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Preparation of PtRu/C electrocatalysts using citric acid as reducing agent and OH⁻ ions as stabilizing agent for Direct Ethanol Fuel Cell (DEFC)

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1. INTRODUCTION

Fuel cells employing ethanol directly as combustible (Direct Ethanol Fuel Cell, DEFC) 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, DEFCs use a liquid fuel, thus simplifying the fuel delivery system [1–5]. The ethanol could be produced in large quantities from biomass and it is much less toxic than methanol. However, its complete oxidation to CO₂ is more difficult due to the difficulties in C–C bond breaking and the formation of CO intermediates that poison the platinum anode catalysts [6–8]. Carbon-supported platinum is commonly used as anode catalyst in low-temperature fuel cells. However, pure Pt is not an efficient anodic catalyst for the direct ethanol fuel cells, because it is rapidly poisoned by strongly adsorbed species coming from the dissociative adsorption of ethanol. Due to the low activity of platinum for practical DEFC applications, elements like ruthenium have been added to promote electroactivity [8]. Studies have been shown that the catalytic activity of PtRu/C electrocatalysts is strongly dependent on the method of preparation. Thus, new preparation methods of PtRu/C electrocatalysts have been one of the major topics studied on the electro-oxidation of alcohols [9]. Citric acid and sodium citrate have been used as stabilizing agent in the preparation of electrocatalysts. Guo *et al.* [10] prepared a well-dispersed Pt/C electrocatalyst by the reduction of chloroplatinic acid with sodium borohydride, with citric acid as a stabilizing agent in ammonium hydroxide solution. The results indicate that the oxygen reduction reaction activity of the obtained catalyst was comparable to that of commercial Pt/C catalyst. Lin *et al.* [11] prepared platinum nanoparticles of 2–3 nm average size by methanol reduction using sodium citrate as the stabilizer. Shimazaki *et al.* [12] prepared PtRu nanoparticles in aqueous media using citric acid as a capping agent and NaBH₄ as a reducing agent with the aid of pH control. Guo *et al.* [13] prepared PtRu/C nanocatalysts by changing the molar ratio of citric acid to platinum and ruthenium metal salts and using sodium borohydride as a reducing agent. The obtained materials were tested as anode of a direct methanol fuel cell (DMFC) and showed a slightly higher performance than the commercial catalyst. In this work, PtRu/C electrocatalysts were prepared using citric acid (CA) as reducing agent and OH⁻ ions as stabilizing agent. The obtained materials were tested for ethanol oxidation.

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2. EXPERIMENTAL

PtRu/C electrocatalysts (20 wt% of metal loading) were prepared in a single step using $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (Aldrich) and $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ (Aldrich) as metals sources and Vulcan XC72R as carbon support. The metal sources, the citric acid (CA:PtRu molar ratio of 1:1) and a solution of KOH 1 mol L^{-1} (OH^- :PtRu molar ratio of 10:1) were dissolved in water and the carbon support was added. The resulting mixtures was treated in an ultrasound bath for 10 min and submitted to reflux for 3 h under open atmosphere. Finally, the mixtures were filtered and the obtained solids were washed with water and dried at $70 \text{ }^\circ\text{C}$ for 2 h.

The Pt:Ru atomic ratios were obtained by EDAX analysis using a scanning electron microscope Philips XL 30 with a 20 keV electron beam and equipped with EDAX DX4 microanalyser.

Transmission electron microscopy (TEM) was carried out using a Carl Zeiss CEM 902 apparatus with a Proscan high-speed slow-scan CCD camera and digitalized (1024×1024 pixels, 8 bits) using the AnalySis software.

Chronoamperometry experiments were performed at $25 \text{ }^\circ\text{C}$ with 1.0 mol L^{-1} of ethanol in 0.5 mol L^{-1} H_2SO_4 solutions saturated with N_2 using a Microquimica (model MQPG01, Brazil) potentiostat/ galvanostat. [14].

The membrane electrode assemblies (MEA) were prepared by hot pressing a pretreated Nafion 117 membrane placed between either a PtRu/C (50:50), PtRu/C (80:20) prepared by citric acid or PtRu/C (50:50) E-TEK anode (1 mg Pt cm^{-2} catalyst loading) and a 20 wt% Pt/C E-TEK cathode (1 mg Pt cm^{-2} catalyst loading) at $125 \text{ }^\circ\text{C}$ for 2 min under a pressure of 225 kgf cm^{-2} . The direct ethanol fuel cell performances were determined in a single cell with an area of 5 cm^2 . The temperature was set to $90 \text{ }^\circ\text{C}$ for the fuel cell and for the oxygen humidifier. The fuel was 2 mol L^{-1} of ethanol solution delivered at approximately 1 mL min^{-1} and the oxygen flow was regulated at 500 mL min^{-1} and pressure of 2 bar. Polarization curves were obtained by using a TDI RBL 488 electronic load.

3. RESULTS AND DISCUSSION

In a previous work [15] the effect of CA:PtRu molar ratio in the preparation of PtRu/C electrocatalysts using citric acid as reducing agent was studied (CA:PtRu molar ratio of 1:1, 1:5 and 1:10). The obtained materials showed an average nanoparticle size of approximately 10 nm. The great size of the PtRu nanoparticles obtained in preparation of PtRu/C electrocatalysts using citric acid as reducing agent was also observed by Pillai and Kamat [16] in the preparation of Ag nanoparticles using citrate as reducing agent. They attributed the nanoparticles growth to the complexation of citrate ions by silver seeds as soon as they were formed in the initial reduction step. In this work, we studied the addition of OH^- ions to the reaction medium with the aim to decrease of the crystallite sizes of the PtRu/C electrocatalysts prepared using citric acid as reducing agent (Table 1). In the preparation of the electrocatalysts the OH^- ions could be adsorbed on the PtRu nanoparticles surface inhibiting their growth [17].

Table 1. Pt:Ru atomic ratios and mean particle sizes of the PtRu/C electrocatalysts prepared using citric acid as reducing agent (20 wt% metal loading, CA:PtRu molar ratio of 1:1 and OH⁻:PtRu molar ratio of 10:1) and PtRu/C E-TEK electrocatalyst.

Pt:Ru atomic ratio - nominal	Pt:Ru atomic ratio - EDX	Average particle size by TEM (nm)
50:50	48:52	2.6
80:20	78:22	2.2
50:50 E-TEK	46:54	3.8

For both prepared PtRu/C electrocatalysts the obtained Pt:Ru atomic ratios determined by EDX analysis were similar to the nominal ones. The average particle sizes for both catalysts were around 2.5 nm (Table 1).

Compared to the PtRu/C electrocatalysts prepared without addition of OH⁻ ions into the reaction medium [15], which have average particles size of around 10 nm, a great decrease of the sizes of the obtained nanoparticles and a good distribution on the carbon support were observed.

The PtRu/C electrocatalysts performances for ethanol oxidation were studied by chronoamperometry in 1.0 mol L⁻¹ of alcohol in 0.5 mol L⁻¹ H₂SO₄ at an anodic potential of 500 mV versus RHE (Fig. 1).

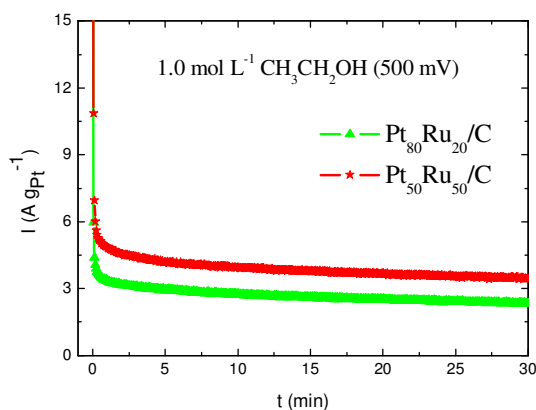


Figure 1. Current–time curves at 5 mV in 0.5 mol L⁻¹ H₂SO₄ containing 1.0 mol L⁻¹ of ethanol for PtRu/C electrocatalysts.

The current values were normalized per gram of platinum, considering that alcohol adsorption and dehydrogenation occur only on platinum sites at room temperature [18]. For ethanol-oxidation (Fig. 1) the electrocatalysts prepared with Pt:Ru atomic ratio of 50:50 showed a superior performance. Similar results were observed using PtRu/C prepared by spontaneous deposition of platinum on carbon-supported

ruthenium nanoparticles [19], where for ethanol oxidation good performance was observed with low platinum coverage. For ethanol electro-oxidation it has been observed that it's increase with more ruthenium content [8, 20].

Figure 2 show the performances of direct ethanol fuel cell (DEFC) using PtRu/C electrocatalysts prepared using CA and commercial Pt/C and PtRu/C from E-TEK as anodes. All PtRu/C electrocatalysts were more active than Pt/C E-TEK for DEFC studies, which could be attributed to the bifunctional mechanism [19]. For DEFC studies the maximum power density of PtRu/C (50:50) (22 mW cm⁻²) prepared using CA was greater than PtRu/C E-TEK (17 mW cm⁻²) and PtRu/C (80:20) prepared using CA (11 mW cm⁻²) and with higher open-circuit voltage (OCV) values than all.

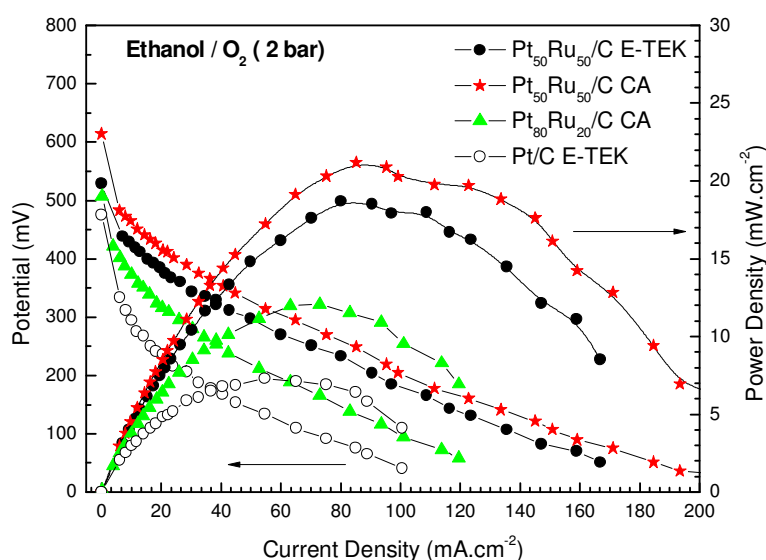


Figure 2. Electrical performances of a 5 cm² DEFC at 90 °C using PtRu/C electrocatalysts (CA) and commercial Pt/C and PtRu/C (50:50) from E-TEK anodes (1 mg Pt cm⁻² catalyst loading) and Pt/C E-TEK cathode (1 mg Pt cm⁻² catalyst loading), Nafion 117 membrane, ethanol (2.0 mol L⁻¹), oxygen pressure (2 bar).

4. CONCLUSIONS

Active PtRu/C electrocatalysts for ethanol oxidation could be prepared using citric acid (CA) as reducing agent and OH⁻ ions as stabilizing agent. The addition OH⁻ ions leads to a decrease of the average nanoparticles sizes. The Pt:Ru atomic ratio has an important effect on the catalytic activity of the prepared PtRu/C electrocatalysts for ethanol oxidation. On the DEFC studies the PtRu/C (50:50) electrocatalyst prepared using CA showed so or more active than PtRu/C (50:50) commercial electrocatalyst from E-TEK.



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REFERENCES

- [1] E.R. Gonzalez, *Química Nova*, 23 (2000) 262.
- [2] H. Wendt, M. Gotz, M. Linardi, *Química Nova*, 23 (2000) 538.
- [3] E.V. Spinacé, A.O. Neto, E.G. Franco, M. Linardi, E.R. Gonzalez, *Química Nova*, 27 (2004) 648.
- [4] H. Wendt, E.V. Spinacé, A.O. Neto, M. Linardi, *Química Nova*, 28 (2005) 1066.
- [5] C. Lamy, A. Lima, V. Lerhum, F. Delime, C. Coutanceau, J.M. Léger, *Journal of Power Sources* 105 (2002) 283.
- [6] F. Vigier, C. Coutanceau, A. Perrard, E.M. Belgsir, C. Lamy, *Journal of Applied Electrochemistry*, 34 (2004) 439.
- [7] A.O. Neto, R.R. Dias, V.A. Ribeiro, E.V. Spinacé, M. Linardi, *Eclética. Química*, 31 (2006) 81.
- [8] A.O. Neto, M.J. Giz, J. Perez, E.A. Ticianelli, E.R. Gonzalez, *Journal of the Electrochemistry Society*, 149 (2002) A272.
- [9] H. Liu, C. Song, L. Zhang, J. Zhang, H. Wang, D.P. Wilkinson, *Journal of Power Sources*, 155 (2006) 95.
- [10] J.W. Guo, T.S. Zhao, J. Prabhuram, C.W. Wong, *Electrochimica Acta*, 50 (2005) 1973.
- [11] L. Chia-Shiang, R. K. Maksudur, D. L. Shawn, *Journal of Colloid and Interface Science*, 299 (2006) 678.
- [12] Y. Shimazaki, Y. Kobayashi, S. Yamada, T. Miwa, M. Koono, *Journal of Colloid and Interface Science*, 292 (2005) 122.
- [13] J.W. Guo, T.S. Zhao, J. Prabhuram, R. Chen, C.W. Wong, *Electrochimica Acta* 51 (2005) 754
- [14] A. O. Neto, A. Y. Watanabe, M. Brandalise, M. M. Tusi, R. M. de S. Rodrigues, M. Linardi, E. V. Spinacé, C.A.L.G.O. Forbicini, *Journal of Alloys and Compounds*, 476 (2009) 288.
- [15] A.O. Neto; E.V. Spinacé, M. Linardi; R.W.R.V. Silva, *Boletim Técnico da Faculdade de Tecnologia de São Paulo*, 18 (2005), 62.
- [16] Z.S. Pillai, P.V. Kamat, *Journal of Physical Chemistry B* 108 (2004) 945.
- [17] Y. Wang, J. Zhang, X. Wang, J. Ren, B. Zuo, Y. Tang, *Topics in Catalysis* 35 (2005) 35.
- [18] H.A. Gasteiger, N. Markovic, P.N. Ross, E.J. Carins, *Journal of the Electrochemical Society* 141 (1994) 1795.
- [19] E.V. Spinacé, A.O. Neto, M. Linardi, *Journal of Power Sources* 129 (2004) 121.
- [20] E.V. Spinacé, A.O. Neto, M. Linardi, *Journal Power Sources* 124 (2003) 426.

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The most important references:	Neto, A.O. ; Vasconcelos, T.R.R. ; VERJULIO-SILVA, R. W. R. ; Linardi, M. ; Spinace, E.V. . Electro-oxidation of ethylene glycol on PtRu/C and PtSn/C electrocatalysts prepared by alcohol-reduction process. Journal of Applied Electrochemistry, Londres, v. 35, p. 193-198, 2005. BRANDALISE, M. ; VERJULIO-SILVA, R. W. R. ; TUSI, M. M. ; CORREA, O. V. ; FARIAS, L. A. ; Linardi, M. ; SPINACÉ, E. V. ; OLIVEIRA NETO, A. . Electro-oxidation of ethanol using PtRuBi/C electrocatalyst prepared by borohydride reduction. Ionics (Kiel), 2009. VERJULIO-SILVA, R. W. R. ; SPINACÉ, E. V. ; LINARDI, Marcelo ; OLIVEIRA NETO, A. . Preparação de eletrocatalisadores PtRu/C pelo método de redução por ácido cítrico para aplicação como ânodo na oxidação direta de metanol em células a combustível. Boletim Técnico da Faculdade de Tecnologia de São Paulo, São Paulo, v. 18, p. 62-71, 2005.

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