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Enhanced electro-oxidation of ethanol using $PtSn/CeO_2$–C electrocatalyst prepared by an alcohol-reduction process

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ABSTRACT

$PtSn/CeO_2$–C electrocatalysts were prepared by an alcohol-reduction process using ethylene glycol as solvent and reduction agent and CeO_2 and Vulcan Carbon XC72 as supports. The electrocatalysts were characterized by EDX and XRD. The electro-oxidation of ethanol was studied at room temperature by chronoamperometry. $PtSn/CeO_2$–C electrocatalyst with 15 wt% of CeO_2 showed a significant increase of performance for ethanol oxidation compared to PtSn/C catalyst. Preliminary tests at 100 °C on a single cell of a direct ethanol fuel cell (DEFC) also confirm the results obtained by chronoamperometry.

1. Introduction

Direct alcohol fuel cells (DAFCs) are attractive as power sources for mobile 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 system [1–3]. Methanol has been considered the most promising fuel, because it is more efficiently oxidized than other alcohols, however, slow anode kinetics have been observed [4,5]. Ethanol offers an attractive alternative as fuel because it is produced in large quantities from biomass and it is much less toxic than methanol. On the other hand, its complete oxidation to CO_2 and water is more difficult than that of methanol due to the difficulties in C–C bond breaking and to the formation of CO-intermediates that poison the platinum anode catalysts [6–8]. In this manner, its complete oxidation remains a great challenge and the principal products formed are acetaldehyde and/or acetic acid [9–10]. Thus, new catalyst materials and new catalyst preparation method developments have been one of the major topics studied on the electro-oxidation of methanol and ethanol [5,7,11]. PtSn/C electrocatalyts have been described to be more active than PtRu/C electrocatalysts for ethanol electro-oxidation and their performances depend greatly on the preparation procedure and Pt:Sn atomic ratio [12–14].

We have demonstrated that PtSn/C electrocatalyst prepared by an alcohol-reduction process, where the major part of tin was found as a SnO_2 phase, was very active for methanol and ethanol oxidation [15]. Bocarsly and co-workers [16] found that a nanoparticulate catalyst containing Pt and SnO_2 allowed the partial conversion of ethanol to CO_2 and water and the elevation of the operating temperature of direct ethanol fuel cell (DEFC) to 130 °C facilitated the production of CO_2 and provided an improvement of current–voltage response.

Recently, Qin and co-workers [17–19] showed that the addition of CeO_2 to platinum catalysts could produce active anode catalysts for methanol and ethanol electro-oxidation. These catalysts were prepared by different procedures: physically mixing Pt/C catalyst with CeO_2, by adsorbing Pt nanoparticles on CeO_2 coated carbon nanotubes and by co-precipitation of Pt(IV) ions and Ce(III) on carbon support and reduction with $NaBH_4$. Wang et al. [20] also observed an enhancement of the electroactivity for methanol electro-oxidation adding CeO_2 to PtRu/C catalyst. The material denoted as $PtRu/Ce_xC$ was prepared by precipitation–decomposition method, where Pt(IV), Ru(III) and Ce(III) ions in aqueous solution were co-deposited on Vulcan XC-72 by the addition of NaOH and the resulting material was treated in flowing of H_2/N_2.

In this study $PtSn/CeO_2$–C electrocatalysts were prepared by an alcohol-reduction process [15,21,22] substituting part of the carbon support by CeO_2. The obtained materials were tested for ethanol oxidation using electrochemical techniques and the most active catalyst was also tested in direct ethanol fuel cell.

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2. Experimental

PtSn/CeO_2–C (Pt:Sn atomic ratio 50:50) eletrocatalysts were prepared by using $H_2PtCl_6 \cdot H_2O$ and $SnCl_2 \cdot 2H_2O$ as metal sources and ethylene glycol as solvent and reducing agent. The platinum and tin metal loadings were always kept at 20 wt%. Carbon Vulcan XC72 and CeO_2 were used as supports and the quantity of CeO_2 was varied between 0 wt% and 20 wt% [15,21,22]. In a typical procedure, the metal sources were dissolved in ethylene glycol/water (75/25, v/v) and Carbon Vulcan XC72 and CeO_2 supports were 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.

Pt:Sn 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 microanaliser.

XRD analyses were performed using a Rigaku diffractometer model Multiflex with a CuK_α radiation source.

Electrochemical studies were carried out using the thin porous coating technique [23]. An amount of 20 mg of the electrocatalysts was added to a solution of 50 mL of water containing 3 drops of 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 working electrodes have a geometric area of 0.3 cm^2 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 ethanol in 0.5 mol L^{-1} H_2SO_4 solutions saturated with N_2 using a Microquimica (model MQPG01, Brazil) potenciostat/galvanostat.

The membrane electrode assemblies (MEA) were prepared by hot pressing a pretreated Nafion 117 membrane placed between either a PtSn/C or a PtSn/CeO_2–C 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 °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 100 °C for the fuel cell and 80 °C for the oxygen humidifier. The fuel was 2 mol L^{-1} ethanol solution delivered at approximately 2 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

PtSn/CeO_2(0–20 wt%)–C electrocatalysts were prepared in a single step (co-reduction of mixed ions) using ethylene glycol as solvent and reducing agent. CeO_2 and carbon Vulcan XC72 were used as supports. The Pt:Sn atomic ratios of the obtained electrocatalysts were similar to the nominal atomic ratios used in preparations. The X-ray diffractograms of the electrocatalysts are shown in Fig. 1. PtSn/C and PtSn/CeO_2–C diffractograms showed a broad peak at about 25° that was associated with the Vulcan XC72 support material and four peaks at approximately $2\theta = 40°$, 47°, 67° and 82°, which are associated with the (111), (200), (220) and (311) planes, respectively, of the fcc structure characteristic of platinum and platinum alloys [21,23]. The (220) reflections of Pt(fcc) crystalline structure were used to calculate the average crystallite sizes using the Scherrer equation [24] and the calculated values were in the range of 2–3 nm. In the diffractograms of these samples it was also observed two peaks at approximately $2\theta = 34°$and 52° that were identified as a SnO_2 phase [14,15]. The diffractogram of CeO_2 support showed the cubic fluorite structure [18,19] with and an average crystallite size of 25 nm. The three most intense peaks of CeO_2 phase at $2\theta = 28.8°$, 47.5° and 56.3° [18] could be observed in the diffractograms of PtSn/CeO_2–C electrocatalysts and their intensities increase with the increase of the CeO_2 content on these samples.. Thus, from the XRD measurements it was observed that Pt (fcc), SnO_2 and CeO_2 phases coexist in PtSn/CeO_2–C electrocatalysts.

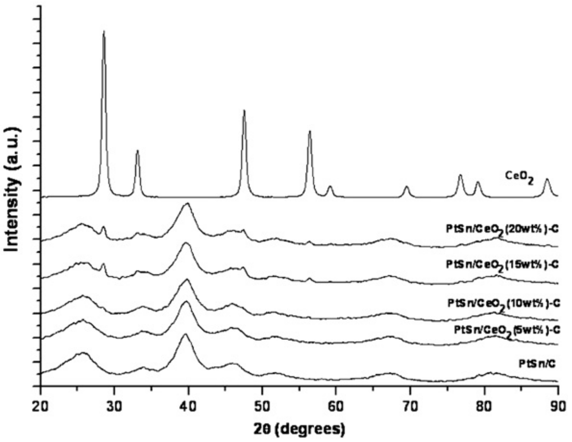

Fig. 1. X-ray diffractograms of CeO_2, PtSn/C and PtSn/CeO_2–C electrocatalysts.

The chronoamperometry curves of the electrocatalysts at 0.5 V are shown in Fig. 2. It can be seen in all current–time curves of PtSn/C and PtSn/CeO_2 electrocatalysts an initial current drop in the first 5 min followed by a slower decay. PtSn/C and PtSn/CeO_2(5 wt%)–C showed a similar behavior, however, a significant increase of performance was observed with the increase of CeO_2 content until 15 wt%. An increase of performance was also observed by Wang et al. [20] for methanol oxidation using PtRu/C catalyst with a loading of 15 wt% of CeO_2.

Fig. 3 shows the performances of single cell with PtSn/C and PtSn/CeO_2(15 wt%)–C as anode catalysts. The open circuit voltage of the fuel cell containing PtSn/C electrocatalyst was 0.71 V, while the corresponding value for PtSn/CeO_2–C electrocatalyst increases to 0.79 V. The maximum power density of PtSn/CeO_2–C electrocatalyst (50 mW cm^{-2}) is greater than that of PtSn/C electrocatalyst (40 mW cm^{-2}). Thus, as observed by electrochemical techniques

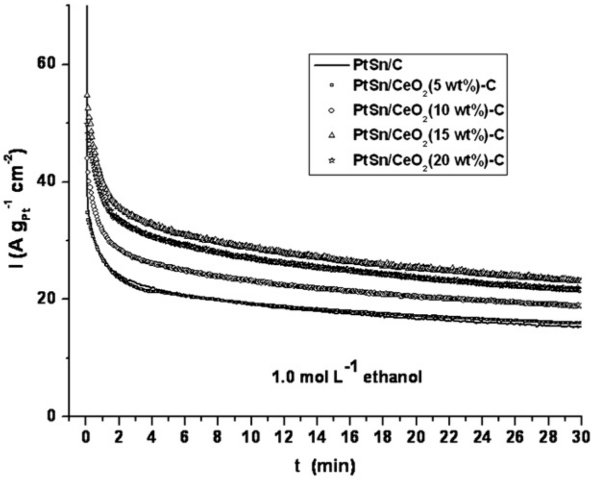

Fig. 2. Current–time curves at 0.5 V in 0.5 mol L^{-1} H_2SO_4 containing 1.0 mol L^{-1} of ethanol for PtSn/C and PtSn/CeO_2–C electrocatalysts.

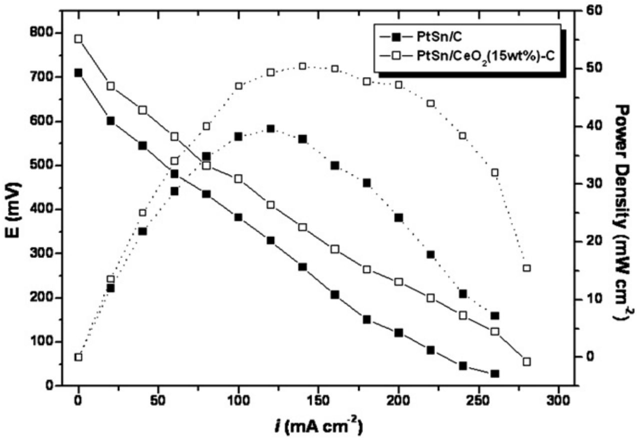

Fig. 3. Electrical performances of a 5 cm^2 DEFC at 100 °C using PtSn/C and PtSn/CeO$_2$–C electrocatalysts anodes (1 mg Pt cm^{-2} catalyst loading) and Pt/C E-TEK cathode (1 mg Pt cm^{-2} catalyst loading, 20 wt% catalyst on carbon), Nafion 117 membrane, ethanol (2.0 mol L^{-1}), oxygen pressure (2 bar).

the use of PtSn/CeO$_2$–C electrocatalyst also increased the cell performance.

The enhancement of activity for alcohol electro-oxidation resulting from the addition of CeO$_2$ to platinum catalysts was attributed by Qin and co-workers [17–19] to the bifunctional mechanism, where CeO$_2$ favors the formation of chemisorbed oxygen species and promotes the oxidation of adsorbed carbon monoxide on the surface of platinum. Similar results were described by Takahashi et al. [25,26] for methanol electro-oxidation using Pt–CeO$_2$ electrodes supported on carbon black. They concluded that the released oxygen species from the surface of CeO$_2$ particles contribute to oxidation of adsorbed CO species on the Pt surface. Díaz et al. [27] using nanocrystalline Pt/CeO$_2$ composite electrodes observed an enhancement of methanol and ethanol electro-oxidation, which was explained either by inhibiting CO adsorption or by ceria's oxygen storage facilitating the oxidation of adsorbed CO. Some studies of carbon monoxide oxidation over Pt–CeO$_2$ [28] and Pt–SnO$_2$ [29] suggested that the high activity of these catalysts was associated with oxygen spillover from the oxides onto the platinum sites.

Wang et al. [20] using PtRu/Ce$_x$C catalysts prepared by co-precipitation method attributed the enhancement of electroactivity for methanol oxidation to the effect of CeO$_2$ as a textural promoter that increases the dispersion of PtRu nanoparticles. XRD measurements showed that the sizes of PtRu nanoparticles decrease with the increase of CeO$_2$ content. In our case, a decrease of the size of Pt nanoparticles was not observed by XRD measurements and could not explain the increase of performance of PtSn/CeO$_2$–C electrocatalyst. However, it was described that PtSn/CeO$_2$ catalysts operating in a continuous-flow fixed-bed reactor showed high catalytic performances for the complete oxidation of ethanol to CO$_2$ in the temperature range between 320 K and 400 K [30].

4. Conclusions

PtSn/CeO$_2$–C electrocatalysts prepared by an alcohol-reduction process exhibited higher performance for ethanol oxidation than PtSn/C electrocatalyst. The best results were found with a loading of 15 wt% of CeO$_2$. Further work is now necessary to investigate the PtSn/CeO$_2$–C catalyst surface by different techniques and to elucidate the mechanism of ethanol electro-oxidation on PtSn/CeO$_2$–C electrocatalysts. It is also necessary to know if the catalyst is effective to oxidize ethanol to CO$_2$, not only to intermediate products like acetaldehyde and acetic acid, under Direct ethanol fuel cell (DEFC) operating conditions. It is also interesting to test these catalysts in DEFC using membranes that could operate at temperatures above 100 °C.

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References

[1] H. Wendt, E.V. Spinacé, A.O. Neto, M. Linardi, Quim. Nova 28 (2005) 1066.
[2] C. Lamy, A. Lima, V. Lerhum, F. Delime, C. Coutanceau, J.M. Léger, J. Power Sources 105 (2002) 283.
[3] U.B. Demirci, J. Power Sources 169 (2007) 239.
[4] T. Iwasita, Electrochem. Acta 47 (2002) 3663.
[5] H. Liu, C. Song, L. Zhang, J. Zhang, H. Wang, D.P. Wilkinson, J. Power Sources 155 (2006) 95.
[6] F. Vigier, C. Coutanceau, A. Perrard, E.M. Belgsir, C. Lamy, J. Appl. Electrochem. 34 (2004) 439.
[7] E. Antolini, J. Power Sources 170 (2007) 1.
[8] S. Song, P. Tsiakaras, Appl. Catal., B 63 (2006) 187.
[9] H. Wang, Z. Jusys, R.J. Behm, J. Power Sources 154 (2006) 351.
[10] S. Rousseau, C. Countanceau, C. Lamy, J.M. Léger, J. Power Sources 158 (2006) 18.
[11] 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.
[12] C. Lamy, S. Rousseau, E.M. Belgsir, C. Coutanceau, J.-M. Léger, Electrochim. Acta 49 (2004) 3901.
[13] W. Zhou, Z. Zhou, S. Song, W. Li, G. Sun, P. Tsiakaras, Q. Xin, Appl. Catal., B 46 (2003) 273.
[14] E.V. Spinacé, L.A.I. do Vale, R.R. Dias, A.O. Neto, M. Linardi, Stud. Surf. Sci. Catal. 162 (2006) 617.
[15] A.O. Neto, R.R. Dias, M.M. Tusi, M. Linardi, E.V. Spinacé, J. Power Sources 166 (2007) 87.
[16] J. Mann, N. Yao, A. Bocarsly, Langmuir 22 (2006) 10432.
[17] J. Xi, J. Wang, L. Yu, X. Qin, L. Chen, Chem. Commun. (2007) 1656.
[18] J. Wang, J. Xi, Y. Bai, Y. Shen, J. Sum, L. Chen, W. Zhu, X. Qin, J. Power Sources 164 (2007) 555.
[19] Y. Bai, J. Wu, X. Qin, J. Yi, J. Wang, J. Li, W. Zhu, L. Chen, Appl. Catal., B 73 (2007) 144.
[20] K-W. Wang, S-Y. Huang, C-T. Yeh, J. Phys. Chem. C 111 (2007) 5096.
[21] E.V. Spinacé, A.O. Neto, T.R.R. Vasconcelos, M. Linardi, J. Power Sources 137 (2004) 17.
[22] E.V. Spinacé, A.O. Neto, T.R.R. Vasconcelos, M. Linardi, Patent BR200304121-A.
[23] A.O. Neto, M.J. Giz, J. Perez, E.A. Ticianelli, E.R. Gonzalez, J. Electrochem. Soc. 149 (2002) A272.
[24] V. Radmilovic, H.A. Gasteiger, P.N. Ross Jr., J. Catal. 154 (1995) 98.
[25] M. Takahashi, T. Mori, A. Vinu, H. Kobayashi, J. Drennan, D.R. Ou, J. Mater. Res. 21 (2006) 2314.
[26] M. Takahashi, T. Mori, F. Xe, A. Vinu, H. Kobayashi, J. Drennan, J. Am. Ceram. Soc. 90 (2007) 1291.
[27] D.J. Díaz, N. Greenletch, A. Solanki, A. Karakoti, S. Seal, Catal. Lett. 119 (2007) 319.
[28] C. Hardacre, T. Rayment, R.M. Lambert, J. Catal. 158 (1996) 102.
[29] K. Grass, H.G. Lintz, Stud. Surf. Sci. Catal. 112 (1997) 135.
[30] X. Tang, B. Zhang, Y. Li, Y. Xu, Q. Xin, W. Shen, J. Mol. Catal. A 235 (2005) 122.