SHORT COMMUNICATION

Electro-oxidation of ethanol using PtSnRh/C electrocatalysts prepared by an alcohol-reduction process

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Abstract PtRh/C (90:10), PtRh/C (50:50), PtSn/C (50:50), and PtSnRh/C (50:40:10) electrocatalysts were prepared by an alcohol-reduction process using ethylene glycol as solvent and reduction agent and Vulcan Carbon XC72 as supports. The electrocatalysts were characterized by energy-dispersive X-ray analysis, X-ray diffraction, and transmission electron microscopy. The electro-oxidation of ethanol was studied by cyclic voltammetry chronoamperometry at room temperature and on a single cell of a direct ethanol fuel cell at 100 °C. Cyclic voltammetry and chronoamperometry experiments showed that PtSnRh/C and PtSn/C electrocatalysts have similar performance for ethanol oxidation at room temperature, while the activity of PtRh/C electrocatalysts was very low. At 100 °C on a single cell, PtSnRh/C showed superior performance compared to PtSn/C and PtRh/C electrocatalysts.

Keywords PtSnRh/C electrocatalyst ·
Alcohol-reduction process · Ethanol oxidation ·
Direct ethanol fuel cell

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

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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. However, its complete oxidation to CO_2 is more difficult than that of methanol due to the difficulty of C–C bond breaking and to 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 cell. Platinum itself is known to be rapidly poisoned on its surface by strongly adsorbed species coming from the dissociative adsorption of ethanol. Efforts to mitigate the poisoning of Pt have been concentrated on the addition of co-catalysts to platinum [7–9]. In this manner, materials based on PtSn have been considered the most active electrocatalysts for ethanol electro-oxidation. However, due to the difficulty of C–C bond breaking, the principal products formed are acetaldehyde and acetic acid [9, 10].

Souza et al. [11] studied the electro-oxidation of ethanol on Pt, Rh, and PtRh electrodes. It was found that Rh was the less active electrocatalyst; on the other hand, the addition of small amounts of Rh to Pt increased the CO_2/acetaldehyde ratio. It was concluded that the presence of Rh was important to improve the C–C bond breaking but was not sufficient to produce a good catalyst. Thus, PtRh/C electrocatalysts were considered promising candidates for ethanol oxidation if a third element was added to improve the overall reaction rate. Recently, Kowal et al. [12] prepared a $PtRhSnO_2$/C electrocatalyst by depositing Pt and Rh atoms on carbon-supported SnO_2 nanoparticles (multiple step process), and good results for ethanol electro-oxidation were obtained. We have

prepared PtSn/C electrocatalysts in a single step by an alcohol-reduction process [10, 13, 14]. The obtained materials have been investigated by some techniques, which revealed that metallic Pt with face-centered cubic (fcc) structure and a SnO_2 phase coexist in PtSn/C electrocatalyst. The best performance for ethanol oxidation was obtained with Pt/Sn atomic ratio of 50:50 [10, 14]. In this work, PtSnRh/C electrocatalyst (Pt/Sn/Rh atomic ratio of 50:40:10) was prepared by an alcohol-reduction process and tested for ethanol electro-oxidation [14].

Experimental

Pt/C, PtRh/C (Pt/Rh atomic ratio of 90:10 and 50:50), PtSn/C (Pt/Sn atomic ratio of 50:50), and PtSnRh/C (Pt/Sn/Rh atomic ratio of 50:40:10) electrocatalysts (20 wt.% of metal loading) were prepared in a single step by an alcohol-reduction process [10, 13, 14]. In this methodology, $H_2PtCl_6 \cdot 6H_2O$ (Aldrich), $SnCl_2 \cdot 2H_2O$ (Aldrich), and $RhCl_3 \cdot xH_2O$ (Aldrich) were used as metal sources, Carbon Vulcan XC72 as support, and water/ethylene glycol (25/75, v/v) solution as solvent and reducing agent.

The atomic ratios were obtained by energy-dispersive X-ray (EDAX) analysis using a Philips XL30 scanning electron microscope with a 20-keV electron beam and equipped with EDAX DX-4 microanalyzer. X-ray diffraction (XRD) analyses were performed using a Rigaku diffractometer model Miniflex II with a CuKα a radiation source.

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 ($1,024 \times 1,024$ pixels, 8 bits) using the Analysis software. The particle size distributions were determined by measuring the nanoparticles from micrographs using Image Tool software.

Cyclic voltammetry and 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) potentiostat/galvanostat and the thin porous coating technique [10]. The reference electrode was a reference hydrogen electrode (RHE) and the counter electrode was a platinized Pt plate.

The membrane electrode assemblies were prepared by hot pressing a pretreated Nafion 117 membrane placed between either a PtRh/C (90:10), PtRh/C (50:50), PtSn/C (50:50), or PtSnRh/C (50:40:10) 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 (DEFC) 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.

Table 1 Nominal atomic ratio, atomic ratio obtained by EDX, and crystallite size of the Pt/C, PtRh/C, PtSn/C, and PtSnRh/C electrocatalysts

Electrocatalysts	Nominal atomic ratio	Atomic ratio EDX	Crystallite size (nm)
PtRh/C	50:50	56:44	2.0
PtRh/C	90:10	88:12	2.0
PtSn/C	50:50	52:48	2.5
PtSnRh/C	50:40:10	51:38:11	2.0

Results and discussion

Pt/C, PtRh/C (90:10 and 50:50), PtSn/C (Pt/Sn 50:50) and PtSnRh/C (Pt/Sn/Rh 50:40:10) electrocatalysts were prepared in a single step (co-reduction of mixed metal ions) using ethylene glycol as solvent and reducing agent in the presence of Vulcan XC72 [10, 13, 14]. For all prepared electrocatalysts, the obtained atomic ratios were similar to the nominal atomic ratios used in preparations (Table 1).

The X-ray diffractograms of Pt/C, PtRh/C, PtSn/C, and PtSnRh/C electrocatalysts are shown in Fig. 1. All 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)
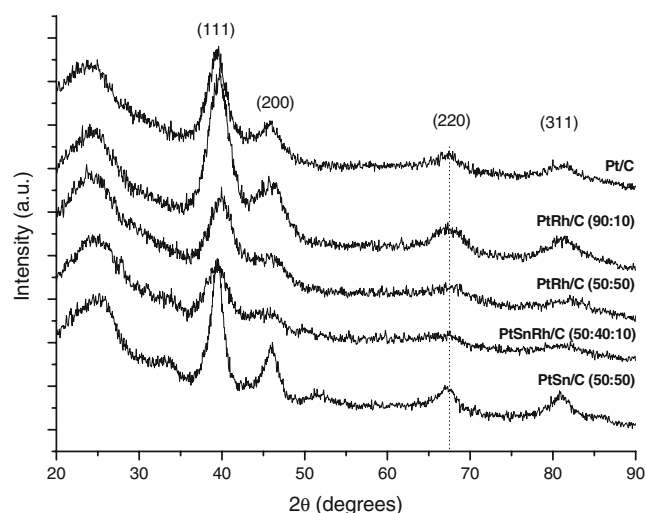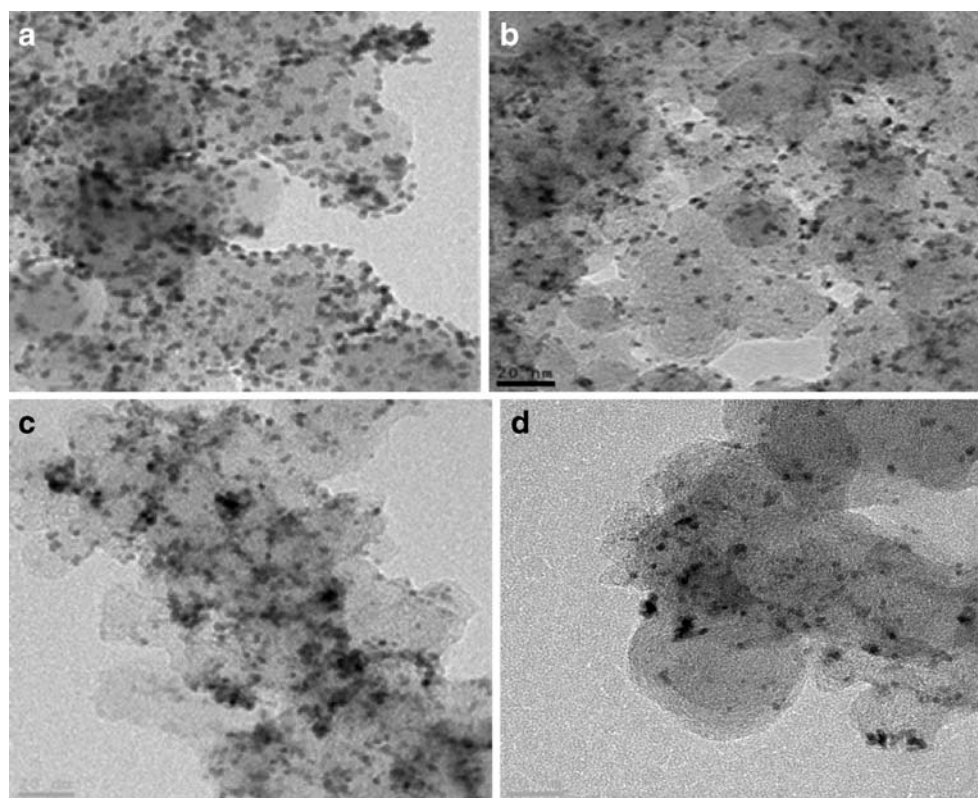

Fig. 1 X-ray diffractograms of Pt/C, PtRh/C, PtSn/C, and PtSnRh/C electrocatalysts

Fig. 2 Transmission electron micrographs (20 nm) of PtRh/C (90:10; **a**), PtRh/C (50:50; **b**), PtSn/C (50:50; **c**), and PtSnRh/C (50:40:10; **d**) electrocatalysts

planes, respectively, of the fcc structure characteristic of platinum and platinum alloys [10, 11]. In the diffractograms of PtSn/C and PtSnRh/C, two peaks were also observed at approximately $2\theta=34°$ and $52°$ that were identified as a SnO_2 phase [10]. The (220) reflections of Pt(fcc) crystalline structure were used to calculate the average crystallite sizes using the Scherrer equation [10], and the calculated values were in the range of 2–2.5 nm. It was observed that the

(220) diffraction peak of PtRh/C (50:50) was dislocated to higher angle compared to Pt/C and PtRh/C (90:10) indicating an alloy formation between Pt and Rh. Similarly, the (220) diffraction peak of PtSnRh/C electrocatalyst was also dislocated to higher angle compared to PtSn/C electrocatalyst.

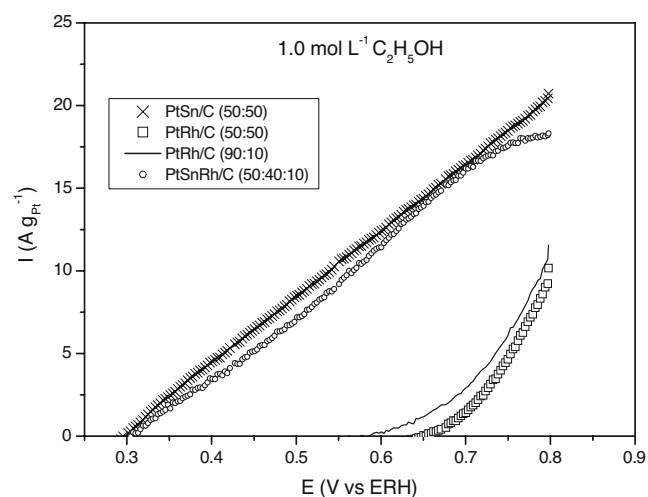TEM micrographs of PRh/C (90:10; Fig. 2a), PtRh/C (50:50; Fig. 2b), PtSn/C (Fig. 2c), and PtSnRh/C (50:40:10;

Fig. 3 Cyclic voltammograms of PtRh/C, PtSn/C, and PtSnRh/C electrocatalysts in 1 mol L^{-1} ethanol solution in 0.5 mol L^{-1} H$_2$SO$_4$ with a sweep rate of 10 mV s^{-1}, considering only the anodic sweep
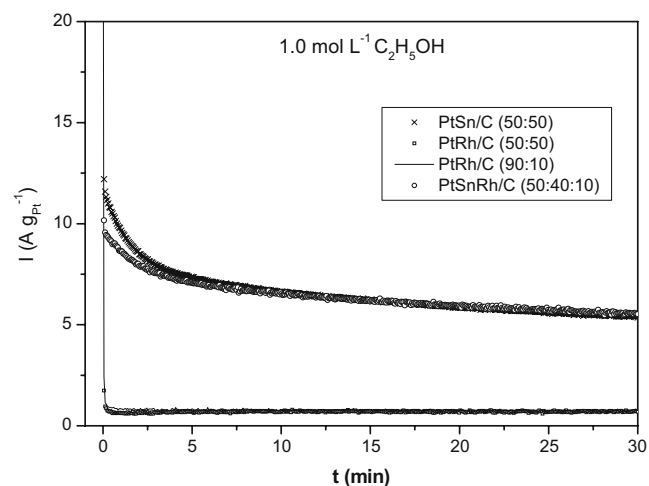

Fig. 4 Current–time curves at 0.5 V in 1 mol L^{-1} ethanol solution in 0.5 mol L^{-1} H$_2$SO$_4$ for PtRh/C, PtSn/C, and PtSnRh/C electrocatalysts

Fig. 2d) electrocatalysts showed a good distribution of the Pt particles on the carbon support with particle sizes of 3.0 ± 1.0 nm, which is in agreement with XRD results.

The cyclic voltammetry of PtRh/C, PtSn/C, and PtSnRh/C in 1.0 mol L^{-1} of ethanol is shown in Fig. 3. The anodic cyclic voltammetry responses were plotted after subtracting the background currents, and the current values were normalized per gram of platinum, considering that ethanol adsorption and dehydrogenation occur only on platinum sites at ambient temperature [14]. PtSn/C (50:50) and PtSnRh/C (50:40:10) electrocatalysts showed similar performance in all range of potential, and the ethanol electro-oxidation started at approximately 0.3 V. For PtRh/C (90:10) and PtRh/C (50:50) electrocatalysts, the onset potential was shifted to more positive potentials (+300 mV), and the current values were smaller than that of PtSn/C and PtSnRh/C electrocatalysts. PtRh/C (50:50) showed lower currents in relation to PtRh/C (90:10) in agreement with the work of Souza et al. [11]. In contrast, Colmati et al. [15] prepared PtSnRh/C (Pt/Sn/Rh atomic ratios of 1:1:0.3 and 1:1:1) by reduction of the metal precursors with formic acid, and the obtained materials were characterized as ternary alloys. Linear sweep voltammetry measurements indicated that, for potentials higher than 0.45 V versus RHE, the ternary Pt–Sn–Rh alloy catalysts possess the higher activity for ethanol electro-oxidation, while for potentials lower than 0.45 V versus RHE, the electrochemical activity of the ternary catalysts was lower than that of the binary Pt–Sn catalyst. These PtSnRh/C electrocatalysts were characterized as a ternary alloy. Thus, these results indicated that the performance depends strongly on the catalyst preparation methodology.

The chronoamperometry experiments were carried out to examine the performance electrochemical and stability

of eletrocatalysts. The PtRh/C, PtSn/C, and PtSnRh/C chronoamperometry curves of the electrocatalysts at 0.5 V are shown in Fig. 4. For PtRh/C electrocatalysts, a great initial current drop and a very low performance for ethanol oxidation at room temperature can be seen, while PtSn/C and PtSnRh/C electrocatalysts showed a similar and good performance for ethanol oxidation at 0.5 V versus RHE. The current values obtained for PtSn and PtSnRh/C electrocatalysts were always higher than those obtained for PtRh/C in agreement with cyclic voltammetry experiments.

Figure 5 shows the performances of single cell with Pt/C, PtRh/C, PtSn/C, and PtSnRh/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 PtSnRh/C electrocatalyst increases to 0.74 V. The maximum power density of PtSnRh/C electrocatalyst (42 mW cm^{-2}) is greater than that of PtSn/C electrocatalyst (35 mW cm^{-2}). The PtSnRh/C electrocatalyst prepared by an alcohol-reduction process had Sn as a SnO$_2$ phase while Rh was alloyed with Pt; the synergy between the three constituents of the electrocatalyst could explain the best activity of this catalyst for ethanol oxidation. Similar results were described by Kowal et al. [12]. They showed that PtRhSnO$_2$/C electrocatalyst was effective in splitting the C–C bond of ethanol at room temperature and led its oxidation to CO$_2$. The catalytic activity was attributed to the synergy between the three constituents of the electrocatalyst, where SnO$_2$ strongly adsorbs water and precludes the Pt and Rh sites from reacting with H$_2$O to form M-OH, making Pt and Rh sites available for ethanol oxidation. The authors concluded that SnO$_2$ reacts with H$_2$O and provides OH species to oxidize the dissociated CO at Rh sites, while Pt facilitates ethanol dehydrogenation. Thus, the good activity for ethanol oxidation of the PtSnRh/C electrocatalyst

Fig. 5 I–V curves of a 5-cm^2 DEFC (left arrow) and the power density (right arrow) at 100 °C using PtRh/C, PtSn/C, and PtSnRh/C electrocatalyst anodes (1 mg Pt cm^2 catalyst loading) and Pt/C E-TEK electrocatalyst cathode (1 mg Pt cm^2 catalyst loading, 20 wt.% catalyst on carbon), Nafion® 117 membrane, and ethanol (2.0 mol L^{-1}). Oxygen pressure=2 bar
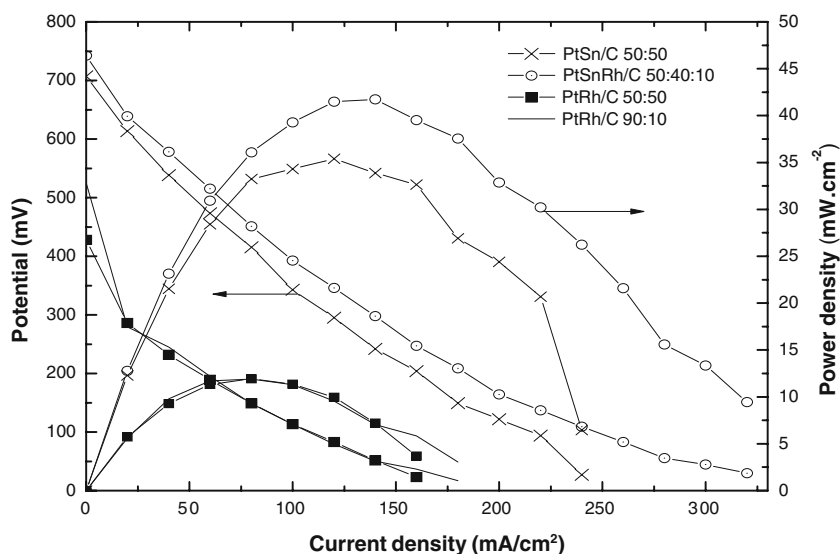
prepared in a single step by an alcohol-reduction process could be attributed to the similar characteristic of the catalyst prepared by Kowal et al. [12] in a multiple step process.

Conclusions

The alcohol-reduction process showed to be an effective method for producing in a single step active PtSnRh/C electrocatalyst for ethanol oxidation. The XRD measurements showed that Sn was found as a SnO_2 phase, while Rh forms an alloy with Pt. The electrochemical experiments showed that PtSn/C and PtSnRh/C electrocatalyst were more active than PtRh/C and Pt/C electrocatalysts for ethanol oxidation at room temperature. Preliminary tests at 100 °C on a single DEFC showed that PtSnRh/C electrocatalyst was more active than PtSn/C electrocatalysts for ethanol oxidation. Further work is now necessary to investigate the PtSnRh/C electrocatalyst surface by different techniques and to elucidate the mechanism of ethanol electro-oxidation.

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