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Preparation of PtSn/C-Rh and PtSn/C-CeO_2 for Ethanol Electro-Oxidation

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PtSn/CeO_2–C electrocatalyst and PtSn/Rh-C were prepared in a two step. In the first step a Carbon Vulcan XC72 + 15%CeO_2 and Vulcan XC72 + 15%Rh supports were prepared using a modified polymeric precursor method under controlled synthesis conditions. In the second step PtSn electrocatalyst was prepared by an alcohol-reduction process using ethylene glycol as solvent and reducing agent and supported on Vulcan XC72 + 15%CeO_2 and Vulcan XC72 + 15%Rh. The obtained electrocatalysts were characterized by XRD and cyclic voltammetry. The electro-oxidation of ethanol was studied by cyclic voltammetry and chronoamperometry at room temperature. PtSn(50:50)/CeO_2–C electrocatalyst showed a significant increase of performance for ethanol oxidation compared to PtSn/C catalyst and others electrocatalysts prepared.

Keywords: alcohol reduction process, PtSn/ CeO_2–C, PtSn/Rh-C, ethanol oxidation, fuel cells.

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 [1-4]. Methanol has been considered the most promising fuel, because it is more efficiently oxidized than other alcohols, however, slow anode kinetics have been observed [1]. Ethanol is an attractive fuel for low temperature fuel cells because it can be produced in large quantities from agricultural products or other biomass, as well as because it is 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 problems in C–C bond breaking and to the formation of intermediates that poison the platinum anode catalysts [5,6]. Platinum is commonly used as anode catalyst in low temperature fuel cells; however, pure Pt is not an efficient anodic catalyst for the direct alcohol fuel cell. Platinum itself is known to be rapidly poisoned on its surface by strongly adsorbed species coming from the dissociative adsorption of alcohols [7,8]. Thus, the addition of co-catalysts to platinum is essential to improve the oxidation [9,10]. It has been shown that ruthenium oxides can enhance the catalytic activity for ethanol electro-oxidation through synergetic interaction with Pt. The Pt sites act as adsorption and dehydrogenation centers for ethanol, while the ruthenium oxides sites provide oxygen-containing species at lower potentials than those on a pure Pt surface [11]. Recently, Neto et al [12] showed that PtSn/C electrocatalyts was more active than PtRu/C electrocatalysts for ethanol electro-oxidation. The performances of PtSn/C depend greatly on the preparation procedure and Pt:Sn atomic ratio, but the principal products formed yet are acetaldehyde and acetic acid, consequently the development of new electrocatalysts and new preparation methods are necessary [12].

Souza et al. [13] studied the electro-oxidation of ethanol on PtRh electrodes. It was found that Rh was the less active electrocatalyst that Pt; but the addition of small amounts of Rh to Pt increased the CO_2/acetaldehyde ratio and 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. [14] 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. The highest activity for ethanol oxidation was observed for Pt–Rh–SnO_2/C electrocatalyst with atomic ratio Pt:Rh:Sn = 3:1:4. The synergistic effect between them facilitates total oxidation of ethanol, which is facilitated by the formation of PtRh uniform solid solution and Sn exists as SnO_2 in entire potential region [15].

Neto et al. [4] prepared PtSnRh/C (50:40:10) electrocatalysts (single step process) by an alcohol-reduction process and the XRD results showed Sn as a SnO_2 phase, while Rh forms an alloy with Pt. The tests at 100°C on a single DEFC showed that PtSnRh/C electrocatalyst was more active than PtSn/C electrocatalysts for ethanol oxidation.

Colmati et al. prepared [16] Pt–Sn–Rh (1:1:0.3 and 1:1:1) catalysts by reduction with formic acid. The XRD results suggest the formation of a ternary Pt–Sn–Rh alloy and activity for the electro-oxidation of ethanol of the ternary Pt–Sn–Rh catalysts above 0.45V is higher than that of the binary Pt–Sn and Pt–Rh catalysts, while for potentials lower than 0.45V, the Pt–Sn catalyst presented the highest activity for the ethanol oxidation. The authors conclude that for fuel cell applications the anode must operate between 0.3 and 0.5V versus RHE, so the Pt–Sn catalyst seems to be more effective than Pt–Sn–Rh. These results were different from the paper of Neto et al. [4] and Kowal et al. [15-16] indicating that activity is dependent on the preparation method.

In another paper Qin and co-workers [17-18] showed that the addition of CeO_2 to platinum catalysts could produce active anode catalysts for 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 $NaBH_4$. Additionally, De Souza et al. [19] using $PtCeO_2/C$ electrocatalysts showed that $Pt-CeO_2/C$ (1:3) had a higher ethanol electro-oxidation activity compared to both Pt/C and PtRu/C ETEK materials. The higher catalytic activity was attributed to several intrinsic features, such as reduced poisoning by the strongly bounded intermediates, maximum utilization of the catalyst surface for particle sizes 4 nm and the indirect bifunctional mechanism which is a possible effect for the electrocatalytical behavior observed using $PtCeO_2/C$ electrocatalysts for ethanol oxidation.

Neto et al. [20-21] showed that $PtSn/CeO_2$–C electrocatalysts prepared by an alcohol-reduction process (single step process) was more active for ethanol oxidation than the analogous PtSn/C catalyst. The best results for ethanol oxidation were found with a loading of 15 wt% of CeO_2. The $PtSn/CeO_2$–C electrocatalysts too showed metallic Pt with face-centered cubic (fcc) structure a SnO_2 phase and peaks of CeO_2 phase at 2h = 28.8°, 47.5° and 56.3°.

The aim of this work was to use the modified polymeric precursor method (PPM) developed by De Souza et al. [22] to produce a support with Carbon Vulcan XC72 + 15%CeO_2 (C-CeO_2) and Vulcan XC72 + 15% Rh (C-Rh) and in the second step to prepare PtSn by an alcohol-reduction to obtain structure a SnO_2 phase and to use C-CeO_2 and C-Rh as support.

2. EXPERIMENTAL PART

PtSn/C-85% 15% CeO_2 (Pt:Sn atomic ratio of 50:50 and 75:25) and PtSn/85% C-15%Rh (Pt:Sn atomic ratio of 50:50 and 75:25) electrocatalysts (20 wt.% metal loading) were prepared in a two step using $H_2PtCl_6{\cdot}6H_2O$, $SnCl_2.2H_2O$ as metal, $RhCl_2{\cdot}xH_2O$ (Aldrich), $CeCl_3$ (Aldrich) and Vulcan XC72 as support. The C-CeO_2 and C-Rh supports were prepared using a modified polymeric precursor method [22] and PtSn prepared by an alcohol reduction process, where the metal sources (Pt and Sn) were dissolved in ethylene glycol/water (75/25, v/v) and Carbon Vulcan XC72 with 15%CeO_2 and Vulcan XC72 with 15%Rh prepared as supports were added [20-22]. 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 X-ray diffraction (XRD) analyses were performed using a Rigaku diffractometer model Miniflex II using Cu Kα radiation source (l=0.15406 nm). The diffractograms were recorded from 2θ = 20° to 90° with a step size of 0.05° and a scan time of 2 s per step.

Electrochemical studies of electrocatalysts were carried out using the thin porous coating technique [20]. An amount of 20 mg of the electrocatalyst was added to a solution of 50 mL of water containing 3 drops of a 6% solution polytetrafluoroethylene (PTFE) suspension. The resulting mixture was treated in an ultrasound bath for 10 min, filtered and transferred to the cavity (0.30 mm deep and 0.47 cm^2 area) of the working electrode. In voltammetry cyclic 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 electrocatalyst present in the working electrode multiplied by its percentage of platinum. The reference electrode was a RHE (reversible hydrogen electrode) and the counter electrode was a platinized Pt plate. Electrochemical measurements were made using a Microquimica (model MQPG 01, Brazil) potenciostat/galvanostat coupled to a PC and using the Microquimica software. Cyclic voltammetry and Chronoamperommetry were performed in a 0.5 mol L^{-1} H_2SO_4 and 1.0 mol L^{-1} ethanol solutions saturated with N_2.

3. RESULTS AND DISCUSSION

The X-ray diffractograms of PtSn/C (50:50), PtSn/C (50:50) 85 % C-15% Ce, PtSn/C (75:25) 85 % C-15% Ce, PtSn/C (50:50) 85 % C-15% Rh and PtSn/C (75:25) 85 % C-15% Rh electrocatalysts are shown in Figure 1.

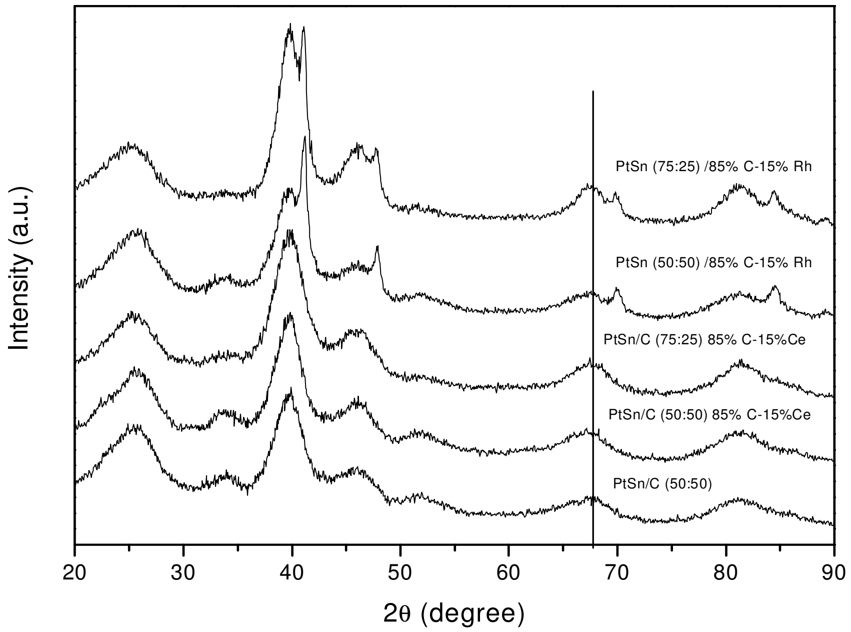

Figure 1. X-ray diffractograms of the PtSn/C, PtSn/C-15% 85%CeO_2 and PtSn/85% C-15%Rh.

All diffractograms of PtSn/C, PtSn/CeO_2–C and PtSn/C-15%Rh showed a broad peak at about 25° that was associated with the Vulcan XC72 support material and four peaks at approximately 2θ = 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. The (220) reflections of Pt (fcc) crystalline structure were used to calculate the average crystallite sizes using the Scherrer equation and the calculated values for all the electrocatalysts were 2 nm [20]. In the diffractograms of these samples it was also observed two peaks at approximately 2θ = 34° and 52° that were identified as a SnO_2 phase. The diffractograms of PtSn/CeO_2–C not showed peaks of CeO_2 phase at 2θ = 28.8°, 47.5° and 56.3° indicating that CeO_2 supported by the modified polymeric precursor method could be amorphous [20]. The diffractograms of PtSn/C-15%Rh showed peaks at about 2θ = 42°, 48°, 72°and 84°corresponding to a metallic rhodium [23].

Figure 2 shows the cyclic voltammograms (CV) in the absence of ethanol of PtSn/C, PtSn/CeO_2–C and PtSn/C-15%Rh electrocatalysts in acid solution.

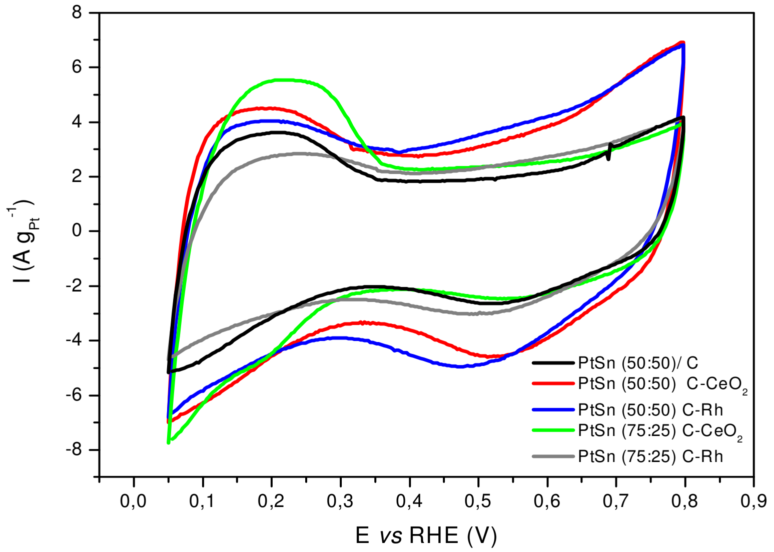

Figure 2. Cyclic voltammograms of PtSn/C (50:50), PtSn/CeO_2–C (50:50), PtSn/CeO_2–C (75:25), PtSn/C-15%Rh (50:50) and PtSn/C-15%Rh (75:25) electrocatalysts in 0.5 mol L^{-1} H_2SO_4, sweep rate: 10 mV s^{-1}.

The cyclic voltammogram for all electrocatalyst do not show a well-defined hydrogen adsorption–desorption region (0.05–0.4 V) and it was observed an increase in the current values in the double layer (0.4–0.8 V), which may be attributed to the formation of oxide species [20-21]. The currents values in the double layer region were high for PtSn/CeO_2–C (50:50) and PtSn/C-15%Rh (50:50) when compared with PtSn/CeO_2–C (75:25) and PtSn/C-15%Rh (75:25) indicating more formation of tin and rhodium oxide species, which agrees with the X-ray diffractograms. The negative scan also showed an increase in the currents in the double layer at about 0.6 V that could be associated with the reduction of oxide species presents in the electrocatalyst. PtSn (75:25)/CeO_2–C electrocatalyst had a more defined hydrogen adsorption–desorption region than PtSn/C and others electrocatalysts. The charge associated to the double layer for PtSn/CeO_2–C too was similar to that observed for PtSn/C. This could to imply that the true active areas of the electrodes are nearly the same, which agrees with the similarity of the particle sizes evaluated from XRD measurements using the Scherrer equation [21].

The chronoamperometry experiments for ethanol oxidation using the PtSn/C, PtSn/CeO_2–C and PtSn/C-Rh electrocatalysts were carried out to examine the electrochemical activity and stability of the electrocatalysts (Fig. 3). The results were obtained in 0.5 mol L^{-1} H_2SO_4 and 1.0 mol L^{-1} C_2H_5OH at an anodic potential of 0.5 V versus RHE.

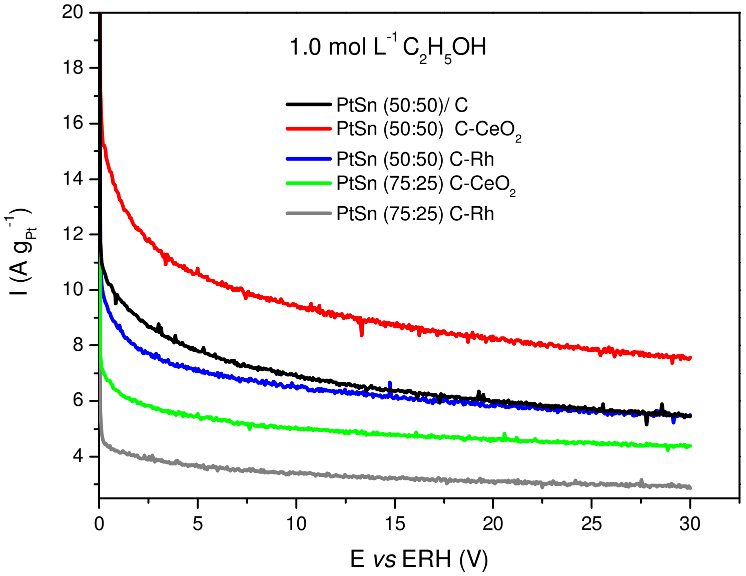

Figure 3. Current–time curves at 0.5 V in 1 mol L^{-1} ethanol solution in 0.5 mol L^{-1} H_2SO_4 for PtSn/C (50:50), PtSn/CeO_2–C (50:50), PtSn/CeO_2–C (75:25), PtSn/C-15%Rh (50:50) and PtSn/C-15%Rh (75:25) electrocatalysts.

In all chronoamperometric curves, there is a sharp initial current drop in the first 2 min followed by a slower decay. The final current values after holding the cell potential at 0.5 V versus RHE for 30 min showed that PtSn/CeO_2–C (50:50) was more active for ethanol electro-oxidation compared PtSn/C and to the others electrocatalysts. The final current values after holding the cell potential at 0.5 V versus RHE for 30 min are following: PtSn/CeO_2–C (50:50) > PtSn/C (50:50) = PtSn/C-15%Rh (50:50) > PtSn/CeO_2–C (75:25) > PtSn/C-15%Rh (75:25).

The superior activity of PtSn/CeO_2–C (50:50) electrocatalysts compared to PtSn/C electrocatalysts probably could be attributed to the bifunctional mechanism, where Pt acts on ethanol adsorption and dissociation, while tin and cerium provides oxygenated species at lower potentials for oxidative removal of the adsorbed intermediates formed during ethanol oxidation [19,20]. In agreement with these results Machida et al. [24] showed that the bifunctional mechanism could be favored by the beneficial synergistic effect of SnO_2 and CeO_2, since cerium oxide is well known in heterogeneous catalysis as a good source of oxygenated species and a presence of these species could favor the ethanol oxidation [19].

The PtSn/C-15%Rh (50:50) and PtSn/C-15%Rh (75:25) electrocatalysts prepared had Sn as a SnO_2 phase while Rh was not alloyed with Pt; these elctrocatalysts not have the similar characteristic of the catalyst prepared by Kowal et al [14] in a multiple step process, consequently these characteristic could explain the worse activity of these catalyst for ethanol oxidation in relation PtSn/C electrocatalyst and another hypothesis is that the high amount of rhodium present in these electrocatalysts could result in lower activity observed.

4. CONCLUSIONS

The proposed method showed that PtSn/CeO_2–C electrocatalysts had higher performance for ethanol oxidation than PtSn/C electrocatalyst probably could be attributed to the bifunctional mechanism. These features should be investigated using in situ techniques to identify the mechanisms occurring. Also, experiments using these electrocatalysts in real conditions (single direct ethanol fuel cell), the identification of the products formed and a more detailed characterization of the electrocatalysts by other techniques like transmission electron microscopy (TEM) and X-Ray Photoelectron Spectroscopy (XPS) should be done in order to explain these results.

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