

Chapter 1

PtSn/C electrocatalysts prepared by different methods for direct ethanol fuel cell

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PtSn/C electrocatalysts with Pt:Sn atomic ratios of 50:50 and 90:10 were prepared by alcohol-reduction process, using ethylene glycol as solvent and reducing agent, and by borohydride reduction. The electrocatalysts were characterized by EDX, XRD and cyclic voltammetry. The electro-oxidation of ethanol was studied by cyclic voltammetry using the thin porous coating technique. The electrocatalysts performance depends greatly on preparation procedures and Pt:Sn atomic ratios.

1. INTRODUCTION

Direct alcohol fuel cells (DAFC) are very attractive as power sources for mobile and portable applications. The alcohol is fed directly into the fuel cell without any previous chemical modification and is oxidized at the anode while oxygen is reduced at the cathode. Methanol has been considered the most promising fuel because it is more efficiently oxidized than other alcohols. Among different electrocatalysts tested in the methanol oxidation, PtRu-based electrocatalysts were the most active [1-3]. In Brazil ethanol is an attractive fuel as it is produced in large quantities from sugar cane and it is much less toxic than methanol. On the other hand, its complete oxidation to CO₂ is more difficult than that of methanol due to the difficulty in C-C bond breaking and to the formation of CO-intermediates that poison the platinum anode catalysts. Thus, more active electrocatalysts are essential to enhance the ethanol electro-oxidation [3].

Recently, Lamy and co-workers [4,5] described that PtSn/C electrocatalysts were more active than PtRu/C electrocatalysts for ethanol oxidation. For electrocatalysts prepared by co-impregnation-H₂ reduction and Bönneiman methods, they found that the optimum tin composition was in the range of 10-20 at.% . In these conditions, the electrode activity was enhanced and the CO-intermediates coming from ethanol dissociative chemisorption were reduced. Xin and co-workers [6-9] prepared PtRu/C and PtSn/C electrocatalysts by a polyol method and tested for ethanol oxidation. It was observed that the addition of some elements, like W, could improve the PtRu/C electrocatalyst activity. However, the activities of the PtRu/C electrocatalysts were inferior to those of PtSn/C electrocatalysts. It was also found that PtSn/C electrocatalysts with Pt:Sn atomic ratios of 60:40 and 50:50 were more active than electrocatalysts with 75:25 and 80:20 atomic ratios. Thus, it seems that the performance of PtSn/C electrocatalysts depends greatly on their preparation procedure.

In this work PtSn/C electrocatalysts with Pt:Sn atomic ratios of 50:50 and 90:10 were prepared by two different methods and tested for ethanol oxidation using cyclic voltammetry.

2. EXPERIMENTAL

PtSn/C electrocatalysts (20 wt%) with Pt:Sn atomic ratios of 50:50 and 90:10 were prepared using H₂PtCl₆·6H₂O (Aldrich) and SnCl₂·2H₂O (Aldrich) as metal sources and Carbon Vulcan XC72R as support by two methods: *i*) the alcohol-reduction process (ARP), where ethylene glycol was used as solvent and reducing agent [10,11]. The metal sources and the carbon support were added to a mixture of ethylene glycol/water (75/25, v/v) and the mixture was refluxed for 3 h and *ii*) by borohydride reduction (BH). In this case, carbon support was suspended in an aqueous solution containing the Pt(IV) and Sn(II) ions and an aqueous solution of sodium borohydride was added dropwise with stirring at room temperature. The suspension was filtered to recover the solid product, which was then washed with water and dried at 70°C for 2h.

The Pt:Sn atomic ratios were obtained by EDAX analysis using a scanning electron microscope Philips XL30 with a 20 keV electron beam and provided with EDAX DX-4 microanalyser. The XRD analyses were performed using a Rigaku diffractometer model Multiflex with a CuK α radiation source.

Electrochemical studies of the electrocatalysts were carried out using the thin porous coating technique [12,13]. An amount of 20 mg of the electrocatalyst was added to a solution of 50 mL of water containing 3 drops of a 6% 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 0.36 cm² area) of the working electrode. The quantity of electrocatalyst in the working electrode was determined with a precision of

0.0001 g. In cyclic voltammetry 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 and the counter electrode was a platinized Pt plate. Electrochemical measurements were made using a Microquimica (model MQPG01, Brazil) potentiostat/galvanostat coupled to a personal computer and using the Microquimica software. Cyclic Voltammetry was performed in a $0.5\ mol\ L^{-1}\ H_2SO_4$ solution saturated with N_2 . The evaluation of ethanol oxidation was performed at $25^\circ C$ in a $0.5\ mol\ L^{-1}\ H_2SO_4$ solution containing $1.0\ mol\ L^{-1}$ of ethanol. For comparative purposes commercial PtRu/C electrocatalyst from E-TEK (20 wt%, Pt:Ru atomic ratio of 50:50, Lot#3028401) was used.

3. RESULTS AND DISCUSSION

The measured Pt:Sn atomic ratios of the obtained electrocatalysts prepared by ARP and BH methods were similar to the nominal atomic ratios used in the preparations (Table 1).

Table 1: Pt:Sn atomic ratios and mean particle size of the prepared electrocatalysts

Method	Pt:Sn atomic ratio - nominal	Pt:Sn atomic ratio - EDX	Particle size ^a (nm)
ARP	50:50	52:48	2.5
ARP	90:10	87:13	3.1
BH	50:50	47:53	4.2
BH	90:10	84:16	7.0

^a Mean particle size calculated from XRD data using the Scherrer equation [14].

The X-ray diffractograms of the electrocatalysts are shown in Fig. 1. The broad peak at about $2\theta = 25^\circ$ was associated with the Vulcan XC72R support material. The PtSn/C electrocatalysts with a Pt:Sn atomic ratio of 90:10, produced by ARP and BH methods, showed five peaks at about $2\theta = 40^\circ, 47^\circ, 67^\circ, 82^\circ$ and 87° characteristic of the fcc structure of platinum and platinum alloys [5,6,9]. The PtSn/C electrocatalysts with a Pt:Sn atomic ratio of 50:50 prepared by ARP and BH methods also showed the peaks characteristic of platinum fcc structure and two peaks at about $2\theta = 34^\circ$ and 52° that were identified as SnO_2 phase. Very recently, it was described that SnO_2 nanoparticles with tetragonal crystalline structure were prepared by heating ethylene glycol solutions containing $SnCl_2$ at atmospheric pressure [15], which is very similar to the conditions used in the preparation of PtSn/C electrocatalysts by ARP method. However, the extent of SnO_2 phase in the

electrocatalysts produced by ARP and BH methods could not be determined by the employed techniques. The mean particle sizes calculated from X-ray diffractograms (Table 1) showed that the nanoparticles of PtSn/C electrocatalysts prepared by ARP method have smaller sizes than the ones prepared by BH method. In the ARP method, ethylene glycol was used as solvent and reducing agent and it also acted as a stabilizing agent preventing growth of nanoparticles [16].

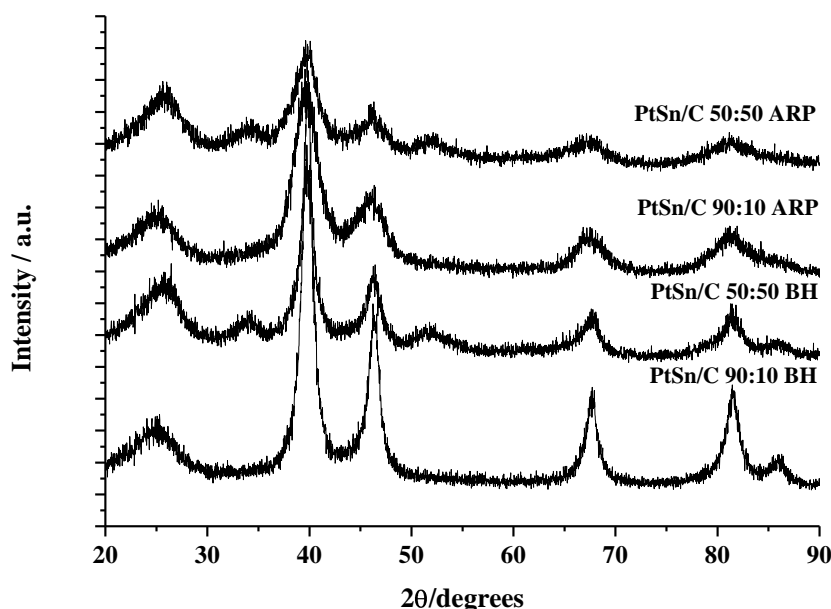


Figure 1: X-ray diffractograms of PtSn/C electrocatalysts

The cyclic voltammograms of PtSn/C electrocatalysts in the absence of ethanol are shown in Fig. 2. The PtSn/C electrocatalysts prepared by ARP method do not have a well-defined hydrogen adsorption-desorption region (0-0.4V), which was characteristic of platinum alloys [17]. The PtSn/C electrocatalyst with a Pt:Sn atomic ratio of 50:50 showed an increase in the currents in the double layer (0.4-0.8V) compared to the PtSn/C electrocatalyst with a Pt:Sn atomic ratio of 90:10. This could be attributed to the presence of tin oxide species [17], as observed on the X-ray diffractogram. The PtSn/C

electrocatalysts produced by BH method do not have a well-defined hydrogen region and this characteristic became more evident for PtSn/C electrocatalyst with a Pt:Sn atomic ratio of 50:50. This sample also showed an increase in the currents in the double layer compared to the electrocatalyst with Pt:Sn atomic ratio of 90:10. These results suggest that the PtSn/C electrocatalyst with Pt:Sn atomic ratio of 50:50 produced by ARP method have a good distribution of Pt and Sn species on the nanoparticles surface, while the PtSn/C electrocatalyst with a Pt:Sn atomic ratio of 50:50 produced by BH method seems to have the nanoparticles surface enriched with tin oxide species.

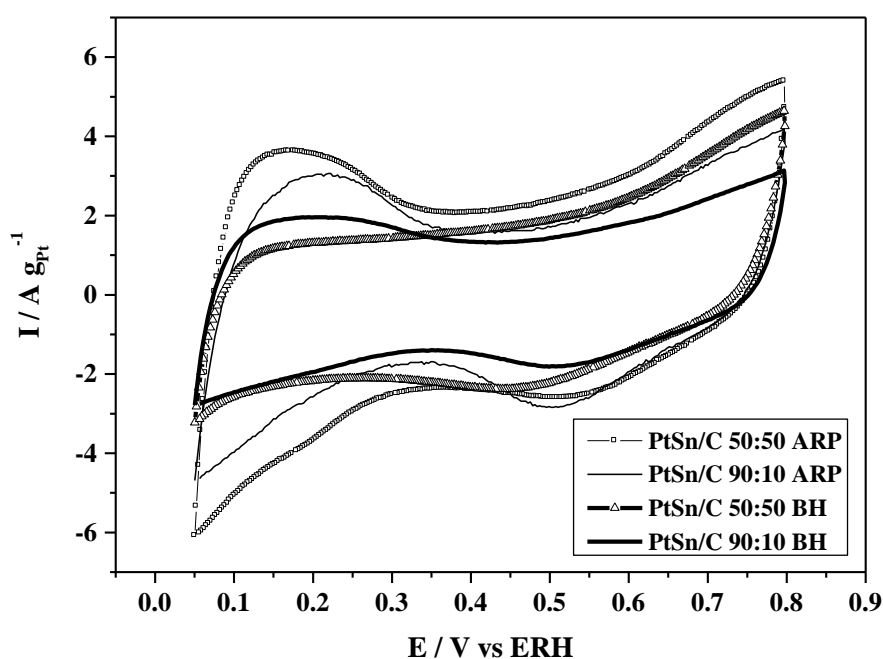


Figure 2: Cyclic voltammetry of PtSn/C electrocatalysts in $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ with a sweep rate of 10 mV s^{-1} .

The performances of PtSn/C electrocatalysts for ethanol electro-oxidation are shown in Fig. 3. The anodic cyclic voltammetry responses were plotted after subtracting the background currents [12,13] and the current values were normalized per gram of platinum, considering that ethanol adsorption and dehydrogenation occur only on platinum sites at room

temperature [18,19]. The performances of PtSn/C electrocatalysts were better for ethanol oxidation than PtRu/C electrocatalyst because the oxidation started at lower potentials and high current values were obtained in the region of interest for direct ethanol fuel cell (0.2–0.6V). The better performances of PtSn/C electrocatalysts have been attributed to changes in the platinum lattice due to the addition of tin and to electronic interaction between platinum and tin, both of which favor C-C bond cleavage, while the CO-intermediates formed during breaking of C-C bond were removed by tin oxide species (bifunctional mechanism) [6,7,20]. The PtSn/C electrocatalyst with a Pt:Sn atomic ratio of 50:50 produced by BH method showed the lowest onset potential ($\sim 0.2V$), which could be attributed to the presence of more tin oxide species on the nanoparticles surface, as observed by XRD and CV experiments. However, the current values in the region of interest for direct ethanol fuel cell were lower than those observed for PtSn/C electrocatalyst with a Pt:Sn atomic ratio of 90:10 produced by the same method.

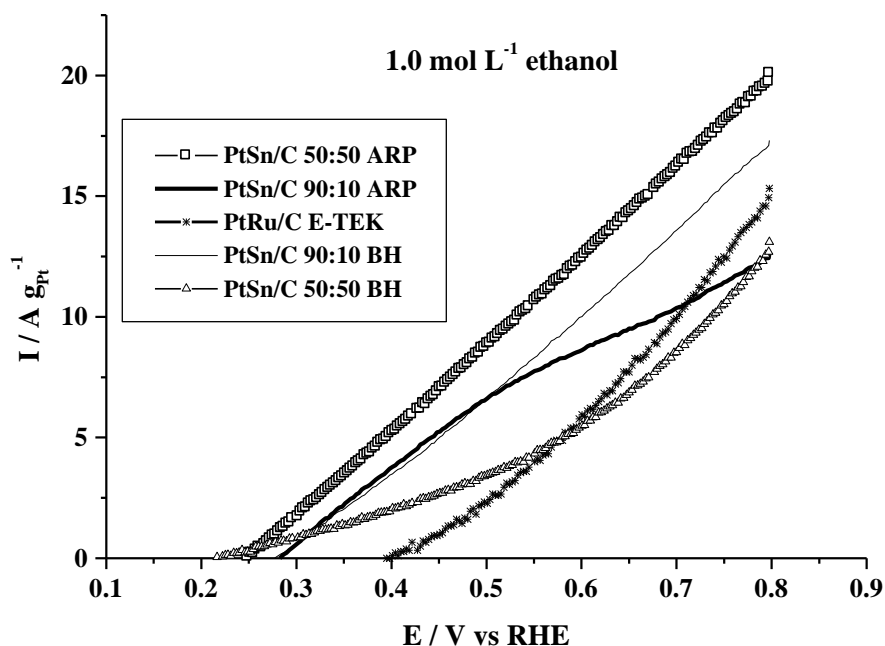


Figure 3: Cyclic voltammetry of PtSn/C and PtRu/C electrocatalysts in $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ containing 1.0 mol L^{-1} of ethanol with a sweep rate of 10 mV s^{-1} , considering only the anodic sweep.

For PtSn/C electrocatalysts prepared by ARP method, the onset potential observed for PtSn/C electrocatalyst with a Pt:Sn atomic ratio of 50:50 ($\sim 0.25V$)

was smaller than the one obtained for PtSn/C electrocatalyst with a Pt:Sn atomic ratio of 90:10 (~ 0.30V), which is similar to that which was observed for electrocatalysts prepared by BH method. On the other hand, PtSn/C electrocatalyst with Pt:Sn atomic ratio of 50:50 showed higher current values than PtSn/C electrocatalyst with Pt:Sn atomic ratio of 90:10 in the region of interest for direct ethanol fuel cell.

4. CONCLUSIONS

The ARP and BH methods were effective for making active PtSn/C electrocatalysts for ethanol oxidation. The X-ray diffractograms of electrocatalysts showed the typical fcc structure of platinum and platinum alloys and for electrocatalysts prepared with a Pt:Sn atomic ratio of 50:50 the presence of SnO₂ phase was also observed. PtSn/C electrocatalysts prepared by ARP method have smaller nanoparticle sizes than the ones prepared by BH method, which could be due to a stabilizing effect of ethylene glycol that prevents nanoparticle growth. The cyclic voltammograms suggest that the electrocatalysts produced by ARP method have a good distribution of Pt and Sn species on the nanoparticles surface, while PtSn/C electrocatalyst with Pt:Sn atomic ratio of 50:50 produced by BH method has the nanoparticles surface enriched with tin oxide species. The best performance for ethanol electro-oxidation was observed for the electrocatalyst with Pt:Sn atomic ratio of 50:50 prepared by ARP method. By the BH method a superior performance was obtained for the electrocatalyst with Pt:Sn atomic ratio of 90:10, showing that the electrocatalysts performance depends greatly on preparation procedures and Pt:Sn atomic ratios.

ACKNOWLEDGMENTS

The authors thank CNPq (Processo n^o 471288/2004-7) and FAPESP (03/03127-0) for financial support.

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