

Preparation of PtSn/C Skeletal-Type Electrocatalysts for Ethanol Electro-oxidation

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PtSnCu/C electrocatalysts were synthesized with 20 wt% of metals loading and different Pt:Sn:Cu atomic ratios by borohydride reduction method using 2-propanol as solvent, $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ as metals sources, NaBH_4 as reducing agent and carbon black Vulcan XC72 as support. In a second step, the electrocatalysts were treated with nitric acid. The obtained materials were characterized by X-ray diffraction and EDX analysis. The electro-oxidation of ethanol was studied by chronoamperometry in acid medium at room temperature. The X-ray diffractograms of the as-synthesized electrocatalysts showed the typical face-centered cubic (FCC) structure of Pt and Pt alloys. After treatment with nitric acid the X-ray diffractograms showed that the FCC structure was preserved and EDX analysis that Sn and Cu were partially removed. The results obtained by chronoamperometry showed for all electrocatalysts an increase of performance for ethanol electro-oxidation after acid treatment.

Introduction

Fuel cells that use alcohols directly as combustible (Direct Alcohol Fuel Cell - DAFC) are attractive as power sources for portable and mobile applications. Methanol is the fuel most studied and also the one with the best results. However, ethanol offers an attractive alternative as fuel because it is produced in large quantities from renewable sources and it is much less toxic than methanol. On the other hand, the complete oxidation of ethanol to CO_2 in fuel cells is still a challenge to be overcome, due to difficulty in breaking the C-C bond. PtSn/C electrocatalysts have been shown to be the most active for ethanol electro-oxidation, however, their activity depends largely on the preparation process (1). A recent study (2) showed that a new class of electrocatalysts (PtCu/C) of high activity, can be obtained by structural modification of the Pt-Cu alloy by partial leaching of Cu by electrochemical treatment (dealloying process). The PtCu/C electrocatalysts treated by this process and applied in reduction of oxygen in PEMFC showed an improvement of 4 times in terms of electrocatalytic activity per mass of Pt and more than 10 times in terms of specific activity if compared to the electrocatalyst Pt/C in the state of the art. When a metal is leached from an alloy, electrochemically or chemically in acidic solutions, this results in a skeletal-type electrocatalyst (3). The present work aims at preparing PtSnCu/C electrocatalysts by borohydride reduction method and activate it through chemical dealloying process (Cu removal by acid treatment) in order to obtain PtSn/C (skeletal-type) electrocatalysts more active for ethanol electro-oxidation.

Experimental

Preparation and characterization of PtSn/C skeletal-type electrocatalysts

The PtSnCu/C electrocatalysts were prepared with 20 wt% of metals loading and different Pt:Sn:Cu atomic ratios by borohydride reduction method. 2-propanol (Merck) was used as solvent, $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (Aldrich), $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (Aldrich) and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (Aldrich) as metals sources, carbon black Vulcan XC72 (Cabot) as support and NaBH_4 (Aldrich) as a reducing agent. Initially, the metal salts were dissolved in 2-propanol and carbon black was dispersed in the solution. It was subsequently added, at once, a solution of NaBH_4 to the mixture, which was kept under stirring for 40 min at room temperature. Finally, the mixture was filtered and the material obtained was washed with water in excess and dried at 70° C for 2 h. In a second step, the PtSnCu/C electrocatalysts were dispersed in concentrated nitric acid (HNO_3) and the mixture was kept under stirring for 70 min at room temperature (chemical dealloying process). Then the mixture was filtered and the material obtained was washed with water in excess and dried at 70° C for 2 h.

The Pt:Sn:Cu atomic ratios were obtained by EDX analysis using a Philips XL30 scanning electron microscope with a 20 keV electron beam and provided with EDAX DX-4 microanalyser.

The X-ray diffraction (XRD) analyses were carried out in a Miniflex II model Rigaku diffractometer using Cu $K\alpha$ radiation ($\lambda = 0.15406$ nm). The diffractograms were recorded at 2θ in the range 20° - 90° with step size of 0.05° and scan time of 2 s per step.

Ethanol Electro-Oxidation

The ethanol electro-oxidation was studied by chronoamperometry using the thin porous coating technique (4). 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 reference electrode was a RHE and the counter electrode was a platinized Pt plate. Chronoamperometry experiments were performed with a Microquimica (model MQPG01) potentiostat/galvanostat using 1.0 mol L⁻¹ of ethanol in 0.5 mol L⁻¹ H_2SO_4 solution saturated with N_2 at 0.5V and at room temperature.

Results and Discussion

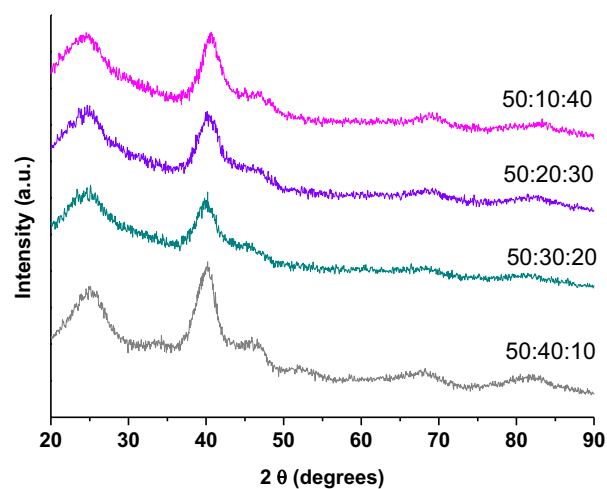
The EDX analysis (Table 1) of the PtSnCu/C electrocatalysts as-synthesized showed that the Pt:Sn:Cu atomic ratios were similar to the nominal values. After acid treatment, the Pt:Sn:Cu atomic ratios were modified indicating that Cu and Sn were partially removed.

The X-ray diffractograms (Figure 1) of the as-synthesized PtSnCu/C electrocatalysts showed a broad peak at about 25°, which was associated with the carbon support Vulcan XC72 and five diffraction peaks at about $2\theta = 40^\circ$, 47°, 67°, 82° and 87°, which are characteristic of face-centered cubic structure (FCC) of Pt and its alloys (4).

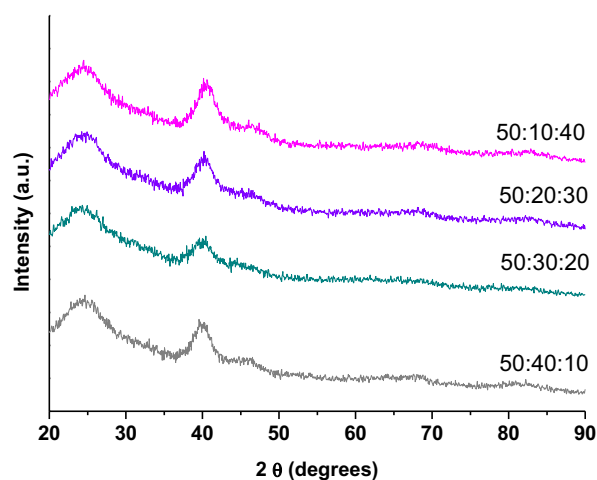
Table 1: Pt:Sn:Cu atomic ratios for PtSnCu/C electrocatalysts as-synthesized and after acid treatment.

Nominal Values	Pt:Sn:Cu Atomic Ratios	Pt:Sn:Cu Atomic Ratios After Acid Treatment
50:40:10	58:32:10	67:27:6
50:30:20	59:24:17	72:20:8
50:20:30	59:18:23	74:14:12
50:10:40	58:10:32	81:6:13

After acid treatment, the X-ray diffractograms of the PtSnCu/C electrocatalysts (Figure 1) showed that the Pt (FCC) structure was preserved.



(A)



(B)

Figure 1: X-ray diffractograms of the PtSnCu/C electrocatalysts as-synthesized (A) and after acid treatment (B).

The chronoamperometry experiments were carried out to examine the performance and stability of the as-synthesized and acid treated PtSnCu/C electrocatalysts for ethanol electro-oxidation (Figure 2). For all electrocatalysts it was observed an increase of performance after acid treatment while the stability remain essentially unchanged.

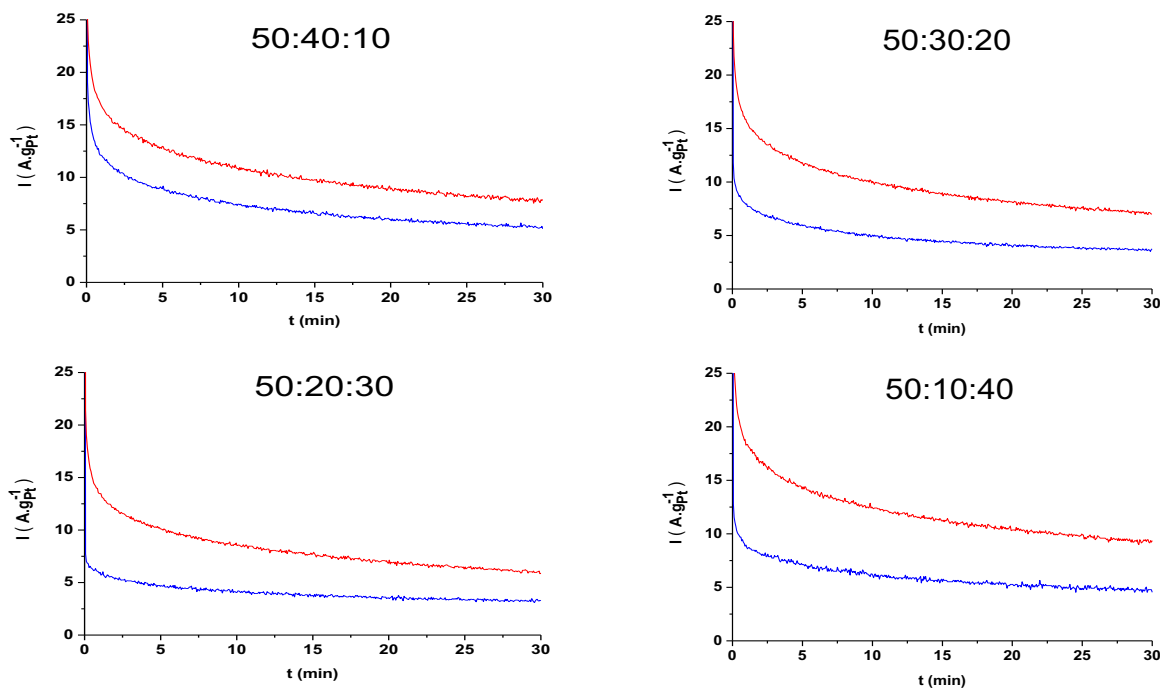


Figure 2: Chronoamperometry curves at 0.5 V in 1.0 mol L⁻¹ ethanol + 0.5 mol L⁻¹ H₂SO₄ for PtSnCu/C electrocatalysts before (■) and after (■) treatment with HNO₃.

The PtSnCu/C electrocatalyst with Pt:Sn:Cu atomic ratio of 50:10:40 after acid treatment showed the highest current value after 30 min and an increase of activity of about 100% compared to the as-synthesized material (Table 2). Comparing the percentage of variation between the final current values before and after acid treatment for all electrocatalysts it could be observed a tendency of an increase of the variation values (%) with the increase of Cu content in the as-synthesized samples. The increase of the electrocatalytic activity could be attributed to the acid treatment, which removes part of the non-noble metals of the PtSnCu/C electrocatalysts creating new structural arrangements and/or crystallographic characteristics on the nanoparticles surface resulting in a more active electrocatalyst (2).

Table 2: Final current values for the PtSnCu/C electrocatalysts before (B) and after (A) acid treatment.

Electrocatalyst	Final Current/B ($A \cdot g_{Pt}^{-1}$)	Final Current/A ($A \cdot g_{Pt}^{-1}$)	Variation (%)
50:40:10	5.1	7.9	56
50:30:20	3.8	7.0	84
50:20:30	3.3	5.9	79
50:10:40	4.5	9.4	107

Conclusions

PtSnCu/C electrocatalysts prepared by borohydride reduction showed a FCC structure of Pt alloys. After acid treatment, Sn and Cu were partially removed and the FCC structure was preserved. The acid-treated electrocatalysts were more active for ethanol electro-oxidation than the as-synthesized electrocatalysts. It was also observed an increase in the percentage of the variation of the final current values before and after acid treatment with the increase of the Cu content in the as-synthesized electrocatalysts. The results showed that PtSnCu/C (skeletal-type) electrocatalysts are very promising for ethanol electro-oxidation.

References

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