

Preparation of PtSn/C skeletal-type electrocatalyst for ethanol oxidation

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Abstract

PtSnCu/C electrocatalyst with Pt:Sn:Cu atomic ratio of 50:30:20 was prepared by borohydride reduction and the obtained material was further treated with nitric acid. The obtained material was characterized by EDX and XRD and tested for ethanol electro-oxidation in acid medium using chronoamperometry. The X-ray diffractogram of as-synthesized PtSnCu/C electrocatalyst showed typical face-centered cubic (fcc) structure of Pt alloy and after acid treatment it was observed that the Pt (fcc) structure was preserved. PtSnCu/C electrocatalyst acid-treated was more active for ethanol electro-oxidation than as-synthesized PtSnCu/C and PtSn/C electrocatalysts.

Keywords: PtSn/C electrocatalyst, skeletal-type, ethanol, fuel cell

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. Methanol has been considered the most promising fuel because it is more efficiently oxidized than other alcohols and PtRu/C electrocatalysts have been shown the best performance for anodic oxidation of methanol. However, 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 CO₂ 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. In this manner, its complete oxidation remains a great challenge and the principal products formed are acetaldehyde and/or acetic acid [1]. PtSn/C electrocatalysts have been shown good performance for ethanol electro-oxidation compared to PtRu/C electrocatalysts, however, their activities depends greatly on the preparation procedure [2]. Recently, Koh and Strasser [3] reported that after Cu dealloying from carbon-supported Pt-Cu alloy nanoparticle electrocatalyst the resulting material showed a significant activity enhancement for oxygen-reduction reaction in fuel cells compared to pure Pt. When a metal is leached from an alloy, electrochemically or chemically in acidic solutions, this results in a skeletal-type catalyst [4]. In this study, PtSnCu/C electrocatalyst (carbon-supported PtSnCu alloy) was prepared by borohydride reduction and the obtained material was treated with nitric acid to remove non-noble metals by chemical leaching in order to obtain a carbon-supported Pt alloy skeletal-type electrocatalyst. The obtained material was tested for ethanol electro-oxidation.

2. Experimental

2.1. Synthesis and characterization of the electrocatalysts

Pt/C, PtSn/C (Pt:Sn atomic ratio of 50:50) and PtSnCu/C (Pt:Sn:Cu atomic ratio of 50:30:20) electrocatalysts were prepared with 20 wt% of metal loading by borohydride reduction. $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ were dissolved in 2-propanol and the carbon support Vulcan XC72 was dispersed in the solution. A solution of sodium borohydride was added and the final mixture was kept under stirring for 40 min at room temperature. Finally, the mixture was filtered and the solid was washed with water and dried at 70°C for 2h. In a second step, the PtSnCu/C electrocatalyst was dispersed in concentrated nitric acid and it was kept for 70 min under stirring at room temperature. After this, the mixture was filtered and the solid was washed with water and dried at 70°C for 2h.

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.

2.2. Electro-oxidation of ethanol

Chronoamperometry experiments were carried out to examine the electrochemical activity and stability of the electrocatalysts. An amount of 20 mg of the electrocatalyst was added to 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 H₂SO₄ solution saturated with N₂ at 0.5V and at room temperature.

3. Results and Discussion

Pt/C, PtSn/C and PtSnCu/C electrocatalysts were prepared by borohydride reduction (Table 1).

Table 1. Pt:Sn and Pt:Sn:Cu atomic ratios and average crystallite sizes of the electrocatalysts

Electrocatalyst	Pt:Sn:Cu atomic ratio (nominal)	Pt:Sn:Cu atomic ratio (EDX)	Crystallite size (nm)
Pt/C	--	--	5
PtSn/C	50:50	53:47	3
PtSnCu/C	50:30:20	52:29:19	2
PtSnCu/C*	--	68:21:11	2

*after acid treatment

The EDX analysis of the as-synthesized PtSn/C (50:50) and PtSnCu/C (50:30:20) electrocatalysts showed similar Pt:Sn and Pt:Sn:Cu atomic ratios to the nominal values. After acid treatment of the PtSnCu/C electrocatalyst the obtained Pt:Sn:Cu atomic ratio was 68:21:11 indicating that Cu and Sn atoms were partially removed. The X-ray diffractograms of Pt/C, PtSn/C and PtSnCu/C electrocatalysts are shown in Fig. 1. The XRD diffractogram of the Pt/C electrocatalyst showed a broad peak at about 25° , which was associated to the Vulcan XC72 support material, and five diffraction peaks at about $2\theta = 40^\circ, 47^\circ, 67^\circ, 82^\circ$ e 87° , which are characteristic of the face-centered cubic (fcc) structure of Pt [5]. Peaks that could be attributed to Sn or Cu oxides were not observed in the diffractograms. However, for PtSn/C electrocatalysts it was observed a shift of the peaks relative to Pt(fcc) phase to lower angles compared to those of Pt/C electrocatalyst indicating an alloy formation between Pt and Sn. PtSnCu/C electrocatalyst showed a shift of the peaks relative to Pt(fcc) structure to higher angles compared to those of PtSn/C electrocatalyst, which could be attributed to the incorporation of copper atoms into the PtSn (fcc) lattice. After the acid treatment, the X-ray diffractogram of the PtSnCu/C electrocatalyst showed that the Pt (fcc) structure was preserved.

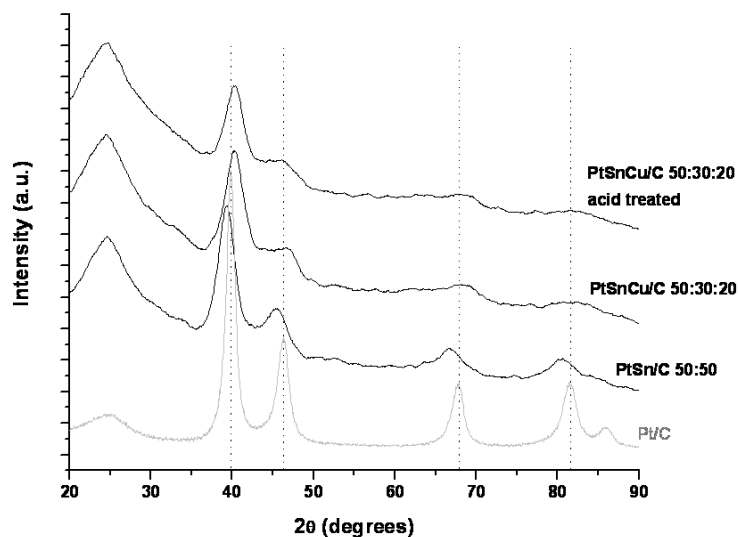


Figure 1. X-ray diffractograms of PtSn/C and PtSnCu/C electrocatalysts.

The average crystallite sizes were calculated using the Scherrer equation [5] (Table 1). A decrease of the crystallite size was observed for PtSn/C electrocatalyst (3 nm) compared to Pt/C electrocatalyst (5 nm). The addition of Cu to PtSn/C electrocatalyst also leads to a decrease of the crystallite size to 2 nm, while this value did not change after acid treatment of the PtSnCu/C electrocatalyst.

The chronoamperometric curves of PtSn/C electrocatalysts in 1 mol L^{-1} ethanol in $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ at 0.5 V for 30 min are shown in Figure 2. The current values were normalized per gram of platinum, considering that ethanol adsorption and dehydrogenation occur only on platinum sites at room temperature [5].

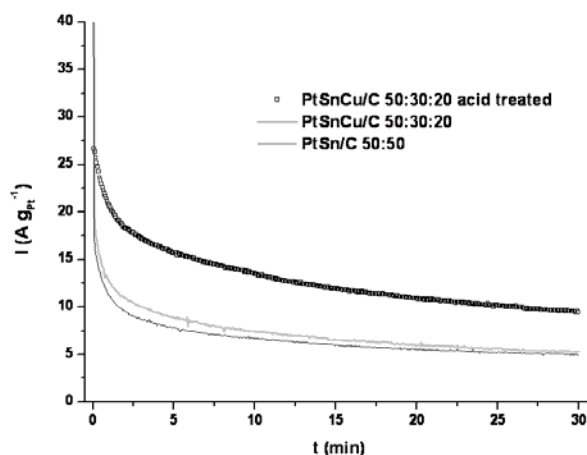


Figure 2. Current-time curves at 0.5 V for PtSn/C and PtSnCu/C electrocatalysts in 1.0 mol L⁻¹ ethanol in 0.5 mol L⁻¹ H₂SO₄.

The PtSnCu/C acid-treated electrocatalyst was more active for ethanol electro-oxidation than the as-synthesized PtSn/C and PtSnCu/C electrocatalysts. The increase of electrocatalytic activity for ethanol oxidation could be attributed to the acid treatment that remove part of the non-noble metals of PtSnCu/C electrocatalyst creating new structural arrangements and/or more active crystallographic facets of Pt atoms at the nanoparticle surface [3].

4. Conclusions

The preliminary results showed that the carbon-supported Pt alloy acid-treated (skeletal-type) electrocatalysts are very promising for ethanol electro-oxidation. Further work is necessary to characterize the catalysts using different surface analysis techniques and to elucidate the mechanism of ethanol electro-oxidation. Also, it is necessary to perform experiments using these electrocatalysts in gas diffusion electrodes for tests in single direct ethanol fuel cells.

References

- [1] E. Antolini, 2007, Catalysts for direct ethanol fuel cells, *J. Power Sources*, 170(1), 1-12.
- [2] E.V. Spinacé, L.A.I. do Vale, R.R. Dias, A.O. Neto, M. Linardi, 2006, PtSn/C electrocatalysts prepared by different methods for direct ethanol fuel cell, *Stud. Surf. Sci. Catal.*, 162, 617-624.
- [3] S. Koh, P. Strasser, 2007, Electrocatalysis on bimetallic surfaces: modifying catalytic reactivity for oxygen reduction by voltammetric surface dealloying, *J. Am. Chem. Soc.*, 129, 12624-12625.
- [4] C. Bock, H. Halvorsen, B. MacDougall, 2008, Catalyst Synthesis Techniques in PEM Fuel Cell Electrocatalysts and Catalyst Layers, J. Zhang (Ed.), Springer, p. 471.
- [5] A.O. Neto, R.R. Dias, M.M. Tusi, M. Linardi, E.V. Spinacé, 2007, Electro-oxidation of methanol and ethanol using PtRu/C, PtSn/C and PtSnRu/C electrocatalysts prepared by an alcohol-reduction process, *J. Power Sources*, 166 (1), 87-91.

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