

# Electro-oxidation of methanol using PtLa/C electrocatalysts prepared by alcohol-reduction process

*Almir Oliveira Neto, EV Spinace, TAB Santoro, MLM Bejarano, EM Arico, CALGO Forbicini and M Linardi*

Instituto de Pesquisa Energéticas e Nucleares-IPEN/CNEN-SP, Av. Professor Lineu Prestes, 2242, Cidade Universitária, 05508-900, São Paulo SP, Brazil.

## INTRODUCTION

Fuel cell employing alcohols directly as combustible (Direct Alcohol Fuel Cell - DAFC) are attractive as power sources for mobile, stationary and portable applications. Compared to hydrogen-fed fuel cells, which need a reforming system, or have hydrogen storage problems. DAFC uses a liquid fuel simplifying the fuel system. Methanol has been considered the most promising fuel, because it is more efficiently oxidized than others alcohols, however, slow anode kinetics are observed [1-4]. In the last years many studies have been made for the development of new electrocatalysts for anodic oxidation of small organic molecules for fuel cell systems, particularly, methanol [5]. It is known that the performance of Pt-based electrocatalysts in methanol oxidation is improved by the presence of elements that form oxide species at low potentials [4,5]. The most stable oxidation state of rare earth elements is the trivalent and they form oxide species in the presence of oxygen [6]. In this work, Pt/C (20wt% Pt) and PtLa/C electrocatalysts (20wt% PtLa) with Pt:La atomic ratios of 70:30 and 50:50 were prepared by alcohol-reduction process (ARP) and tested for methanol oxidation aiming fuel cell application.

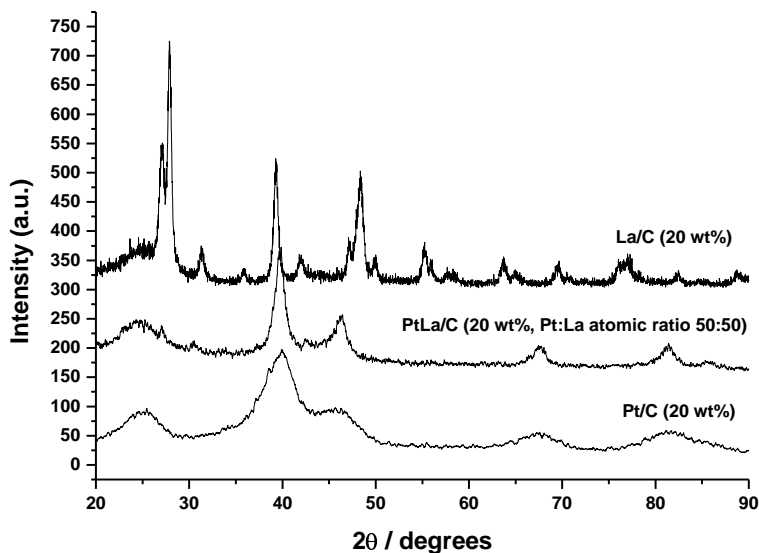
## EXPERIMENTAL

Pt/C, La/C and PtLa/C electrocatalysts were prepared by alcohol-reduction process (ARP) using  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  (Aldrich) and  $\text{LaCl}_3 \cdot x\text{H}_2\text{O}$  (Aldrich) as metal sources, ethylene glycol (Merck) as solvent and reducing agent and carbon Vulcan XC72R as support [7,8]. The Pt:La 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. Electrochemical studies of the electrocatalysts were carried out using the thin porous coating technique [9]. The working electrode was constructed using PTFE cylinder with a cavity 0.15 mm deep and 0.36 cm<sup>2</sup> area. A known amount of the electrocatalysts were treated with a 2% PTFE suspension and transferred quantitatively to the cavity. The reference electrode was a RHE and the counter electrode was a platinized Pt plate. Electrochemical measurements were made using a Microquímica (model MQPG01, Brazil) potentiostat/galvanostat coupled to a personal computer with Microquímica software. Cyclic Voltammetry was performed in a 0.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> solution

saturated with N<sub>2</sub>. The evaluation of methanol oxidation was performed at 25°C using 1.0 mol L<sup>-1</sup> solution. For comparative purposes a commercial Pt/C catalyst from E-TEK<sup>®</sup> (20 wt% Pt, Lot # 3182602) was used.

## RESULTS AND DISCUSSION

Pt/C, La/C and PtLa/C electrocatalysts (20 wt%) were prepared in a single step using ethylene glycol as solvent and reducing agent in presence of carbon Vulcan XC72R [7,8]. As the reduction potential of La is about 3.5 V negative of that for Pt [6], it was not possible to reduce La(III) ions in the conditions used in the chosen methodology. Thus, the electrocatalysts were prepared in alkaline medium (KOH/PtLa molar ratio of 8) in order to deposit La(III) ions as Lanthanum oxide or hydroxide and Pt(IV) ions, which were reduced by ethylene glycol, as metallic Pt on the carbon support. The EDS analysis showed that the Pt:La atomic ratios were similar to the ones used in the preparations. The X-ray diffractogram of the Pt/C, La/C and PtLa/C electrocatalysts are shown in Figure 1. In all diffractograms a broad peak at about 25° was



associated with the Vulcan XC72R support material. The diffractogram of Pt/C electrocatalyst showed peaks at approximately  $2\theta = 40^\circ$ ,  $47^\circ$ ,  $67^\circ$  and  $82^\circ$ , which are associated with the (111), (200), (220) and (311) planes, respectively, of the fcc structure characteristic of platinum [10], while the diffractogram of La/C electrocatalyst showed that La(III) ions were supported as La(OH)<sub>3</sub> [11]. The diffractogram of PtLa/C electrocatalyst with Pt:La atomic ratio of 50:50 showed the peaks characteristic of fcc Pt and the presence of peaks of La (OH)<sub>3</sub>.

Figure 1: X-ray diffractograms of Pt/C, La/C and PtLa/C electrocatalysts prepared by ARP.

Cyclic voltammograms of Pt/C and PtLa/C electrocatalysts are shown in Figure 2. Pt/C electrocatalyst showed the typical hydrogen peaks (0-0.4V), which are similar to that of smooth

platinum and characteristic for this material in acid medium [9]. PtLa/C electrocatalysts do not have a well-defined hydrogen adsorption-desorption region (0 – 0.4V) and showed an increase of current values in the double layer region (0.4-0.8V), which could be attributed to the presence of La oxygenated species.

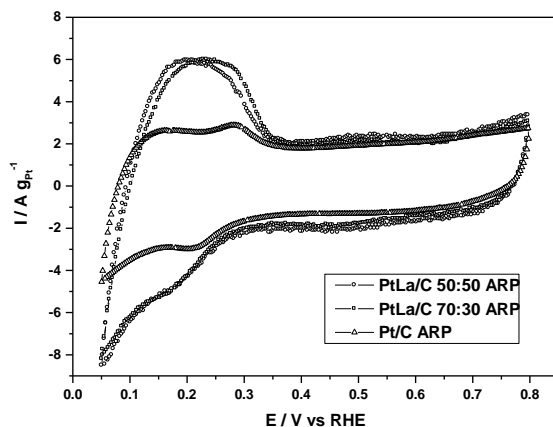


Figure 2: Cyclic voltammetry of the electrocatalysts in 0.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> with a sweep rate of 10 mV s<sup>-1</sup>.

The Pt/C and PtLa/C electrocatalysts performances in methanol oxidation are shown in Figure 3.

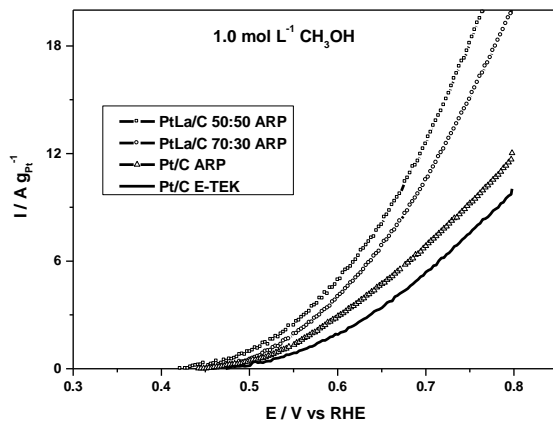


Figure 3: Cyclic voltammetry of the electrocatalysts in 0.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> and 1.0 mol L<sup>-1</sup> of methanol with sweep rate of 10 mV s<sup>-1</sup>, considering only the anodic sweep.

The anodic cyclic voltammetry responses were plotted after subtracting the background currents [12] and the currents values were normalized per gram of platinum, considering that methanol

adsorption and dehydrogenation occur only on platinum sites at ambient temperature [13]. PtLa/C electrocatalysts showed better performance for methanol oxidation than Pt/C E-TEK and Pt/C prepared by ARP.

## CONCLUSIONS

Active PtLa/C electrocatalysts for methanol oxidation could be prepared by alcohol-reduction process in alkaline medium. The X-ray diffractogram of PtLa/C electrocatalysts showed the typical fcc structure of platinum and the presence of La(OH)<sub>3</sub>. The electrochemical studies at ambient temperature showed that PtLa/C electrocatalysts were more active than Pt/C electrocatalysts in the potential range of interest for direct methanol fuel cell (0.3-0.6V). The superior activity of PtLa/C electrocatalysts could be attributed probably to the bi-functional mechanism where Pt acts on methanol adsorption and dissociation and La provides oxygenated species at lower potentials for oxidative removal of adsorbed CO. Further work is necessary to investigate these electrocatalysts in gas diffusion electrodes for tests in single direct methanol fuel cell.

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