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Research Article

Ethanol Electrooxidation on Pt with Lanthanum Oxide as Cocatalyst in a DAFC

T. A. B. Santoro,[1,2] A. Oliveira Neto,[2] C. A. L. G. de O. Forbicini,[2] M. Linardi,[2] J. L. Rodríguez,[1] and E. Pastor[1]

[1] *Departamento de Química Física, Instituto Universitario de Materiales y Nanotecnología, Universidad de La Laguna, C/Astrofísico Francisco Sánchez s/n, 38071 La Laguna, Spain*
[2] *Instituto de Pesquisas Energéticas e Nucleares (IPEN), CNEN-SP, Avenida Professor Lineu Prestes 2242, Cidade Universitária, 05508-900 São Paulo, SP, Brazil*

Correspondence should be addressed to T. A. B. Santoro, thaisabsantoro@yahoo.com.br

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Electrocatalytic activity toward ethanol electrooxidation of Pt particles in PtLa/C catalysts with different Pt : La ratios has been studied with different electrochemical and spectroscopic techniques, and the results were compared to those of Pt/C catalyst. Significant enhancement in the electrocatalytic activity has been achieved by depositing the Pt particles with lanthanum oxides/hydroxides using an alcohol reduction method. Compared to Pt/C catalyst, PtLa/C materials exhibit a lower onset potential and a higher electron-transfer rate constant for the investigated reaction. These studies illustrate the possibility of utilizing Pt/C with La oxides/hidroxides as electrocatalyst for direct alcohol fuel cells (DAFCs).

1. Introduction

In catalysis, numerous applications can be found for lanthanum oxide. It is used as support for metals that catalyze reactions such as methanol decomposition, ammonia oxidation, and methane dry reforming [1–4]. It is also recognized as an active and selective catalyst for several processes [5–7]. It has been shown that lanthanum oxides can substantially modify the chemical behaviour of highly dispersed metal catalysts [6]. In this system, several chemical species are present such as La_2O_3 or $La(OH)_3$ [8], which could be implied in the electrooxidation of alcohols like methanol or ethanol, for example.

In the past decades, direct alcohol fuel cells (DAFCs) have received much attention due to their possible applications in transportation and portable electronic devices [9–15]. Methanol or ethanol can be directly used as fuel in DAFCs without external reformer. Ethanol has higher energy density compared with methanol [15, 16] and it is more attractive as fuel for DAFCs: it is safer and can be produced in great quantities from biomass. However, the ethanol electrooxidation has slow reaction kinetics that is still the main problem for its direct application in an ethanol fuel cell (DEFC). A lot of work has been done with the purpose to prepare catalysts with sufficiently high catalytic activity and CO tolerance for ethanol electrooxidation. It is accepted that the coexistence of some metal oxides with Pt can improve the catalytic activity of Pt-based catalysts for this reaction.

In the present work, the effect of the addition of La oxides/hidroxides to Pt/C is investigated for ethanol electrooxidation [16]. PtLa/C catalyst powders with different compositions were prepared and compared to Pt/C. X-ray diffraction (XRD), cyclic voltammetry (CV), steady-state polarization experiments, and Fourier transform IR spectroscopy (FTIRS) were employed as characterization techniques to provide information on the physicochemical properties as well as on the catalytic activity of these materials towards the electrochemical reactions of ethanol.

2. Experimental

PtLa/C with different Pt : La atomic ratios and Pt/C catalysts were prepared by an alcohol reduction process in alkaline

environment (KOH/Pt : La molar ratio of 8) using Vulcan XC 72R as support. Metal precursors were $H_2PtCl_6 \cdot 6H_2O$ (Aldrich) and $LaCl_3 \cdot xH_2O$ (Aldrich), and ethylene glycol (Merck) was employed as solvent and reducing agent [17–19]. The reduction potential of La is about 3.5 V more negative than that of Pt [20]. Therefore, it is not possible to reduce La(III) ions to La^0 in the conditions of the chosen methodology. Thus, in alkaline medium La(III) ions are deposited as lanthanum oxide and/or hydroxide. On the other hand, Pt (IV) ions can be reduced by ethylene glycol to metallic Pt nanoparticles, which are placed on the carbon support. Characterization of prepared materials by XRD and transmission electron microscopy (TEM) has been described in a previous work where it was proved that La is deposited in the form of oxides and hydroxides by this procedure [21]. The diffractograms of PtLa/C electrocatalysts showed the peaks characteristic of fcc Pt and the presence of the contributions of La_2O_3 at 26°, 29°, 34°, and 56° (JPDF 000–83–1354) and those of $La(OH)_3$ at 27°, 31°, and 43° (JPDF 000–75–1900) [21, 22].

Dispersive X-ray (EDX) analysis using a scanning electron microscope Philips XL30 with a 20 keV electron beam and provided with EDAX DX-4 microanalyser was used to establish the real composition of the materials investigated in the present paper.

The electrochemical measurements for the ethanol oxidation reaction were carried out with a three-electrode flow cell. A hydrogen electrode in the electrolyte solution (RHE) was used as reference and a glassy carbon as counter electrode. The working electrode was prepared with 40 μL of a homogeneous mixture of 4 mg of powder electrocatalyst, ultrasonically dispersed in 1 mL of Milli-Q ultrapure water, and 38 μL of Nafion (Aldrich, 5 wt.%) [23]. This ink was deposited onto a glassy carbon polished surface disc, with geometric area of 0.28 cm^2, and dried in N_2 atmosphere before its utilization.

Electrochemical experiments were performed in a 1 mol L^{-1} CH_3CH_2OH + 0.5 mol L^{-1} H_2SO_4 solution for both PtLa/C and Pt/C electrocatalysts. Cyclic voltammograms (CVs) were recorded in the 0.05–0.90 V potential range at 0.01 Vs^{-1} and the current-time curves at a constant potential of 0.55 V. Activation pretreatment by potential cycling between 0.05 and 0.40 V in the base electrolyte (H_2SO_4 0.5 mol L^{-1}) was applied until a stabilized CV was achieved (the upper potential was set to 0.40 V in order to avoid La dissolution from the alloy). A potentiostat/galvanostat Autolab PGSTAT30 was used for these studies.

Electroactive area was calculated from the hydrogen adsorption/desorption region assuming 0.210 mC/cm^2 for the oxidation of an H adsorbed monolayer. Density current values in the paper are calculated with respect to the electroactive areas.

Fourier transform IR spectroscopy (FTIRS) experiments were carried out with a Bruker Vector 22 spectrometer equipped with an MCT (mercury cadmium telluride) detector. A small glass flow cell with a 60° CaF_2 prism at its bottom was employed. For each spectrum, 128 interferograms were collected at selected potentials with a resolution of 8 cm^{-1}, by applying 0.05 V single potential steps from a reference potential (0.05 V) in the positive going direction. Spectra are represented as the ratio R/R_0, where R and R_0 are the reflectance at the sample and reference spectra, respectively [11]. In this way, positive bands represent the loss and negative bands the gain of species at the sampling potential.

The working electrodes for FTIRS consist of a thin layer of a certain amount of the metal/C catalysts deposited over a polycrystalline gold disk. The geometric area of the disk was 0.85 cm^2. 40 μL of the homogeneous mixture of powder electrocatalyst was pipetted on the top of the gold disk and dried at ambient temperature. The electrolyte was 0.1 mol L^{-1} $HClO_4$ containing 1.0 mol L^{-1} of ethanol.

Table 1: Pt : La ratios from EDX analysis and current density from chronoamperometric curves obtained at 0.55 V.

Electrocatalysts	Atomic ratios (Pt : La)	$CV_{0.55}$ (mA cm^{-2})
PtLa 30 : 70	37 : 63	0.288
PtLa 50 : 50	57 : 43	0.213
Pt	—	0.092

3. Results and Discussion

The real compositions of the catalysts were established from EDX analysis and results are summarized in Table 1. The measured atomic ratios of PtLa/C were close to nominal ones, so it can be deduced that Pt and La oxides/hydroxides were successfully loaded on the carbon support without metal loss.

The cyclic voltammograms for ethanol oxidation on PtLa/C and Pt/C electrodes in 1.0 mol L^{-1} CH_3CH_2OH + 0.5 mol L^{-1} H_2SO_4 solution at room temperature are given in Figure 1. It can be observed that the CVs exhibit the irreversible nature of the ethanol electrooxidation that is characteristic of Pt-based catalysts. The onset for ethanol electrooxidation occurs at approximately 0.50 V but a shift to more negative potentials is clearly apparent when introducing La species in the material, especially in the case of the PtLa/C (30 : 70) catalyst. Moreover, different maximum current densities are achieved during the positive potential scan. The highest current density is apparent for PtLa/C (30 : 70) catalysts, and it is about twice that obtained for Pt/C. The PtLa/C (50 : 50) electrocatalyst also increases the catalytic activity, by a factor of 1.5 when compared to Pt/C. Therefore, the activity order towards ethanol electrooxidation can be established as follows: PtLa/C (30 : 70) > PtLa/C (50 : 50) > Pt/C. Then, the content of La oxides/hydroxides in the PtLa/C catalysts affects the catalytic activity for ethanol electrochemical oxidation allowing the oxidation at lower potentials and increasing the current density values.

Considering that ethanol does not react on La oxides/hidroxides, from these data it can be concluded that the addition of La oxides/hydroxides significantly increases the catalytic activity of Pt towards ethanol electrooxidation. Probably this result is related to the improvement of the kinetics of CO and other adspecies oxidation on Pt through

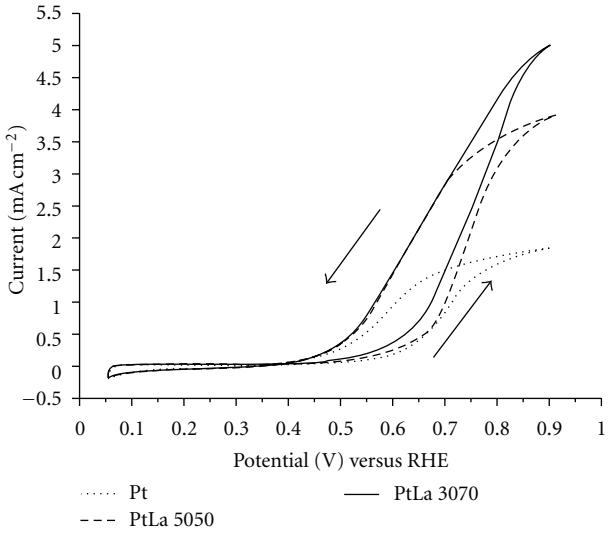

Figure 1: Cyclic voltammograms for ethanol electrooxidation on Pt/C, PtLa/C (50 : 50), and PtLa/C (30 : 70) electrocatalysts in 1.0 mol L^{-1} CH_3CH_2OH + 0.5 mol L^{-1} H_2SO_4 in the 0.05 to 0.90 V potential range at room temperature. Scan rate: 0.010 Vs^{-1}.

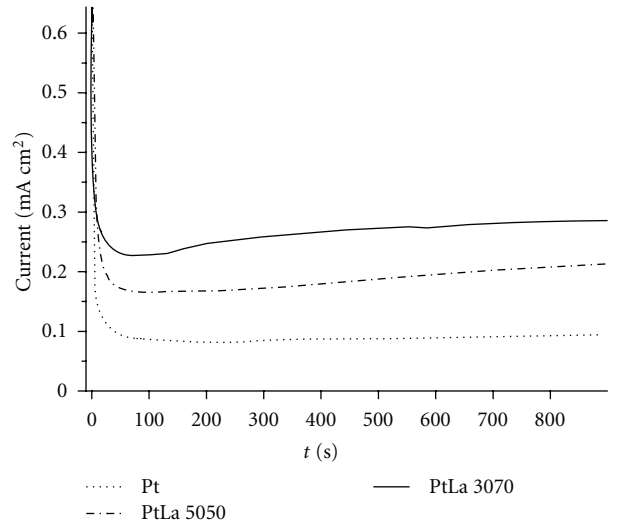

Figure 2: Current-time curves at 0.55 V in 1.0 mol L^{-1} CH_3CH_2OH + 0.5 mol L^{-1} H_2SO_4 solution for Pt/C, PtLa/C (50 : 50) and PtLa/C (30 : 70) electrocatalysts.

a bifunctional mechanism [24] (as no alloy is formed in these materials according to previous results in [21]).

To compare the cyclic voltammetric and the potentiostatic responses of the electrocatalysts, chronoamperometric curves in 1.0 mol L^{-1} CH_3CH_2OH + 0.5 mol L^{-1} H_2SO_4 were recorded at 0.55 V during 900 s. Results are given in Figure 2 and stable current density values summarized in Table 1. The same trend previously established from the CVs is observed.

All current-time curves display an initial fast current drop in the first 90 seconds followed by a slower rise only apparent for PtLa materials. This observation could be explained assuming that a fast poisoning of the Pt surface takes place in the first instants, but, in the presence of La oxides/hydroxides, slower oxidation of the poisons occurs to a certain extent at 0.55 V. Thus, the current increases until achieving a stable value when the concurrence between both processes (poisoning and oxidation of the adspecies) acquires the equilibrium. In other words, PtLa/C electrocatalysts are more resistant to the poisoning caused by ethanol intermediate adspecies causing a significant increase of performance with the augment of La oxides/hidroxides content. This behaviour could be attributed to the oxophilic character of La in $La(OH)_2$ and La_2O_3 [25].

Using CeO_2, an increment in performance was also described by Xua and coworkers [24]. They attributed the activity enhancement for alcohol electrooxidation after the addition of CeO_2 to the Pt catalysts to the bifunctional mechanism, where the formation of chemisorbed oxygen species was favoured by CeO_2 and promotes the oxidation of adsorbed carbon monoxide on the surface of Pt. Neto et al. [26] observed an improvement in ethanol electrooxidation using nanocrystalline Pt/CeO_2 composite electrodes. From the studies of carbon monoxide oxidation over Pt–CeO_2 and Pt–SnO_2, these authors associated the increase in the activity with the oxygen spillover from the oxides onto the Pt sites [26]. In a similar way, it is also possible that, in our case, the release of oxygen from the surface of La oxides/hidroxides particles contributes to facilitating the oxidation of adsorbed CO and other intermediate species on the Pt surface.

To provide complementary information on the electrochemical oxidation of ethanol, Fourier transform IR spectroscopy (FTIRS) was employed as catalyst characterization technique. According to Iwasita et al. [27], possible products during ethanol electrooxidation are CO_2, acetaldehyde, and acetic acid, although ethyl acetate could also be produced by the reaction of acetic acid with ethanol. Figure 3 presents the IR spectra acquired with p-polarized light in 1.0 mol L^{-1} CH_3CH_2OH + 0.5 mol L^{-1} H_2SO_4 solution during the progressive ethanol electrooxidation from 0.05 V up to 0.90 V for PtLa/C (50 : 50) catalyst. $HClO_4$ was used instead of H_2SO_4 in order to avoid the bands related to the adsorption of sulphate/bisulphate species.

In Figure 3, the growing in CO_2 production is indicated by the asymmetric stretching vibration band at 2343 cm^{-1}. The positive going features at 2983 and 2901 cm^{-1} correspond to CH_3CH_2OH and indicate the consumption of the alcohol in the thin layer. At 0.80 V all other contributions in the spectrum are well developed. At 1715 cm^{-1}, the stretching band of the carbonyl group (C=O) is observed. Both acetaldehyde and acetic acid could be responsible for this band, so it is not appropriated for identification purposes [27]. As the potential is stepped to more positive values, two other negative features at 1354 and 1278 cm^{-1} appear in the spectrum, parallel to the carbonyl band. According to Iwasita et al. [27], the spectrum of pure acetic acid presents in this region two bands due to the coupled C–O stretching and OH deformation.

These results confirm that CO_2 and acetic acid are produced during ethanol oxidation. On the other hand, the identification of acetaldehyde in the presence of comparable quantities of acetic acid is difficult. The characteristic features

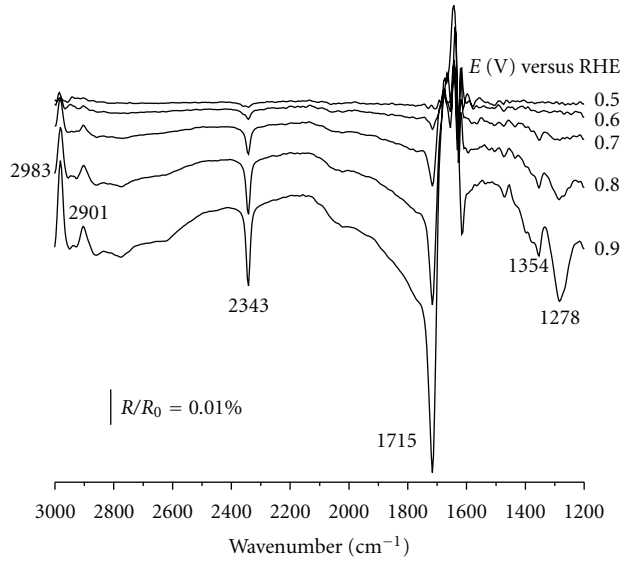

FIGURE 3: In situ FTIR spectra obtained in 1.0 mol L^{-1} CH_3CH_2OH + 0.1 mol L^{-1} $HClO_4$ solution for PtLa/C (50 : 50) electrocatalysts. P-polarized light; resolution: 8 cm^{-1}; E_{ref} = 0.05 V.

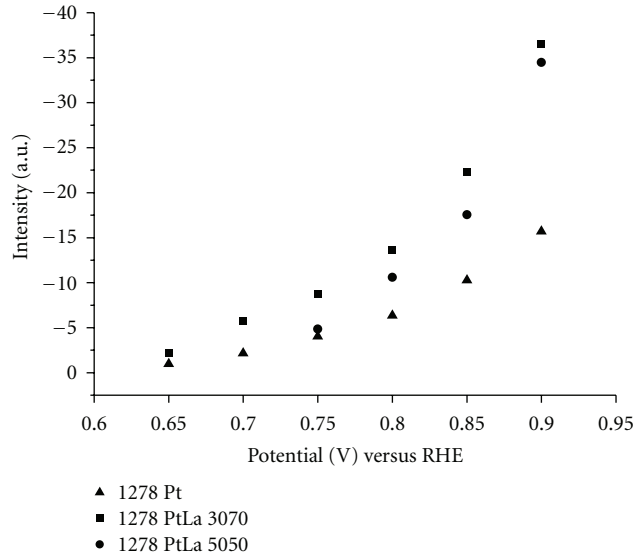

FIGURE 4: Potential dependence of the integrated band intensity (1278 cm^{-1}) from Figure 3 corresponding to acetic acid, for Pt/C, PtLa/C (50 : 50), and PtLa/C (30 : 70) electrocatalysts.

of acetaldehyde are the C=O stretch (in the region of the signal at 1715 cm^{-1}) and the symmetric CH_3 deformation (in the region of the signal at 1354 cm^{-1}). These bands can be then strongly overlapped with those of acetic acid. Assuming that the dual-path mechanism is acting for ethanol electrooxidation, CO_2 and acetic acid can be considered as representative of the two reactions pathways (acetaldehyde is produced in the same route as acetic acid).

The acetic acid (1278 cm^{-1}) and CO_2 (2343 cm^{-1}) productions can be followed integrating their characteristic bands from the spectra in Figure 3 and plotting the result as a function of the potential. The integrated intensity values are given in Figures 4 and 5, respectively. The same procedure for spectra collection has been followed with PtLa/C (30:70) and Pt/C, and the results for their integration are also included in Figures 4 and 5.

The bands at 2343 and 1278 cm^{-1} in Figures 4 and 5 follow similar potential dependences, increasing the intensity as the sample potential is set more positive. It is also observed that the amount of both acetic acid and CO_2 rises with the increment of La oxides/hidroxides content in the catalyst. However, some differences are apparent between the two PtLa/C electrocatalysts and have to be remarked.

In general, the onset electrooxidation potential observed in the CVs in Figure 1 is related to the onset in the CO_2 production (Figure 5) in all catalysts, whereas the formation of acetic acid starts at more positive potentials (Figure 4). This result suggests that it is necessary that adsorbed species initiate their oxidation to CO_2 in order to liberate Pt sites, where ethanol molecules from the solution can further react and produce acetaldehyde and acetic acid. Although the onset potentials for both CO_2 and acetic acid are similar for the three catalysts studied, from a detailed inspection of Figures 4 and 5, it is clearly observed a faster increase in the production of both CO_2 and acetic acid in the presence of

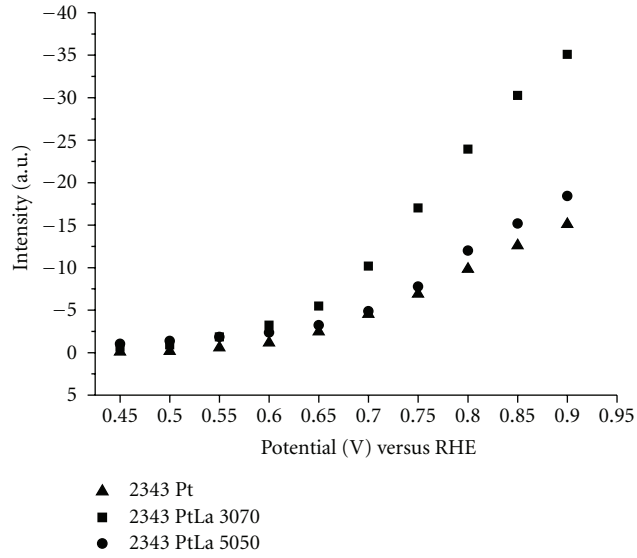

FIGURE 5: Potential dependence of the integrated band intensity (2343 cm^{-1}) from Figure 3 corresponding to CO_2, for Pt/C, PtLa/C (50 : 50), and PtLa/C (30 : 70) electrocatalysts.

La oxides/hydroxides. In the case of Pt : La 50 : 50, the higher currents observed in Figure 1 with respect to Pt are due to the formation of higher amounts of acetic acid (Figure 4). For Pt : La 30 : 70, both CO_2 (Figure 5) and acetic acid (Figure 4) productions are enlarged with respect to Pt, but mainly CO_2 when compared with PtLa 50 : 50. Therefore, it seems that initially the presence of La oxides/hydroxides contributes to enhancing the catalytic activity facilitating the bulk ethanol reaction; but increasing its content in the catalyst, also the electrooxidation of adsorbed intermediates to CO_2 (and, therefore, the cleavage of the ethanol molecule) is favoured.

To produce CO_2 or CH_3COOH, CH_3CH_2OH needs at least a second oxygen atom. The reaction mechanism must involve some form of adsorbed oxygen species, which probably come from La oxides/hidroxides in addition to PtOH from water splitting. Although there is an evident rise in the performance of the catalyst with the increment of La oxides/hidroxides content, this is mainly due to a faster oxidation of bulk ethanol to acetic acid, that is, without breaking the C–C bond. However, it is also shown that with appropriate amounts of La oxides/hydroxides also the efficiency to CO_2 (and, therefore, the cleavage of the molecule) can be enhanced.

4. Conclusions

The combination of electrochemical and spectroscopic techniques has allowed a comparative analysis of the behaviour of Pt/C, PtLa/C (50 : 50) and PtLa/C (30 : 70) electrocatalysts towards ethanol electrooxidation. A significant increase of performance was observed with the increment of La oxides/hidroxides content, indicating that the addition of La species improves the activity of Pt for this reaction. FTIR results show that higher amounts of acetic acid are produced during ethanol oxidation at PtLa/C (50 : 50). Also the formation of CO_2 is favoured if the La oxides/hydroxides content is raised to Pt : La 30 : 70, and, therefore, the presence of these compounds as oxygen source can favour both bulk alcohol reactions (acetic acid formation) and adsorbed species oxidation (CO_2 production).

The onset for ethanol oxidation is observed at 0.50 V, that is, in the potential range used for a DAFC. The enhancement of activity towards alcohol electrooxidation in this potential region due to the addition of La oxides/hidroxides to Pt opens a possibility to utilize these materials as electrocatalysts for these devices. However, the detection of representative amounts of acetic acid clearly indicates that the C–C bond is not completely broken and further optimization of the catalysts is needed to improve the energy efficiency of ethanol electrooxidation.

Acknowledgments

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