Short communication

Preparation, characterization and utilization of a new electrocatalyst for ethanol oxidation obtained by the sol–gel method

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Abstract

This work reports some advances in the development of catalysts for ethanol electro-oxidation. A sol–gel-based method was used to incorporate different metal oxides on a substrate composed of platinum dispersed on carbon (Pt/C), resulting in very active catalysts with high surface area. Ruthenium and iridium oxides were used as modifiers, either alone or combined, maintaining a proportion of 25% in their total mass, as related to the amount of platinum on the substrate. The catalyst behavior was evaluated by polarization curves and the results were compared with commercially available catalysts. The experimental data reveals a superior performance of the sol–gel-based materials, indicating that the proposed method is a promising alternative to prepare catalysts to be used in the direct electrochemical oxidation of ethanol.
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1. Introduction

In the last decade, important improvements have been made in the development of active anode materials to be used as catalysts for the anodic oxidation of small organic molecules for fuel cells systems, particularly, methanol. Direct methanol fuel cells (DMFC) are very attractive systems having a variety of stationary and non-stationary applications. Hydrogen-based fuel cell systems are less convenient in many cases since they require a more sophisticated storage and transportation sub-systems. Apart from methanol, ethanol is another potential fuel candidate for these systems in substitution to hydrogen. Direct ethanol fuel cells (DEFC) is an advanced concept that combines the environmental friendly operation of a conventional cell with a renewable fuel that can be produced from agricultural crops, thus, avoiding the increase of CO_2 in the atmosphere. However, much effort has to be spent to achieve a fully functional DEFC and one of the major challenges is the development of efficient and poison-free catalysts.

The rate of ethanol electro-oxidation is very slow due to the accumulation of CO and other residues on the anode surface at low potentials [1]. Besides, poisoning of the cathode surface can also occur due to ethanol permeation through the Nafion® membrane in a crossover process that also contributes to slow down the rate of the overall reaction [2].

In the case of DMFC, significant advances have been made by improvements in the catalysis of methanol electro-oxidation reaction. The main adsorbed residue formed on Pt catalysts during this reaction in acid medium is CO and its electrochemical transformation to CO_2 is the rate determinant step for methanol oxidation. Meanwhile, Pt is, at present, the best known catalyst for breaking the C−H and O−H bonds, thus, making its presence essential in the composition of anodes for DMFC. The most successfully Pt-based catalyst reported for the anodic oxidation of methanol is a binary alloy composed of Pt–Ru [3–6]. There, carbon monoxide formed during the adsorption of methanol is oxidized at low potentials by the oxides formed on the Ru surface [7].

On the other hand, many aspects of the ethanol electro-oxidation reaction are fundamentally different from the case of methanol, particularly the nature of the adsorbed intermediates. The ethanol electro-oxidation pathway is extremely

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complex and follows parallel reactions producing acetaldehyde, acetic acid and CO_2 (complete oxidation) as final products. In general, ethanol oxidation on Pt follows a dual path mechanism either via the formation of strongly bound species or via the direct oxidation of dissolved ethanol molecules [8]. Several intermediates are formed during this reaction and the most important are: $-CO-CH_3$, $-OCH_2-CH_3$, $=COH-CH_3$ and linearly bonded CO [8].

Only the oxidation of CO is effective on Pt–Ru alloys, whereas most of the other intermediates cannot be completely oxidized by the surface oxides formed on ruthenium [8]. Another important aspect of the ethanol electro-oxidation is that a C—C bond must be broken for a complete oxidation process. The production of acetaldehyde and acetic acid as the final products, instead of CO_2, is a consequence of the inefficient removal of the adsorbed intermediates formed during the process.

Thus, an active catalyst for ethanol oxidation must combine the properties of a surface capable of oxidizing small molecules at low potentials, as observed for the Pt–Ru alloys, with ability of breaking the C—C bond present in ethanol and some of their initial oxidation products (acetaldehyde, etc.). Several metals and metal oxides have been tested for this purpose, including Os [9], IrO_2 [10], SnO_2 [11] and Rh [12]. However, none of them has shown sufficient activity at low potentials to be used as a DEFC catalyst. Nowadays, in spite of the problem of being strongly poisoned by adsorption products, Pt is the best known catalyst for the oxidation of small organic molecules. This is a clear demonstration that the presence of Pt is strictly necessary in the catalyst composition.

Along with the chemical nature of the components, the preparation method is another essential feature in the development of catalysts. Catalysts to be used in fuel cells are normally prepared in the form of particles dispersed in a high surface area carbon. Several methods have been used to anchor the catalyst particles to the substrate, including the chemical reduction of inorganic salts containing the metals of interest with formic acid [13] and more recently, the Bönnemann's method [14]. This latter method involves the reduction of an appropriate inorganic metal salt, usually a chloride, by an organic reductive medium (alkali hydrotriorganoborates). The Bönnemann's method appears to be very attractive since it allows the production of nanostructured particles having well controlled sizes, essential features for the production of catalysts. However, the method is rather complicated, involving several steps and the use of sophisticated apparatus.

An attractive alternative to produce catalysts with the required features is the sol–gel method that has been recently reported as an efficient way to synthesize very active catalysts for the oxidation of methanol [15]. The sol–gel method involves the preparation of a solution containing metal alkoxides or acetylacetonates as precursors in a mixed alcohol/acetic acid solvent, the last one acting as the catalyst for the initial hydrolysis step promoted by residual water. This initial step generates a sol that contains oligomers produced by the condensation of the precursors. A subsequent heat treatment accelerates and completes the three-dimensional chain condensation process leading to the desired metal oxide with the elimination of the organic residues. Thus, the sol–gel method is very suitable to prepare pure and homogeneous metal oxides [15] with high surface area. Besides, the sol–gel method allows the production of materials with complex compositions in a very simple and straightforward way.

The aim of this work is to report preliminary results in the development of Pt/C catalysts modified by the incorporation of different metal oxides by the sol–gel method and its application in the study of ethanol electro-oxidation. The voltammetric performance of the $Pt-RuO_2/C$, $Pt-IrO_2/C$ and $Pt-RuO_2-IrO_2/C$ composite electrodes will be compared with that of commercially available Pt/C and Pt–Ru/C powders.

2. Experimental

The catalysts were prepared by the sol–gel method using as substrate a commercial Pt/C (Etek Inc., USA) powder containing 10% of platinum. IrO_2 and RuO_2 oxides or their mixture were deposited by dissolving the metallic precursors (ruthenium and iridium acetylacetonates) in a solvent containing isopropanol and acetic acid 3:2 (v/v). After that, an appropriate amount of Pt/C (Etek, USA) was added to the resulting sol and the mixture was homogenized by ultrasonic irradiation (20 kHz) produced by a Heat System Ultrasonic W85 Sonicator. The solvent was then slowly evaporated and the resulting powder submitted to a heat treatment at 400 °C in an inert Ar atmosphere for 60 min. The desired amount of modifiers (metal oxides) was calculated in relation to the amount of platinum in the powder, namely 25% (w/w) of the modifying metals with respect to platinum. For materials containing more than one oxide, the amount of each metal was 12.5% (w/w). The results obtained for the composite containing only IrO_2 were much less satisfactory than the others and will not be presented in detail.

Three techniques were employed to physically characterize the catalysts: X-ray diffraction (XRD), energy dispersive analysis of X-rays (EDAX) and atomic absorption spectroscopy (AAS). The instruments were a Rigaku Rotoflex RU 200B using the Cu Kα radiation and $v = 2°$ min^{-1}, a Link Analytical QX 2000 and a Hitachi Z-8100 spectrophotometer. The XRD patterns were also analyzed by the software Winfit 1.2 [16] to determine the mean size of the catalysts crystallites.

The working electrodes were constructed using the thin porous coating (TPC) configuration [17]. These electrodes were prepared by mixing the catalyst powders with a dilute suspension ($\approx$2%, w/w) of a Teflon emulsion (Du Pont TM30) and then following the procedures described elsewhere [17]. A pyrolitic graphite rod ($\phi = 5$ mm) inserted in a Teflon cylinder and leaving a small cavity ($\approx$0.3 mm) at the end was used to support the catalysts. Unless indicated, on the

contrary, all electrochemical measurements were carried out using the TPC electrode configuration. A Pt disk ($\phi = 5$ mm) in a Teflon holder having an electrochemical active area of 0.25 cm^2 was also used for comparative experiments. A three-electrode cell was used for the electrochemical measurements. The counter electrode was a 1 cm^2 platinum foil and the reference system was a hydrogen electrode in the same solution (HESS). All the experiments were carried out at room temperature in a 0.5 mol L^{-1} H$_2$SO$_4$ solutions where known amounts of ethanol were added. The solutions were prepared with analytical grade reagents without further purification and water supplied by a Milli-Q system from Millipore Inc. and were N$_2$-saturated prior to the measurements.

The electrochemical experiments were carried out using a Princeton Applied Research Corporation (PARC) Model 273A potentiostat coupled to an IBM-PC compatible microcomputer. All cyclic voltammetric curves reported here correspond to the stationary responses obtained for electrodes cycled between 0.05 and 1.55 V versus HESS. The Pt electroactive areas of the composite electrodes were evaluated from the voltammetric curves by assuming a value of 210μC cm^{-2} for the hydrogen desorption charge [18].

3. Results and discussion

3.1. XRD characterization

Fig. 1 shows the XRD patterns obtained for the Pt-RuO$_2$/C and Pt-RuO$_2$-IrO$_2$/C composite materials as well as those of the base material (Pt/C 10%, Etek) and the carbon substrate for comparison. The more relevant peaks in those spectra were identified using the reference data obtained from the Joint Committee of Power Diffraction Standards (JCPDS) and are indicated in the figure. It should be mentioned that the signals related to IrO$_2$ and RuO$_2$ cannot be distinguished

Fig. 1. X-ray diffraction patterns of: (a) Pt-RuO$_2$-IrO$_2$/C electrode; (b) Pt-RuO$_2$/C electrode; (c) Pt/C 10% E-Tek commercial powder; (d) Vulcan XC-72 powder.

in the spectrum shown in Fig. 1(a), since their most significant peaks appear at the same diffraction angle. This is in accordance with the results reported by Mattos-Costa et al. [19] in a previous investigation related to the preparation and characterization of mixed iridium and ruthenium oxides using the sol–gel method. Nevertheless, the presence of Ru and Ir in the catalyst is confirmed by the EDAX and AAS analyses (see below). On the other hand, no shifts were observed in the Pt peak locations, strongly suggesting that the metals in the ruthenium oxide or the ruthenium–iridium oxide do not alloy with the Pt as expected.

The XRD patterns (Fig. 1) were also used to estimate the mean crystallite size of the Pt particles on the different materials using the Winfit 1.2 software [16], a MS-Windows program for the extraction of crystalline data by profile shape analysis. The program can be used for the determination of peak widths and shapes, determination of peak intensity data, pattern decomposition, background subtraction and conversion of fixed slit to variable slit geometry and vice versa. Fourier analyses of single lines and combination of peaks yields crystallite size and lattice strain. The size distribution is determined from the second derivative of the Fourier-coefficient plots. In order to evaluate the derivative, a Savitzky–Golay polynomial function was used. The detailed procedure to calculate the mean size of the crystallites can be found elsewhere [16]. To calculate the mean size of the crystallites present in the different materials, the 2θ angle corresponding to 100% I/I_o was used [20]. A value of 2.3 nm was found for the commercial Pt/C 10% (Etek) catalyst. According to Maillard et al. [21], the mean crystallite size of such material calculated by transmission electron microscopy (TEM) was also 2.3 nm. On the other hand, the values found here for Pt-RuO$_2$/C and Pt-RuO$_2$-IrO$_2$/C were 4.8 and 6.9 nm, respectively. A reduction of the crystallite size by changing the preparation conditions in the sol–gel method should be the object of a future investigation.
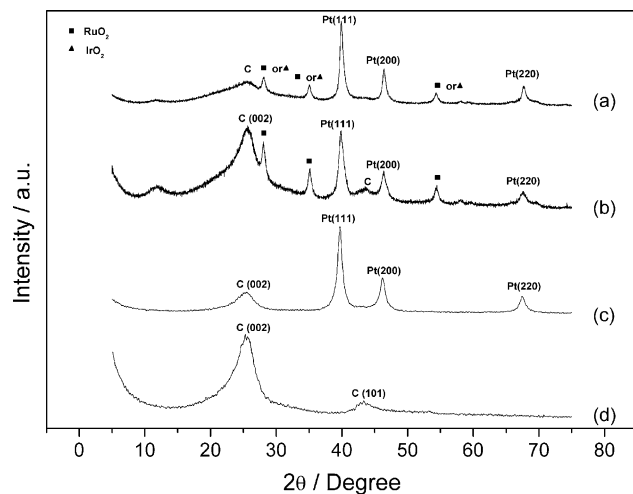
3.2. EDAX and AAS characterization of the catalysts

EDAX and AAS analyses were used to determine the composition of the materials prepared by the sol–gel method. Table 1 summarizes the results obtained for the Pt-RuO$_2$/C and Pt-RuO$_2$-IrO$_2$/C composites. The excellent agreement between the experimental data and the proportions used in the preparation of the composites confirms the validity of the method.

3.3. Electrochemical characterization of the catalysts

Cyclic voltammograms of thin porous coating electrodes prepared with commercial Pt/C 10% were recorded at 5 mV s^{-1} in an aqueous 0.5 mol L^{-1} H$_2$SO$_4$ solution in the absence and in the presence of 0.1 mol L^{-1} ethanol (Fig. 2). In the absence of ethanol, a fair resolution of the platinum surface features can be observed in the cyclic voltammogram. The slow scan rate prevented distortions caused by capacitive

Table 1
Chemical analysis of the catalysts from EDAX and AAS measurements

Catalyst	EDAX composition (mass%)			AAS composition (mass%)		
	Pt	Ru	Ir	Pt	Ru	Ir
Pt-RuO$_2$/C	75.0	25.0	–	75.1	25.2	–
Pt-RuO$_2$-IrO$_2$/C	74.9	12.4	12.8	72.1	12.5	12.7

currents. Using the hydrogen adsorption/desorption charges in the potential range from 0.0 to 0.3 V [18], the approximate Pt electroactive surface area was calculated yielding a value of 69.9 cm^2. This value was used to calculate the current density values plotted in Fig. 2.

On the other hand, the presence of ethanol generates two prominent peaks that can be observed at ca. 0.9 and 1.25 V during the positive scan and a somewhat small reactivation peak in the opposite branch. These results are qualitatively similar to those for smooth platinum, as exemplified in Fig. 3 where the voltammogram was recorded under the similar
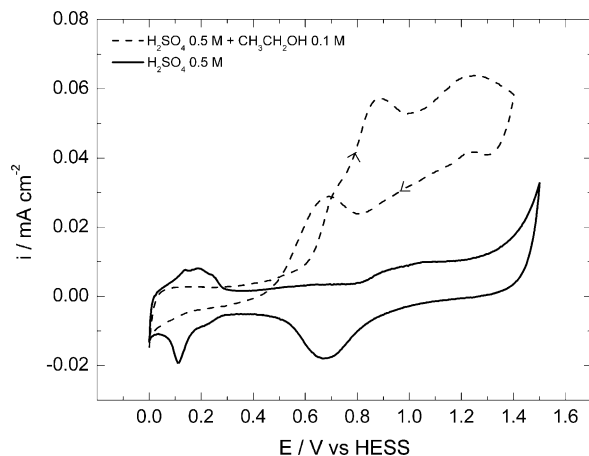

Fig. 2. Steady-state voltammograms of a Pt/C 10% E-Tek commercial powder electrode in 0.5 mol L^{-1} H$_2$SO$_4$ aqueous solution in the absence and in the presence of 0.1 mol L^{-1} ethanol; $v = 5$ mV s^{-1}.
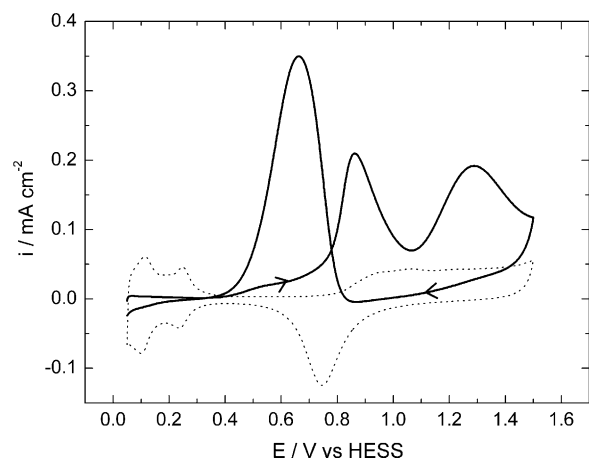

Fig. 3. Steady-state voltammogram for a smooth platinum electrode in 0.5 mol L^{-1} H$_2$SO$_4$ aqueous solution in the absence (- - -) and in the presence of 0.1 mol L^{-1} ethanol (—); $v = 50$ mV s^{-1}.

experimental conditions but at a higher scan rate. Published data concerning the identification of intermediates formed during the oxidation of ethanol [22–24] revealed the great complexity of the system. Meanwhile, it is clear that the nature and quantity of each intermediate formed strongly depends on the electrode composition and morphology [23].

A comparison between Figs. 2 and 3 clearly shows that both the oxidation and the reactivation peaks observed in either Pt/C or smooth platinum occur at approximately the same potentials. However, the reactivation current density observed at ca. 0.6 V for the smooth Pt electrode is considerably larger than that observed for the TPC electrode when compared to the direct oxidation peaks. This is a very interesting aspect of these systems, indicating that the electroactive area is not the only important parameter in dispersed catalysts when compared to equivalent smooth catalysts. Other parameters, such as particle size and distribution on the substrate are also important and may affect the catalyst performance in ethanol electro-oxidation, suggesting that a smooth electrode is more seriously poisoned than a disperse one [25].

It is important to analyze the role of the state of the Pt surface in the voltammetric response for ethanol oxidation. The onset for that process on Pt is around 0.35 V but from this potential up to ~0.75 V, the direct alcohol oxidation in inhibited by the presence of intermediates generated by dissociative adsorption on the surface [8]. Consequently, the oxidation peaks appear when the Pt surface is free from those poisoning intermediates after their oxidation. According to Bagotsky and Vassilyev [26], significant amounts of kinetically reversible surface oxides are already formed at around 0.5–0.6 V on the Pt surface, but the maximum coverage of the electrode with surface oxides is only achieved at around 1.05 V [27]. This is in accordance with the results in Fig. 3.

Based on the previous discussion and the information from the literature [9–12], it is reasonable to assume that the presence of oxides on the electrode surface is necessary to eliminate some adsorbed intermediates, thus, allowing for the direct reaction to occur at reasonable rates. The problem with Pt is related to the high potential values necessary to achieve suitable oxide coverage. The modification of a Pt/C powder with different metal oxides takes into account some properties inherent to these materials that can diminish the poisoning of the Pt surface by promoting the oxidation of intermediates at lower potentials, thus, accelerating the ethanol oxidation reaction.

Some types of metal oxides can be used for the indirect oxidation of organic compounds [28]. Such materials are classified as "non-active" when the oxidation process on them
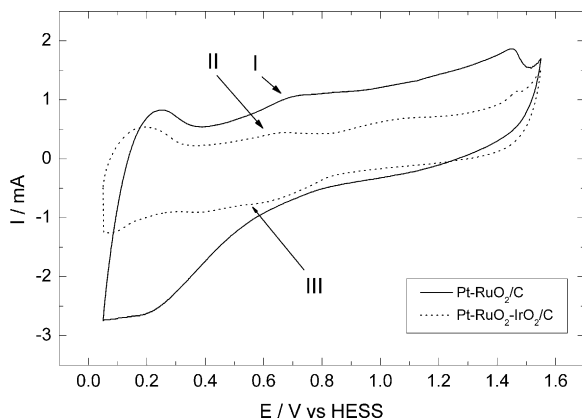
Fig. 4. Steady-state voltammograms of Pt-RuO$_2$/C (—) and Pt-RuO$_2$-IrO$_2$/C (- - -) electrodes in 0.5 mol L^{-1} H$_2$SO$_4$ aqueous solution; $v = 5$ mV s^{-1}.

occurs by the formation of hydroxyl radicals [28]. Otherwise, metal oxides can participate effectively in the oxidation process and in this case, they are classified [28] as "active" and the oxidation process is generally very selective.

Fig. 4 shows the cyclic voltammograms at 5 mV s^{-1} of Pt-RuO$_2$/C and Pt-RuO$_2$-IrO$_2$/C electrodes recorded in 0.5 mol L^{-1} H$_2$SO$_4$. The voltammetric behavior of Ru and Ir oxides in acid electrolytes has been discussed in the literature [19] and the peaks are normally associated to redox processes occurring within these materials at well-defined potentials. The enhanced capacitive currents produced by the carbon present in the substrate hinder the voltammetric signals associated with some of these processes and little information can be extracted from Fig. 4. However, the peaks observed at ca. 0.65 V (I–III in Fig. 4) can be reasonably distinguished and had been attributed to the Ru(III)/Ru(IV) transition[19,29].

On the other hand, the current associated to the processes of hydrogen adsorption/desorption on Pt are notably affected by the presence of Ru and Ir oxides. For this reason, it is not possible here to determine the electroactive area of the materials as it was done in the case of the Pt and Pt/C electrodes. Nevertheless, it can be seen in Fig. 5 that the presence of oxides produces a marked increase in ethanol oxidation currents (measured with respect to the mass of platinum in the composite) in comparison to the Pt/C electrode.

To evaluate the real catalytic effect of the oxides towards ethanol oxidation, linear sweep voltammetry experiments using low scan rate (5 mV s^{-1}) were performed in the potential range from 0.0 to 0.8 V using the experimentally prepared composites. The results were compared with those obtained in equivalent experiments using Pt/C and Pt$_{0.75}$Ru$_{0.25}$/C (E-Tek), commercial samples are presented in Fig. 6.

It can be observed from that figure that the increase of the electroactive area promoted by the addition of the oxides to the Pt/C substrate is not the only effect, as suggested by the results of Fig. 5. The oxide-based catalysts also present a better performance than the Pt/C and Pt–Ru/C catalysts for ethanol electro-oxidation. The onset potentials shift to lower
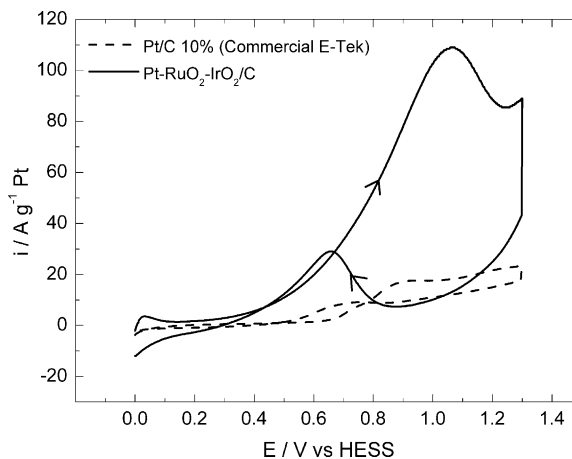

Fig. 5. Comparative steady-state voltammograms of Pt/C 10% E-Tek commercial powder and Pt-RuO$_2$-IrO$_2$/C experimentally prepared composite in 0.5 mol L^{-1} H$_2$SO$_4$ aqueous solution containing 1.0 mol L^{-1} ethanol; $v = 5$ mV s^{-1}.
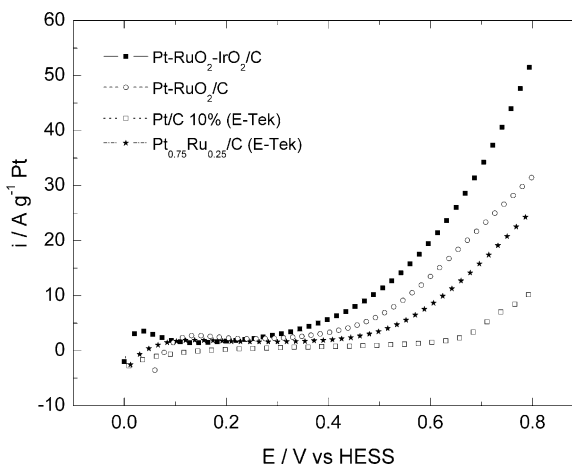

Fig. 6. Linear sweep voltammograms for ethanol oxidation on the different catalysts in 0.5 mol L^{-1} H$_2$SO$_4$ aqueous solution containing 1.0 mol L^{-1} ethanol; $v = 5$ mV s^{-1}.

values when the reaction takes place on the oxide-modified electrodes, indicating that these materials possess a higher catalytic activity. The current values presented in Fig. 6 are once again normalized as a function of the Pt load, a procedure adopted here to allow a comparison with other published results. Analyzing the curve obtained for the oxidation of ethanol on Pt-RuO$_2$-IrO$_2$/C, the measured currents are five times greater than those published in the literature under the same experimental conditions but using different catalysts [30,31].

4. Conclusions

The catalysis of ethanol electro-oxidation was successfully investigated in a new class of materials composed of commercial Pt/C modified by the addition of several noble metal oxides. The procedure used to incorporate the oxides

on the substrate was based on the sol–gel method that proved to be very adequate for this purpose. The onset potential of the electrochemical reaction shifted to less positive values when compared to the same electrode process conducted on Pt/C and Pt–Ru/C catalysts. The increase of the electroactive area by the incorporation of oxides was not the only effect that increased the peak currents in the oxidation processes, indicating a good catalytic activity for these new materials.

Acknowledgement

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