

**Functionalization of Vulcan XC-72 via a soft chemical route by intermittent microwave heating and its use as support of Pt/C electrocatalysts for the ethanol oxidation reaction**

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**ABSTRACT**

The catalytic activity for ethanol oxidation reaction (EOR) in acid media of Pt/C electrocatalysts supported on functionalized Vulcan has been investigated. The functionalization was carried out by submitting the carbon support to intermittent microwave heating using different soft chemical agents, namely acetic acid (ACA), citric acid (CA) and ethylene glycol (EG). Pt nanoparticles were dispersed on the functionalized Vulcan with the aid of the microwave-assisted polyol process, by applying radiation pulses to the sample. XRD analysis showed the formation of crystalline Pt with an average particle size of nearly 2 nm. The nanosized feature was confirmed by HR-TEM evaluation. The characterization of the electrochemical performance of the anodes indicated an enhanced catalytic activity for the EOR of the Pt/C electrocatalysts supported on Vulcan functionalized with EG. This material, labeled Pt/C-EG showed a peak current density on the positive scan of 31.2 mAcm<sup>-2</sup> at 0.93 V. The catalytic activity of Pt/C-EG was followed by that of Pt/C-CA (Vulcan functionalized with citric acid), with a peak current density of 31.44 mAcm<sup>-2</sup> at 1.03 V. The results showed that functionalization of Vulcan with EG and CA is one effective way to enforce the interaction between Pt and carbon support.

**1. Introduction**

During the last decade Direct Alcohol Fuel Cells (DAFCs) have been widely investigated because of their energetic features that make such systems attractive as power sources for small scale stationary and portable applications. [1, 2]. Recently, it has been shown that ethanol is both more convenient and efficient (due it can be easily produced in large amount by the fermentation of sugar containing raw materials and has very good energy density, 8kWhkg<sup>-1</sup>) compared with other alcohols [3, 4]. Some of the most important technological problems of DAFC are related to their low durability and high cost of electrocatalysts used in anodes and cathodes [2]. Pt-based electrocatalysts are used for the electrochemical oxidation of ethanol in Direct Ethanol Fuel Cell (DEFC). However, the abundance of this noble metal in the earth is limited and, therefore is an expensive material. For these reasons, different materials have been used as electrocatalysts support for DAFCs. They provide access to a much larger number of catalytically active atoms than in the corresponding bulk metal [5]. The support material used in fuel cells applications must have a high electrical conductivity and a high corrosion resistance [6]. So far, Vulcan is the most widely used carbon support because of its physicochemical properties which make it adequate for such applications. It has been reported that the catalytic activity, selectivity and stability of fuel cells electrocatalysts are highly influenced by surface microstructure and chemical property of this carbon [7]. Nevertheless, Vulcan that has not being submitted to any surface modification treatment may have a relatively high ash content and has a large hydrophobic surface, which may result in a poor capability to anchor Pt nanoparticles [7]. Therefore, surface chemical modification of Vulcan is necessary in order to enhance a favorable interaction with catalysts nanoparticles. Sunday et al. [8] have studied the performance of Pt/C materials using Vulcan modified by sulphonic acid group. The authors found an enhanced

activity for the methanol electrooxidation of the catalysts dispersed on the sulphonic acid modified Vulcan, compared to the anodes supported on unmodified Vulcan. Shibin Yin et al [2] modified CNT by combining Hydrofluoric acid (HF) treatment and intermittent-microwave assisted  $\text{H}_2\text{O}_2$  treatment and found that this material exhibits a significantly higher electrochemical surface area and higher Pt utilization efficiency compared with Pt/CNT-HF, Pt/CNT- $\text{H}_2\text{O}_2$  and Pt/CNT.

In this work we present the electrochemical evaluation of Pt electrocatalysts, supported on Vulcan XC-72 functionalized by different solutions, namely acetic acid (ACA), citric acid (CA) and ethylene glycol (EG). The functionalization has been carried out by intermittent microwave heating. These materials were evaluated as anodes for the EOR. The results show that the catalytic performance for EOR is highly dependent of carbon functionalization.

## 2. Methodology

### 2.1 Carbon Vulcan XC-72 functionalization

300 mg of Vulcan (Cabot Corp.) were dispersed separately in a round bottom flask containing each of the chemical agents used for functionalization (ACA, CA, EG). The solution was sonicated for 15 min, and stirred for 15 min at room temperature. Afterwards, the flask was placed in the center of a modified household microwave oven in order to be submitted to 25s-on/25s-off pulsed heat treatment for 4 min, with microwave power of 700 W. Then carbon suspension was filtered through a polycarbonate filter membrane (pore size  $0.45\ \mu\text{m}$ ) and thermally treated at 300 K for 1 hour, to remove the adsorbed chemical agent and water. Figure 1 shown the steps followed for the Vulcan treatment with different solutions used.

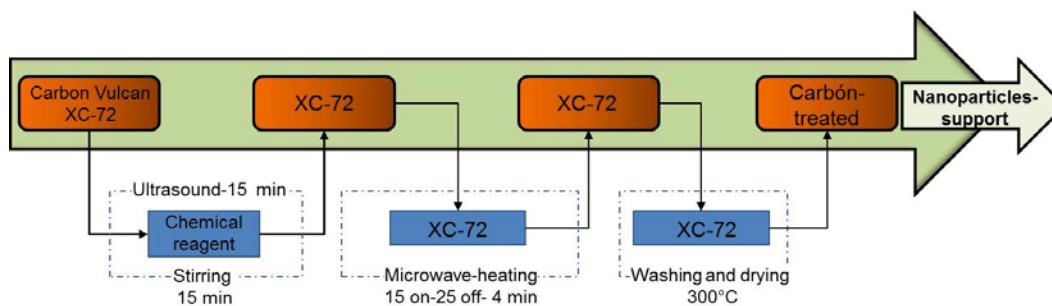


Figure 1 Experimental procedure for carbon functionalization, functionalized Vulcan was labeled C-ACA, C-CA and C-EG, according to the chemical agent.

### 2.2 Deposition of Pt nanoparticles on Vulcan

The dispersion of Pt nanoparticles on functionalized carbon (20% metal content) was carried out by the intermittent-microwave assisted polyol process as follows: 80 mg of carbon were dispersed by ultrasound in 45 mL of ethylene glycol and water (V/V= 90/10) and to this mixture 4 mL of chloroplatinic acid at 0.026 M (dissolved in an EG/ $\text{H}_2\text{O}$  solution) were added drop by drop. The mixture was stirred for 1 hour and the pH adjusted to around 12 by adding 3 mL of 0.5 M NaOH/EG solution. Thereafter, the solution was placed in the microwave oven and heated by applying 700 W for 20 s, followed by pulses 17s-on/165s-off for 16 min. The solution was allowed to cool down to room temperature and left overnight with continuous stirring. Afterwards, 1.2 mL of 0.5 M  $\text{H}_2\text{SO}_4$  was added to the mixture to adjust the pH to 3. The obtained mixture was stirred for another 20 hours. The final products was filtered, washed, and dried at  $85^\circ\text{C}$  for 14 h.

### 2.3 Physical and chemical characterization

XRD patterns were obtained in a scan range from  $10^\circ$  to  $100^\circ$  ( $2\theta$ ) with a Phillips-X'pert diffractometer using  $\text{CuK}\alpha$  radiation source. The average particle size of the Pt/C anodes was obtained analyzing the (220) reflection of each sample. The morphology, particle size and distribution of Pt nanoparticles were obtained from HR-TEM images. The X-ray photoelectron spectroscopy (XPS) was used to analysis the functional groups in the electrocatalysts.

### 2.4 Electrode preparation and electrochemical measurements

The catalytic activity of the Pt/C electrocatalysts for the EOR was evaluated in a three electrode glass cell, using a Voltalab Potentiostat/galvanostat. The electrodes were silver/silver-chloride (Ag/AgCl) and platinum foil as the reference electrode and the counter electrode, respectively. The support electrolyte was a 0.5 M  $\text{H}_2\text{SO}_4$  solution. Ethanol electrooxidation was carried out in  $\text{N}_2$  saturated electrolyte containing 1M ethanol. A thin porous film on a glassy carbon was used as the working electrode. The working electrode (with an area of  $0.196\text{cm}^2$ ) was prepared by deposition of a catalytic ink composed of 5mg of electrocatalysts dispersed in 0.5mL of isopropyl alcohol and 25 $\mu\text{L}$  of Nafion® solution (5 wt%). Then, 10  $\mu\text{L}$  of the ink was spread onto the surface of the glassy carbon. Each electrocatalysts was activated by performing 40 cycles in the potential range between -0.175 and 0.975 V vs Ag/AgCl with a scan rate of  $50\text{ mVs}^{-1}$ . Then, cyclic voltammograms were acquire at the scan rate of  $20\text{ mVs}^{-1}$  and reported in this work (all potential reported in this paper are referenced to the EEH).

## 3. Results and discussions

### 3.1 Physical and chemical characterizations

The XRD patterns of synthesized electrocatalysts are shown in figure 2. The diffraction peak at  $2\theta = 25^\circ$  is attributed to the carbon support (graphite structure). Others peaks at  $2\theta = 39.7, 46.2, 67.4$  and  $81.2^\circ$  correspond to crystalline FCC Pt reflections (111), (200), (220), and Pt (311), respectively. The average crystallite size of Pt nanoparticles is calculated by determining the Full Width at Half Maximum (FWHM) for (220) reflection and using the Scherrer equation:

$$d = \frac{0.9\lambda_{k\alpha}}{B_{2\theta}\cos\theta} \quad (1)$$

Where  $d$  is the average crystallite size, 0.9 is the shape factors for spherical crystallites,  $\lambda$  the radiation wavelength ( $1.5406\text{\AA}$ ),  $B_{2\theta}$  the Full Width at Half Maximum, and  $\theta$  the angle at maximum intensity of the Pt (220). The crystallite sizes obtained are 1.3, 1.8, 2.2 and 2.3 nm for Pt/C-untreated, Pt/C-ACA, Pt/C-CA and Pt/C-EG, respectively.

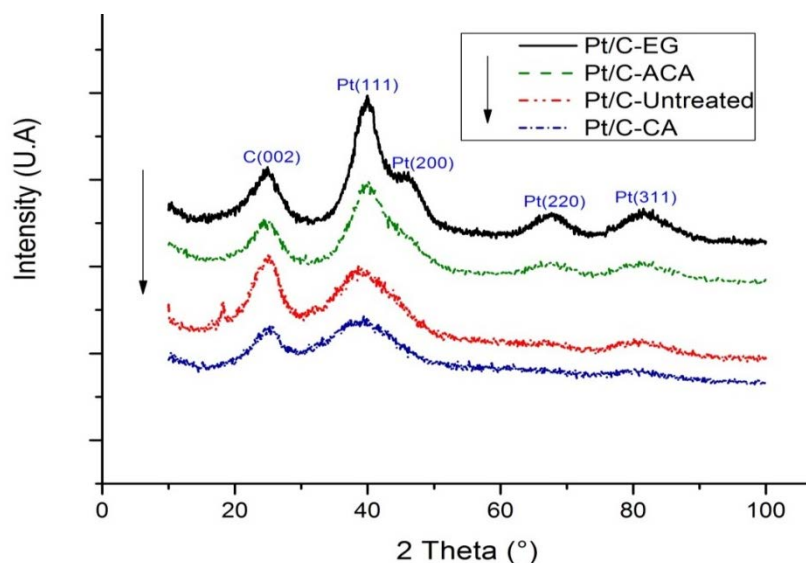


Figure 2 XRD patterns of prepared electrocatalysts, Pt/C

Figure 3 (a y b) shows HR-TEM images of Pt/C-EG and Pt/C-CA electrocatalysts. In both cases, the morphology shows homogeneous dispersion of the nanoparticles on the carbon support. From these images, it can be concluded that the materials have nanosized characteristics. This is important because such properties are key factor for enhancing the electrocatalytic activity of the anodes for EOR.

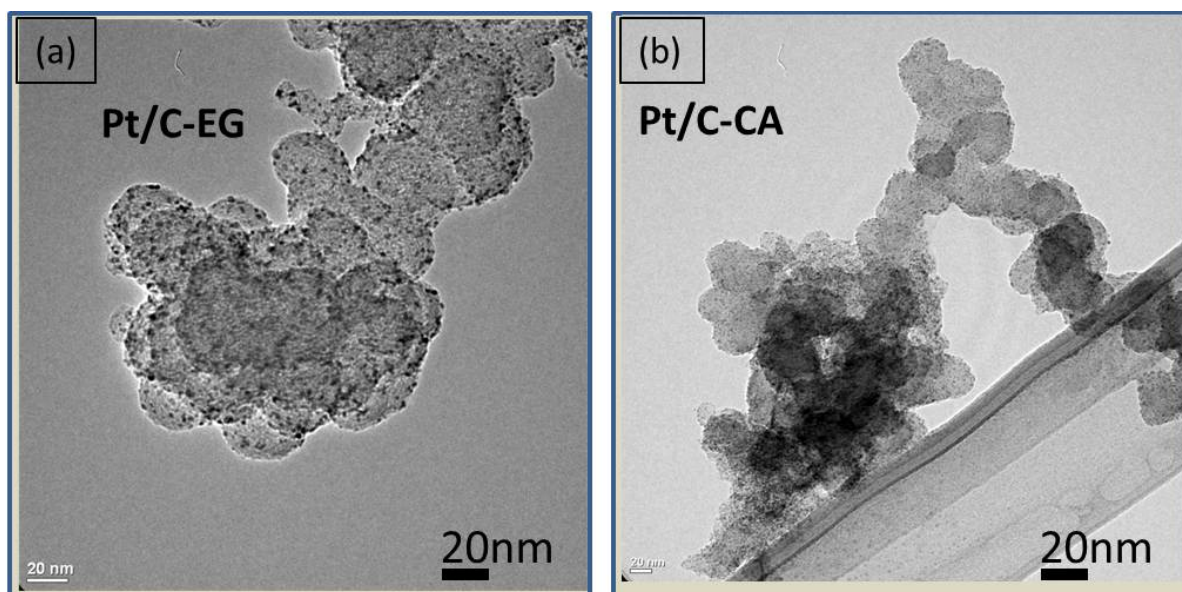


Figure 3 HR-TEM micrograph of the Pt/C electrocatalysts a) Pt/C treated with ethylene glycol, b) Pt/C treated by citric acid

The mass fraction of Pt in Pt/C electrocatalysts prepared by microwave assisted polyol process is measured by EDX and the loads of Pt for the electrocatalysts are 5, 6.8, 2 and 4.5 % for Pt/C-untreated, Pt/C-ACA, Pt/C-CA and Pt/C-EG, respectively. Has can be seen any materials synthesized had the desired metal loading; this can be due to the process of synthesis performed, that it's the irradiation time, dispersion time.

### 3.2 Surface Characterization

Figure 4 shows the O 1s, C 1s and Pt 4f XPS spectra for Pt/C electrocatalysts (figure 4 a-f). The results confirm the existence of functional groups on modified carbon. The XPS studies clearly demonstrated that the carbon treated with CA, ACA and EG led to the formation of large amounts of oxygen-containing functional groups (highly O1s signal compared with the untreated carbon, see figure 4(a, b)). On the other hand, the C1 s peaks of the electrocatalysts are shown in figure 4(c-d) and its observed changes as shift in the binding energy for O 1s and changes in the amplitude of the signal for O1s, that depends on the functionalization of carbon support. The peak corresponding to Pt/C-CA has the highest intensity, while the Pt/C-untreated has the lowest one. The regional Pt 4f spectra of the electrocatalysts are shown in figure 4(e-f), showing the Pt 4f7/2 and Pt 4f 5/2 peaks (71.4 and 74.7 eV, respectively). The deconvolution of the Pt 4f spectrum corresponding to Pt/C-EG is shown in figure 4(f). Two pairs of doublets are formed after fitting of the experimental data. The first doublet contains a low energy band centered at 71.6 and high energy band at 74.8 eV, indicating that the Pt is present in its metallic Pt, i.e., Pt<sup>0</sup> [9]. The second, less intense doublet is composed of two peaks at higher binding energy positions (72.7 and 76.1) revealing the existence of Pt<sup>2+</sup>, i.e., Pt-oxides species. Table 1 presents a comparative of percentage of Pt<sup>0</sup> and Pt<sup>2+</sup> calculated for the electrocatalysts.

Table 1 Pt species observed from XPS analysis for Pt/C electrocatalysts synthesized

Catalysts	Pt(0) species (%)	Pt(II) species (%)
Pt/C-CA	77.3	22.6
Pt/C-ACA	79.1	20.88
Pt/C-EG	77.1	22.8
Pt/C-Untreated	87.1	12.8



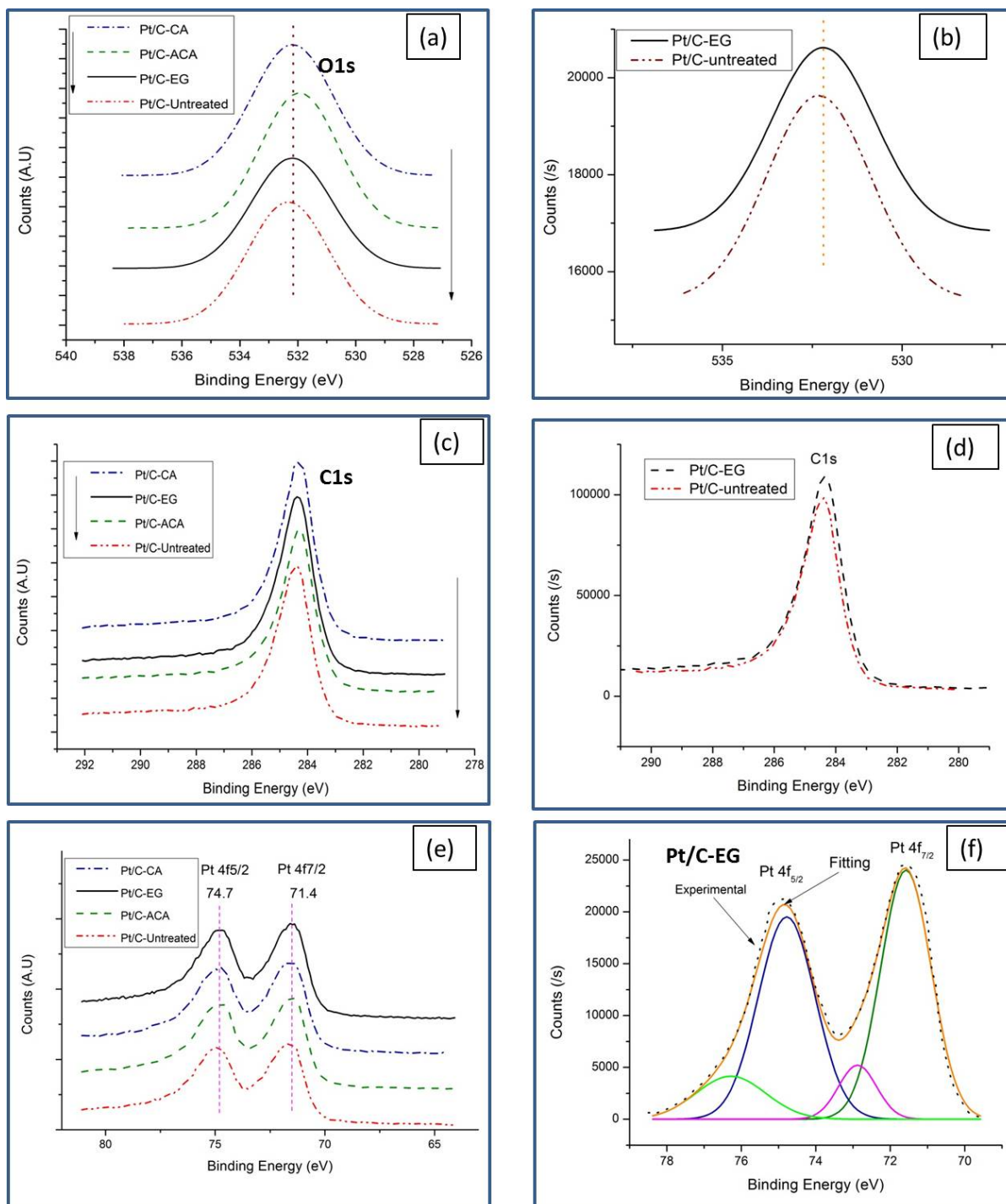


Figure 4 XPS spectra of Pt/C electrocatalysts. A,B) Species O1s; C,D) species C1s and E,F) Pt4f

### 3.3 Electrochemical characterization

Figure 5 shows the CVs of the Pt/C electrocatalysts in N<sub>2</sub>-saturated electrolyte at the scan rate of 20 mVs<sup>-1</sup>. The Electrochemically Active surface area (ESA) of Pt/C electrocatalysts can be determined by integrating the charge associated with the peak area in the hydrogen desorption region and using the well-known equation (2):

$$S_{ESA} = \frac{\text{charge } [\mu\text{Ccm}^{-2}]}{Q_0[\mu\text{Ccm}^{-2}\text{Pt}] \times \text{Ptloading}[\text{mgcm}^{-2}]} \times 10^4 \quad (2)$$

Where the charge correspond to the integrated charge in the hydrogen adsorption-desorption peak area in the CV curve;  $Q_0$  is the charge constant of 210  $\mu\text{Ccm}^{-2}$  for hydrogen adsorption on poly-crystallite Pt [10]; and Pt loading is the amount of Pt on the working electrode.

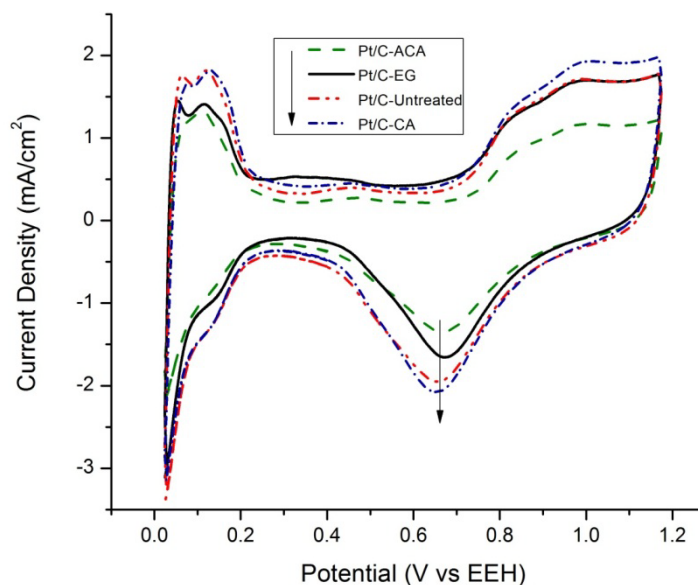


Figure 5 Cyclic voltammograms for Pt/C-AAC, Pt/C-EG, Pt/C-untreated and Pt/C-AC. Scan rate of 20mVs<sup>-1</sup> at room temperature in 0.5 M H<sub>2</sub>SO<sub>4</sub>, disk electrode area 0.196 cm<sup>2</sup>

The Chemical Specific Surface Area (CSA) of the electrocatalysts was calculated using the following equation, based on the assumption of a spherical morphology:

$$S_{CSA} = \frac{6 \times 10^4}{\rho d} \quad (3)$$

Where  $\rho$  is the density of platinum metal (21.4 gcm<sup>-3</sup>) and  $d$  is the diameter of the particle determined from XRD analysis. The ratio between  $S_{ESA}$  AND  $S_{CSA}$  gives the Pt utilization factor:

$$\text{Pt utilization efficiency (\%)} = \frac{S_{\text{ESA}}}{S_{\text{CSA}}} \times 100 \quad (4)$$

The SESA, SCSA and Pt utilization values for the different electrocatalysts are summarized in table 2. It can be seen that Pt/C-EG and Pt/C-EG present the highest Pt utilization, 35.14 and 30.42, respectively. Pt/C-untreated and Pt/C-ACA have lower Pt utilization: 20.73 and 22.59, respectively.

Table 2 Physico-chemical and electrochemical characterization for the Pt/C electrocatalysts

Pt/C	Particle size/nm	Pt loading rate %	SESA $\text{m}^2\text{g}^{-1}$	SCSA $\text{m}^2\text{g}^{-1}$	Pt utilization %
Pt/C-untreated	1.3	13.1	48.73	215.67	22.59
Pt/C-ACA	1.8	6.8	32.29	155.76	20.73
Pt/C-CA	2.2	2	44.78	127.44	35.14
Pt/C-EG	2.3	4.5	37.8	121.90	30.42

The polarization curves of the EOR at the Pt/C electrocatalysts are shown in figure 6. The anodes delivering higher ethanol oxidation with values of 31.44 and 31.2  $\text{mAcm}^{-2}$  are Pt/C-CA and Pt/C-EG, respectively. This increase in performance for ethanol electrooxidation may be due by an increase in the number of surface hydroxyl group, during the chemical treatment, that facility the removal of CO intermediate, that is adsorbed on Pt surface [11]. Figure 6-b shown the onset potential for the four electrocatalysts. From this figure we can see that all electrocatalysts have the same onset potential, about 0.3 V. So, we analyze the onset potential for a current density of 6  $\text{mAcm}^{-2}$ . Pt/C-EG present the lowest onset potential (0.61 V), meanwhile the Pt/C-ACA has the greatest potential (0.64 V) at the same current density.

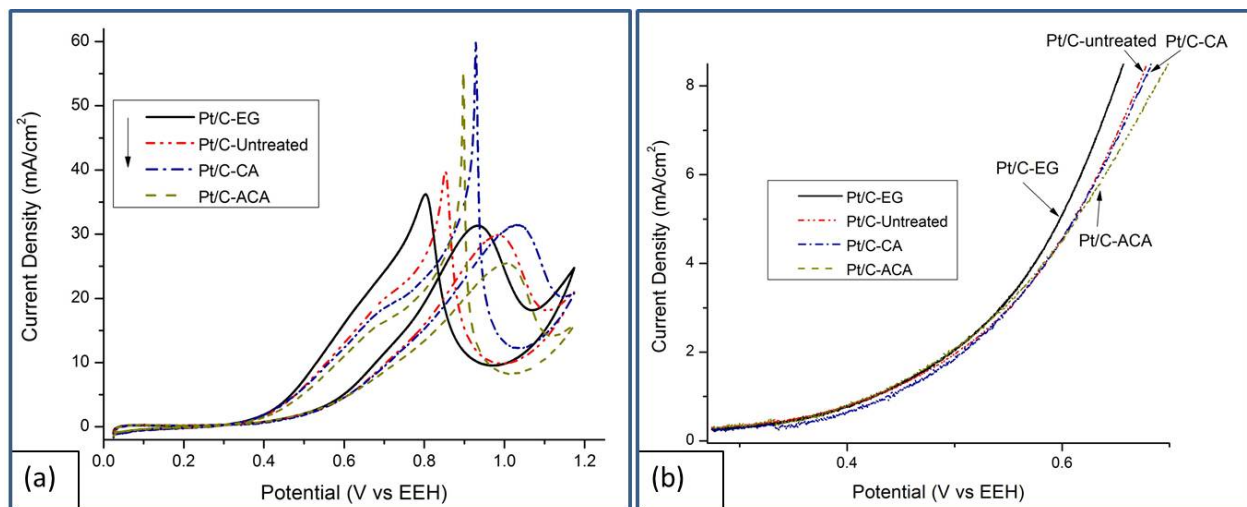


Figure 6 Cyclic voltammograms of ethanol electrooxidation in  $\text{N}_2$ -saturated solution of 0.5 M  $\text{H}_2\text{SO}_4$ +1M  $\text{C}_2\text{H}_6\text{O}$  at 25°C.



The chronoamperometric curves at a constant potential of 0.87 V in an N<sub>2</sub>-saturated solution of 0.5 M H<sub>2</sub>SO<sub>4</sub>+1M C<sub>2</sub>H<sub>6</sub>O at 25°C are showed in figure 7. The final current density at 600 s is 13.92, 13.35, 12.3 and 11.96 mAcm<sup>-2</sup> for Pt/C-AC, Pt/C-EG, Pt/C-AAC and Pt/C-untreated, respectively. It is clear that the Pt/C-AC electrocatalysts has de maximal current density in accordance with the results of ethanol electrooxidation. This high stability along the time may be due to the better interaction between the Pt particles and the carbon.

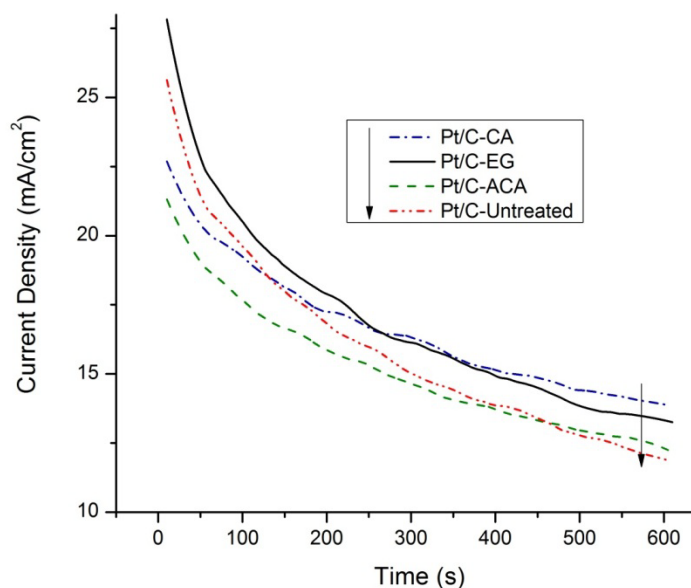


Figure 7 chronoamperometric curves of ethanol electrooxidation on the Pt/C electrocatalysts prepared on functionalized supports.

#### 4. Conclusions

Carbon Vulcan XC-72 was functionalized by using different chemicals reagent assisted by intermittent microwave irradiation. The influence of this chemical modification on the physicochemical and electrochemical properties of catalysts was investigated. The XPS spectra showed an increase of O1s and C1s species due to chemical modification of carbon support and modified the Pt state in the electrocatalysts. The electrochemical measurements indicated that Pt/C-CA exhibits a significantly higher Pt utilization efficiency in comparison with Pt/C-untreated, Pt/C-EG and Pt/C-ACA. The Pt/C-EG has a significantly enhanced in EOR in comparison with the other samples. Therefore, the results indicate that EG and CA functionalization is one of effective ways to enforce the interaction between Pt and carbon support.

#### 5. Acknowledgments

The authors wish to thank Conacyt for financial support through grant 164251.

**XIII Congreso Internacional de la Sociedad Mexicana del Hidrógeno  
Aguascalientes, México, 2013**

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