

Functionalization of Vulcan XC-72 by IMH and its Effect as Support for Pt Electrocatalysts for the EOR

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ABSTRACT

In this study, Vulcan XC-72 was functionalized by an intermittent microwave heating (IMH) method in two different soft chemical agents, namely citric acid (CA) and methanol (MeOH). The results showed physical and chemical changes in the structure of functionalized Vulcan. Pt/C electrocatalysts were synthesized by pulse IMH assisted polyol method using the treated carbons as support. The electrochemical activity and stability of the Pt/C materials were investigated by cyclic voltammetry and chronoamperometry measurements. The electrochemical results showed higher catalytic activity and stability of Pt nanocatalyst supported on some of the functionalized carbons for the Ethanol Oxidation Reaction (EOR), compared to a Pt/C electrocatalysts dispersed on non-treated Vulcan. The higher performance shown by Pt/C electrocatalysts dispersed on functionalized supports has been attributed to: i) a better distribution of nanoparticles, and ii) an enhanced interaction between Pt nanoparticles and the oxygenated species formed over the surface of the treated carbon. The results suggest that functionalization of Vulcan with MeOH and CA using the IMH method could become a promising process for the development of highly active Pt/C catalyst for the EOR due to its simplicity and low cost.

Keywords: functionalization of Vulcan; citric acid and methanol; EOR



1. Introduction

Direct Alcohol Fuel Cells (DAFCs) have attracted a great interest as power source for small scale stationary and portable applications due to the simplicity of fuel handling, low operation temperature, high power density, and fuel availability [1-5]. The most common fuels such as methanol, ethanol, ethylene glycol, propanol, and others possess physicochemical properties that make them good candidates for DAFCs [6, 7]. Since it is easily produced from biomass by fermentation of sugar containing raw materials, ethanol (C_2H_5OH) is considered an excellent fuel for low temperature Direct Ethanol Fuel Cells (DEFCs). Ethanol has a relatively low toxicity, high mass energy density, and high availability [8, 9]. However, ethanol molecules have two bonded carbon atoms, and as a result the EOR is complex [10].

At the present, Pt-alone catalysts are still considered to be used as anodes for DEFCs because such catalysts can adsorb and dehydrogenate small organic molecules [11,12]. High surface-area Pt-supports have been proposed to be used in DEFCs because their morphology provide access to a much larger number of active atoms, related to the corresponding bulk metal [13]. The ideal support must have the following characteristics: i) high electrical conductivity; ii) high corrosion resistance under fuel cell operation environment; and iii) must promote the transport of reactants onto the catalysts layer [14]. Carbon materials are recognized as attractive Pt supports because they have high surface area and good chemical stability [15]. Nevertheless, as-received carbon black typically has high ash content and a hydrophobic surface, that results in low capability to anchor Pt nanoparticles [16]. Therefore, several studies have been carried out to modify and functionalize the surface of carbon supports to enhance its interaction with nanoparticles, thus increasing its catalytic activity.

In this study, carbon Vulcan XC-72 was functionalized in CA and MeOH solutions using an IMH process. The functionalized materials were used as support to synthesize Pt/C anodes. Their performance was evaluated for the EOR in acid media.

2. Experimental

2.1. Carbon functionalization

Vulcan XC-72 (Cabot[®], specific surface area of $237 \text{ m}^2 \text{ g}^{-1}$) was chemically treated with CA and MeOH as soft chemical agents, in order to create functional groups that enhance the catalytic activity of Pt/C electrocatalysts. Table 1 presents the design of experiment proposed to achieve the functionalization of the support. As can be seen, it considered three different concentrations of the chemical agents (0.05, 0.1 and 0.15 M) with two irradiation time (4 and 8 min).

The procedure to carry out the functionalization is described as follows: Carbon powder (300 mg) was dispersed in a round bottom flask for 1 h in a solution of the corresponding chemical agent, namely CA or MeOH, by ultrasound. Afterwards, the carbon mixture was placed in the center of modified domestic microwave-oven and heated using a 25 s power-on/15 s power-off cycle for 4 or 8 min under magnetic stirring. The resulting solution was allowed to cool down and then was filtered and dried at 200°C for 30 min, to remove any traces of chemical agent and water.



Table 1. Design of experiments for the functionalization of carbon support.

Catalysts	Chemical agent	Concentration (mol L^{-1})	Irradiation time (min)
Pt/C-CA1	CA	0.05	4
Pt/C-CA2	CA	0.05	8
Pt/C-CA3	CA	0.1	4
Pt/C-CA4	CA	0.1	8
Pt/C-CA5	CA	0.15	4
Pt/C-CA6	CA	0.15	8
Pt/C-MeOH1	MeOH	0.05	4
Pt/C-MeOH2	MeOH	0.05	8
Pt/C-MeOH3	MeOH	0.1	4
Pt/C-MeOH4	MeOH	0.1	8
Pt/C-MeOH5	MeOH	0.15	4
Pt/C-MeOH6	MeOH	0.15	8

2.2. Synthesis of Pt/C

Pt/C catalysts having 20 wt. % Pt loading were synthesized by the IMH polyol method as follow: 56 mg of treated Vulcan were dispersed by ultrasound in an EG/H₂O solution (v/v= 90/5) and to this mixture 37 mg of H₂PtCl₆ 6H₂O dispersed in an EG/H₂O solution were added drop by drop. The colloidal solution was stirred for 1 h and the pH was adjusted to around 12 using a NaOH/EG solution. After that, the mixture was put in the microwave-oven and submitted to 600 W of irradiation continuously for 58 s, followed by pulses of 4 s power-on/15 s power-off for 40 min. The mixture was left cool off overnight with continuous stirring. Then, the pH was adjusted to 3 using H₂SO₄/EG solution. The final products were filtered and washed with water.

2.3. Catalysts characterization

X-ray patterns were obtained in a Phillips-X'Pert diffractometer using CuK α radiation (λ = 0.15406 nm) source. The scan was from 10 to 100° (2 θ).

The chemical composition of catalysts was determined by SEM-EDS in an XL30 Phillips Microscope, operating at 20 kV.

Electrochemical measurement were performed on an Voltalab PGZ 301 potentiostat/galvanostat in a standard three electrode cell using Ag/AgCl as the reference electrode and platinum foil as counter electrode. The working electrode was a thin layer of the synthesized catalysts and Nafion[®] dispersed on a glassy carbon support (0.196 cm² geometrical area). Cyclic voltammetry and chronoamperometric curves were carried out in N₂-saturated 0.5 M H₂SO₄ without and with ethanol. The constant potential during chronoamperometry measurements was 0.87 V vs. SHE.



3. Results and discussion

3.1. Physicochemical characterization

Figure 1 shows the XRD patterns of the Pt/C catalysts synthesized by IMH using carbon supports pre-treated with CA (1a) and MeOH (1b). In both cases, the patterns of Pt dispersed on non-treated Vulcan are also shown as reference. The diffraction peaks at about $2\theta = 25^\circ$ are associated to the graphite structure of Vulcan, plane (002). The diffraction peaks nearly to 39.7° , 46.2° , 67.4° and 81.2° are attributed to the Pt (111), (200), (220) and (311) planes, respectively. The (220) plane was used to calculate the size particle according to the Scherrer's formula [4] and the results are summarized in Table 2.

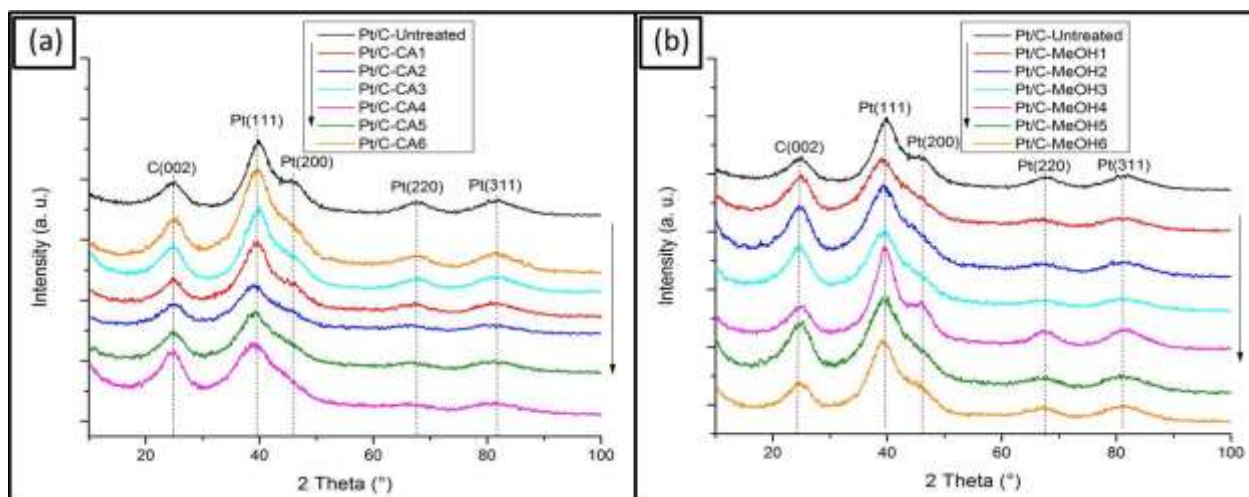


Fig 1. XRD patterns of a) Pt nanoparticles supported on carbon functionalized by CA; b) Pt nanocatalysts supported on carbon functionalized by MeOH.

From Figures 1(a), (b) it can be observed that the patterns corresponding to the Pt/C-CA and Pt/C-MeOH catalysts show some differences related to Pt/C-Untreated, which give as a result dissimilar characteristics regarding crystallinity and particle size. This can be more readily seen in the (220) plane. Overall, the patterns of Pt/C on treated Vulcan show a wider peak. Such characteristic may be due to the interaction of Pt nanoparticles with treated carbon during their nucleation and growth. The particle sizes of the catalysts (2.5 nm and smaller) are given in Table 2.

The results of the EDS analysis show that the metal loading on the Pt/C materials is closed to the nominal composition, i.e., 20 wt. %. Table 2 summarizes the Pt loadings obtained from the catalysts.

3.2. Electrochemical characterization

Figure 2 shows the CVs of the Pt/C nanocatalysts dispersed on Untreated, CA-treated and MeOH-treated Vulcan. The curves have very similar general shapes and current densities characteristics. Only the Pt/C-MeOH4 catalyst shows a noticeable smaller current density profile than the rest of the materials (Fig.



2d). The electrochemically active surface area (EAS) of the synthesized Pt/C materials can be determined by integrating the charge associated with the area of the hydrogen adsorption-desorption region, from the CVs in Figure 2, using the equation (1):

$$\text{EAS} = \frac{Q}{Q_0 \times Pt_{\text{loading}}} \quad (1)$$

where Q is to the integrated charge in the hydrogen adsorption-desorption area from the CVs, Q_0 is the theoretical charge required for the adsorption of a monolayer of hydrogen on polycrystalline Pt ($210 \mu\text{C cm}^{-2}$) [17], and Pt_{loading} is the amount of Pt dispersed on the working electrode.

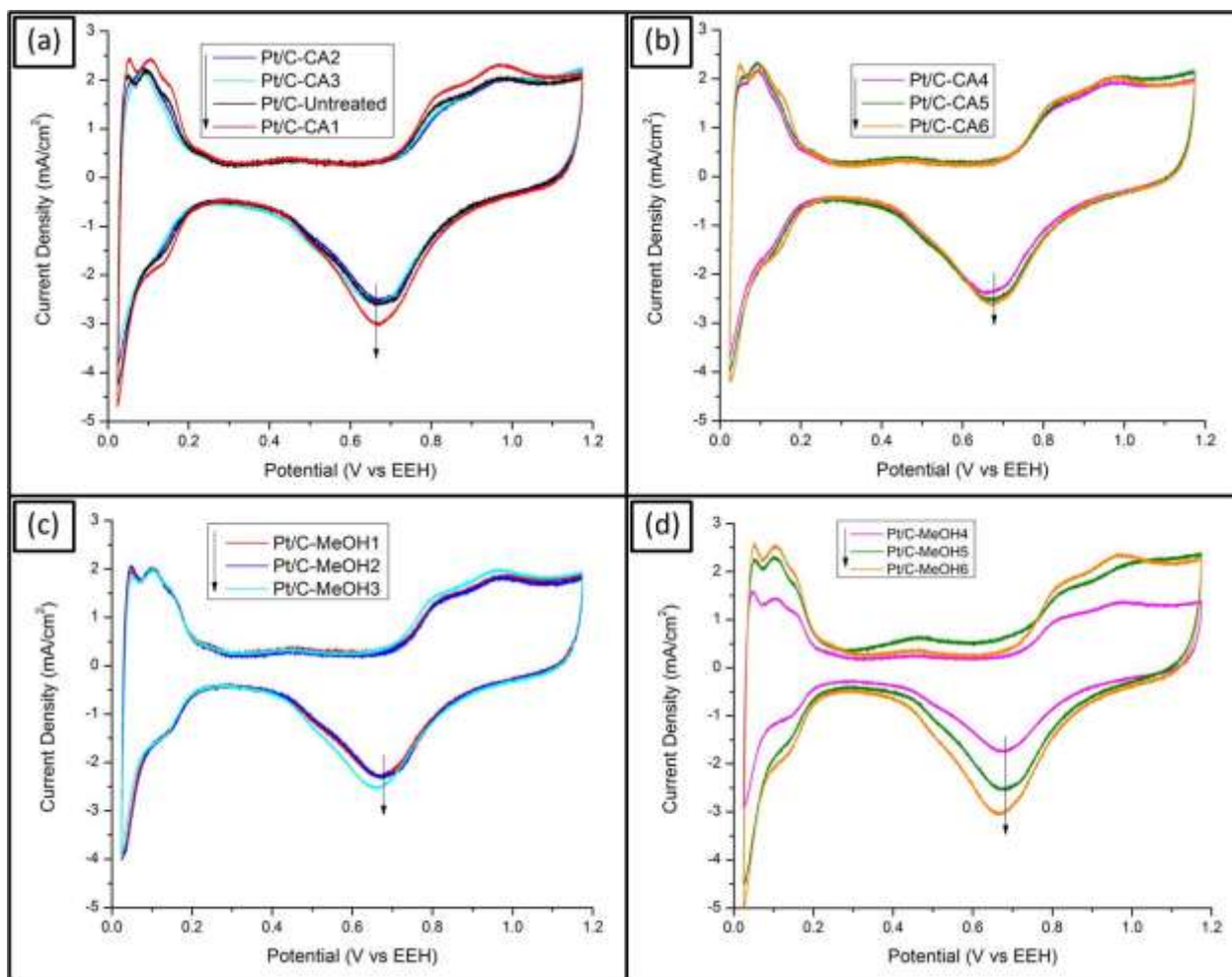


Fig 2. CVs of Pt/C nanocatalysts. (a) and (b) Pt/C (treated by CA) and Pt/C-Untreated; (c) and (d) Pt/C (treated by MeOH). Scan rate of 20 mV s^{-1} at room temperature in $0.5 \text{ M H}_2\text{SO}_4$.



The EAS of the catalysts are summarized in Table 2. It can be seen that Pt/C-CA1, Pt/C-CA6, Pt/C-MeOH5 and Pt/C-MeOH6 present higher EAS values than Pt/C-Untreated: 66.9, 65.3 and 63.7, 62.8 $\text{m}^2 \text{g}^{-1}$, respectively, against 59.6 $\text{m}^2 \text{g}^{-1}$ of the latter. Meanwhile, Pt/C-CA3 and Pt/C-MeOH4 have the lower EAS values: 48.2 and 42.7 $\text{m}^2 \text{g}^{-1}$ respectively.

Table 2. Pt content, particle size and EAS values of the Pt/C catalysts

Catalysts	Pt loading (%)	Particle size from XRD (nm)	EAS ($\text{m}^2 \text{g}^{-1}$)
Pt/C-Untreated	20.6	2.1	59.6
Pt/C-CA1	21.5	1.9	66.9
Pt/C-CA2	19.5	2.1	55.6
Pt/C-CA3	20.8	2.0	48.2
Pt/C-CA4	17.9	---	53.5
Pt/C-CA5	20.0	1.8	58.7
Pt/C-CA6	19.9	1.8	65.3
Pt/C-MeOH1	20.1	1.8	56.2
Pt/C-MeOH2	17.7	1.7	58.7
Pt/C-MeOH3	18.8	1.9	52.4
Pt/C-MeOH4	19.9	2.5	42.7
Pt/C-MeOH5	17.74	1.5	63.7
Pt/C-MeOH6	18.64	1.7	62.8

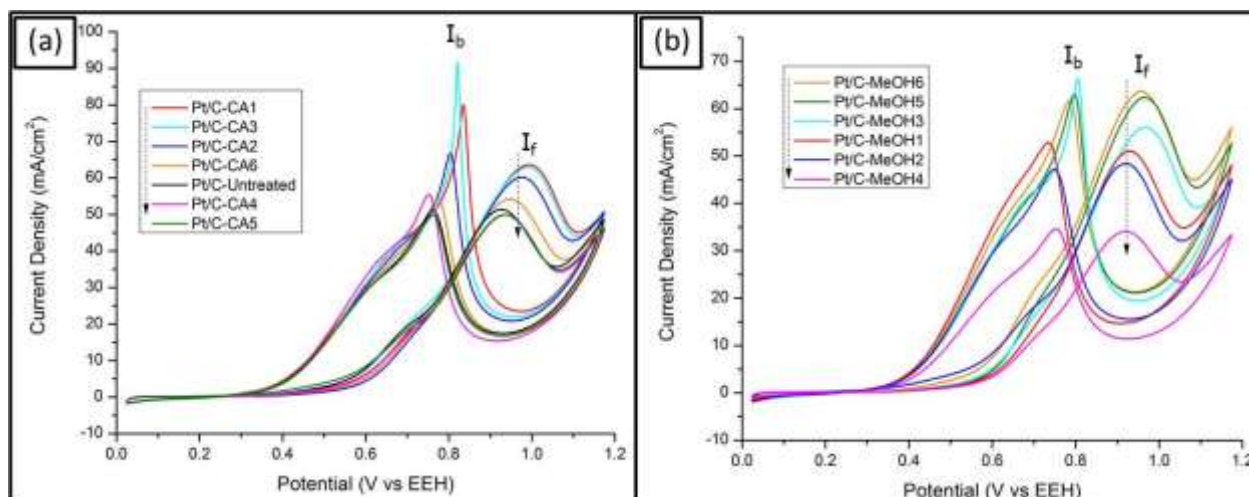


Fig 3. CVs of the EOR. a) Pt/C (functionalized by CA) and Pt/C-Untreated. b) Pt/C (functionalized by MeOH). Electrolyte: N_2 -saturated 0.5 M H_2SO_4 + 1 M $\text{C}_2\text{H}_6\text{O}$.



The polarization curves of the EOR at the Pt/C catalysts are shown in Figure 3. The anodes with the higher catalytic activity for the EOR are Pt/C-MeOH6, Pt/C-CA1, Pt/C-CA3 and Pt/C-MeOH5, with current density values of 63.7, 63.5, 63.1 and 62.3 mA cm⁻², respectively (see Table 3). The higher performance for the EOR of some of the Pt catalysts supported on treated Vulcan suggests that its functionalization with CA and MeOH increases the number of surface functional groups, resulting in a more homogeneous dispersion of Pt nanoparticles on the support and therefore on the catalytic activity for the anodic reaction. Most of the catalysts in Table 3 have onset potentials of the EOR roughly around 0.3 V vs. SHE, with the exception of Pt/C-CA3 and Pt/C-MeOH5 with a higher value.

The catalyst tolerance to CO and other reaction intermediaries can be evaluated by the ratio of the anodic current densities in the forward (I_f) and reverse (I_b) scans [18, 19]. A high I_f/I_b ratio suggests that the catalyst efficiently oxidizes ethanol in the anodic scan, producing small amounts of intermediaries that will be oxidized in the cathodic direction. Table 3 summarizes the I_f/I_b ratio of the Pt/C catalysts. It is observed that Pt/C-MeOH6 has the highest I_f/I_b value, followed closely by Pt/C-Untreated, Pt/C-CA5, Pt/C-CA6, Pt/C-MeOH2. However, it should be noted as mentioned before that Pt/C-MeOH6 shows a higher current density of the EOR.

Considering these three EOR parameters, it is clear that Pt/C-MeOH6 is the most active catalyst among those enlisted in Table 3. The performance of Pt/C-MeOH6 may be attributed to the surface composition (presence of functional groups) of the treated Vulcan and its interaction with Pt nanoparticles, thus enhancing the catalytic activity for the EOR.

Table 3. Electrocatalysis parameters of the Pt/C catalysts for the EOR.

Catalysts	Onset potential (V)	Peak current density (mA cm ⁻²)	I_f/I_b ratio
Pt/C-Untreated	0.30	51.0	1.0
Pt/C-CA1	0.30	63.5	0.80
Pt/C-CA2	0.35	60.2	0.90
Pt/C-CA3	0.31	63.1	0.68
Pt/C-CA4	0.30	49.9	0.90
Pt/C-CA5	0.29	49.8	1.0
Pt/C-CA6	0.30	54.0	1.0
Pt/C-MeOH1	0.31	50.9	0.96
Pt/C-MeOH2	0.28	48.3	1.0
Pt/C-MeOH3	0.28	55.8	0.85
Pt/C-MeOH4	0.29	33.8	0.98
Pt/C-MeOH5	0.34	62.3	0.98
Pt/C-MeOH6	0.30	63.7	1.03

Figure 4 shows the chronoamperometric curves of the EOR at the four most active Pt/C catalysts (supported on CA or MeOH treated Vulcan) and Pt/C-Untreated. The Pt/C-CA1 shows a more stable current density after 600 s. Meanwhile, Pt/C-MeOH6, Pt/C-MeOH5 and Pt/C-CA2 show similar current density-time characteristics. Thus, Pt/C-MeOH6 which has high electrocatalysis values in Figure 3 and



Table 3 also demonstrates a good stability for the EOR. On the other hand, Pt/C-Untreated presents a more important current density decay in the first 100 s and maintains a lower performance over the testing. These results suggest that Pt nanoparticles supported on treated Vulcan have a better stability compared with Pt supported on untreated carbon for the EOR.

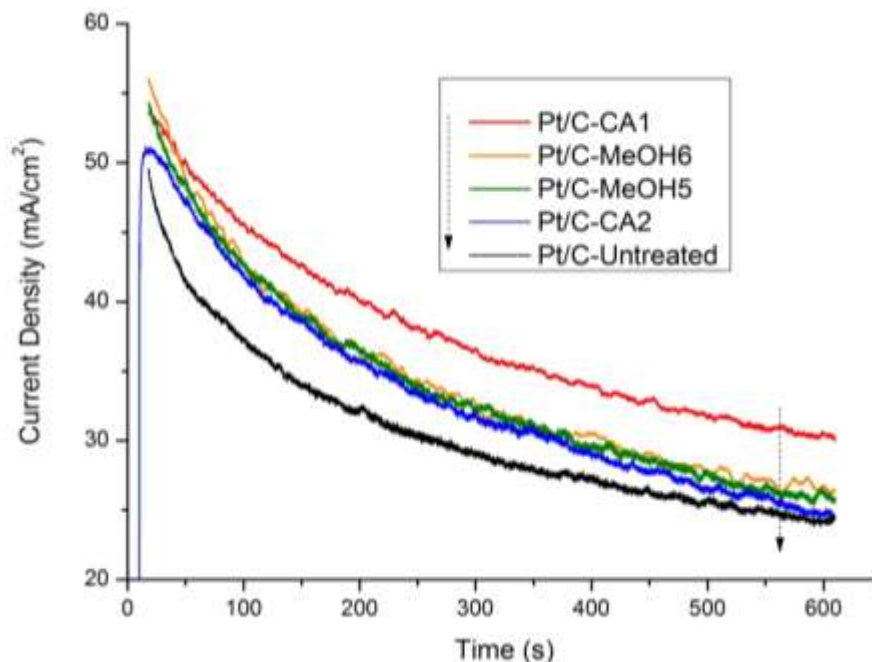


Fig 4. Chronoamperometric curves of the EOR at the Pt/C catalysts. Constant potential: 0.87 V vs. SHE. Electrolyte: N₂-saturated 0.5 M H₂SO₄ + 1 M C₂H₆O.

4. Summary and perspectives

Commercial carbon Vulcan XC-72 was functionalized in different concentrations of MeOH and CA using the IMH process. The treated carbon was used as support for Pt nanoparticles. The electrochemical characterization indicates that the performance of Pt/C catalysts is influenced by the conditions of functionalization and synthesis parameters. The Pt/C-MeOH6 sample, synthesized using carbon functionalized in 0.15 mol l⁻¹ methanol for 8 min showed the highest catalytic activity for the EOR among the materials studied in this work.

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