

The effect of physicochemical Pretreatment of Supported Pt Nanoparticles for the ORR. A Novel Carbon from Natural Source.

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ABSTRACT

Materials used as nanoparticles supports play an important role in the performance, efficiency and stability of catalysts applied in polymer fuel cells. Carbon supports have been employed for their excellent properties like good electronic conduction, high surface area, relative crystallinity and resistance to acids and alkalis moderate. The surface modification of carbon by physicochemical treatment (functionalization) has a favorable effect on the performance and stability of the catalyst to improve the metal-support interaction through anchoring sites which in turn favor the distribution of the metal particles on the carbon matrix. The shape and particle size are influenced by the properties of the support and these characteristics are directly related (together with the diffusion of gases and ionomer interaction conductor) with the catalytic activity towards the reactions of interest. Pre-treated Carbon Vulcan with nitric acid is the most used support for nanoparticles in polymer fuel cell. However its origin derived from the combustion of waste oil (non-renewable energy source) makes it unattractive for future applications by issues of environmental pollution, furthermore the sulfur content and other impurities can degrade and decrease the lifetime of the metal catalysts. In this study we present the research for a new type of carbon obtained by a simple process from natural sources. This carbon was treated by different physicochemical methods and then Pt nanoparticles were synthesized and supported by chemical reduction with NaBH₄ on the different pre-treated carbons. This work plan is performed with the main target to evaluate the potential use of natural carbon as a novel support material and to analyze the effect of different treatments on the catalytic activity of nanoparticles towards the ORR. The study is complemented by physical characterization techniques like XRD, FTIR, Raman, SEM, EDAX, HRTEM and electrochemical techniques by RDE in acid medium. All the results are compared with Pt/Vulcan Carbon XC-72R pre-treated.

Keywords: Novel natural carbon; Oxygen reduction reaction; Physicochemical pretreatment to carbon.

1. Introduction

Catalytic processes play an important role in the development of new chemicals, many of them of great value added worldwide. Catalysis involves accelerating the reaction rate and favor selectivity of the chemical reactions of interest. [1] In our particular case, the oxygen reduction reaction (ORR) is of



relevant importance in the performance of a proton exchange membrane fuel cell (PEMFC) because the cathodic region (place wherein said reaction is carried out) limiting the efficiency of system given that the kinetics reaction is very slow compared to the hydrogen oxidation reaction at the anodic region [2]. Platinum is, until today, the best catalyst to the ORR. To increase its catalytic activity is necessary to form Pt nanoparticles on the order of 2 to 3 nm. With decreasing size of the nanoparticles is achieved to increase the number of active sites on which the reaction is carried out, this results in an increase of the Platinum Electrochemical Surface Area (ECSA) and improved the catalytic activity [3,4]. Generally nanoparticles are dispersed on a conductive support material of high surface area such as carbonaceous matrices [5]. Supports have the aim to be a matrix which promotes a good homogeneous distribution by reducing the effects of agglomeration of the metal particles (this results in an improvement of the catalytic activity), also have a great influence on the stability of the catalyst itself and allow to reduce costs by not using full loads of catalytic metal [5]. The materials used as supports have highly porosity and they must have preferably the following characteristics [1]:

- High surface area to promote a good dispersion of the catalyst.
- Suitable size and distribution of pores for the successful diffusion of the reactant gases and byproducts.
- Good electrical conductivity to transfer electrons between the electrodes.
- Chemical and electrochemical corrosion stability.
- Suitable surface chemistry (functionalization) to facilitate the interaction with the catalytic material during the synthesis process.
- Hydrophilicity (affinity to water).
- Low level of surface impurities.
- Ease recovery of catalytic metal at the end of their life cycle.
- Abundant and affordable.

In this sense many materials have been investigated in order to obtain a better support for metal catalysts. Some like graphite and the significant improvement of its activity by chemical treatments for use in microbial fuel cells [6]; metal oxide nanowires as WO_3 (tungsten trioxide) which has had a significant interest in recent years as supported of Pt nanoparticles showing a higher catalytic activity than Pt/C and excellent tolerance to CO [7]; carbon nanotubes used as a 3D structural network which confers high stability and high catalytic properties of materials [8,9]; graphene sheets whose high number of edges and small pores allows to the formation of the catalyst active sites [10]; mesoporous carbons, aerogels and xerogels whose pore sizes ranging between 2 and 50 nm [8,11-13] give a greater surface area as Ketjen Black EC 300J carbon with $829 \text{ m}^2 \text{ g}^{-1}$ [14]; among other materials supports.

Among all the supports mentioned above, Vulcan Carbon XC-72R is the most widely material used as catalyst supports for PEM fuel cell applications [8,11]. It is obtained from the pyrolysis of hydrocarbons from the oil fractionation and natural gas sources that are fed to a furnace at 1400°C with flowing air. This process maintains a low ash content of about 1% by weight [8]. Vulcan carbon has $254 \text{ m}^2 \text{ g}^{-1}$ of surface area and maintains a certain degree of crystallinity and good electronic conductivity; however belongs to the category of microporous carbon because their pores are below 2 nm in diameter in spite of maintaining a mean particle size of 30 nm; this is a disadvantage because the pores are too small to accommodate Pt nanoparticles with similar sizes (2-3 nm) and therefore metal particles reside primarily on the carbon surface making them prone to agglomeration effects or detachment of the support [11]. Nevertheless Vulcan Carbon XC-72R continues to hold as the ideal support and his substitute has not been discovered yet, thus opening a wide research around the world whose objective is the search for new materials that



allow replace it, and as far as possible implement process more friendly with environmental to carbon generation such as obtaining carbon from natural sources [15,16].

When carbon is used as nanocatalyst support without performing a surface modification does not have binding sites suitable for anchoring the metal ion precursors or the metal nanoparticle directly during the synthesis process [5]; which leads to a low dispersion of nanoparticles and a high probability of agglomeration which has a direct negative effect on the catalytic activity, especially working in conditions where it has a high metal loading and even when working with magnetic metals. To avoid such problems is carried out a process known as functionalization or modification of the carbon surface conducted through chemical agents or heat treatments. Derbyshire et al. [17] found that the surface chemistry of carbon associated with the surface functional groups which are formed during chemical pre-treatments given to the carbon plays an important role in the distribution of metal catalysts, and consequently there is an improvement in its catalytic properties. Many functional groups can be incorporated into carbon and which are based on elements such as oxygen, nitrogen, hydrogen, carbon, sulfur, phosphorus and some halogens [18], the most investigated are those groups containing C-O. It is difficult to establish the precise nature of surface oxygen groups on the carbonaceous material; however, the most common types of such groups are carboxylic, phenolic, lactones, ethers, quinones, carbonyl, anhydrides and others groups which are the result of oxidative processes given to carbon mainly with HNO_3 , H_2SO_4 , KOH , H_2O_2 or with O_2 and O_3 in gas phase [8, 18 - 20]. The presence of such groups reduces the hydrophobic character of the carbon material, thereby making the surface more accessible to the metal precursors during the impregnation process with aqueous solutions and serve as anchoring sites for fixing metal nanoparticles and preventing agglomeration during the reduction process [1, 8, 19, 20].

The objective of this study is primarily focused on presenting a new type of carbon obtained from natural sources such as camphor by a simple process (which is patent pending). Secondly it is desired to elucidate the effect of the functionalization treatment given to the new carbon support on the catalytic activity of Pt nanoparticles toward the oxygen reduction reaction. This materials was both physically evaluated by HRTEM, SEM, XRD, Raman spectroscopy and FTIR and electrochemically by Rotating Disk Electrode (EDR) techniques.

2. Experimental

2.1 Preparation of a new carbon from natural source

The new type of carbon was obtained from a natural source such as the camphor (Camphor Carbon = CC) by a simple procedure which we cannot give specifics details because the methodology is patent pending. Amounts of 160 mg from powder carbon obtained (CC) were subjected to different methods: 1) Camphor carbon without any treatment (CC). 2) Thermal treatment under inert conditions at 400°C for four hours (CC-TT). 3) Chemical treatment with 160 ml of 1M HNO_3 under reflux conditions for four hours with magnetic stirring (CC- HNO_3). 4) Chemical treatment with 160 ml of 0.5M KOH under reflux conditions for four hours with magnetic stirring (CC-KOH). In methods 2 and 3 it was observed that the initial carbon without functionalization had hydrophobic characteristics and precipitates after a few minutes. However, with the heating and the first drops of refluxing, a more homogeneous mixture was observed, this is evidence of a more hydrophilic carbon. Once reflux time finish, carbons were filtered and



washed under vacuum conditions with deionized water until the filtrate had a pH near neutrality. The final product was dried in a furnace at 120 °C for 2 hours under N₂.

2.2 Preparation Vulcan Carbon XC-72R for comparison

Vulcan Carbon XC-72R (Cabot) was used in order to compare the properties of new carbon. Vulcan Carbon was subjected to chemical treatment following a modified procedure reported by Senthil-Kumar et al. [20]. Vulcan Carbon powder (2 g) was dispersed in 500 ml of 5% v/v HNO₃. The mixture was brought to reflux conditions and magnetic stirring at 120 °C for 16 hours. The material was recovered by vacuum filtration and washed with deionized water until the filtrate reached a pH near neutrality. The final product was dried in a furnace at 120 °C for two hours under N₂. This material was identified simply as Vulcan.

2.3 Preparation of Platinum nanoparticles catalysts supported on carbon

Supported catalysts of platinum nanoparticles were prepared with reference to the method reported by Zeng et al. [21] which was modified and adapted to our laboratory conditions. In a typical procedure: In a 250 ml three necked flask 48 mg of any of the previously treated carbons were dispersed in 50 ml of deionized water. Subsequently 91 mg of Sodium Citrate Di-hydrate and 31 mg of K₂PtCl₆ (Citrate:K₂PtCl₆ = 5:1) were dissolved in 20 ml of deionized water and then were added to the first mixture. The mixture was dispersed under ultrasonic bath for 15 minutes and then was kept under magnetic stirring for two hours under N₂ flow to deoxygenate the solution. The mixture was heated by oil bath while maintaining the inert atmosphere and upon reaching 80 °C an excess reducing solution (14 mg of NaBH₄/5 ml of deionized water) was added via syringe. The mixture was maintained at reflux for one hour. The final product was recovered by centrifugation and several washes were performed with water-acetone mixture. Finally the material was dried in a furnace at 120 °C for 2 hours under N₂. The yields in all cases were above 95%. Thus, five carbon supported catalysts with metal loading estimated at 20% weight were obtained with the following identifications: Pt/Vulcan, Pt/CC, Pt/CC-TT, Pt/CC-HNO₃ and Pt/CC-KOH.

2.4 Physical characterization

2.4.1 UV-Vis spectroscopy

With the purpose to observe the reduction reaction evolution of [PtCl₆]²⁻ species, a UV-Vis spectra was obtained from a control synthesis which not contained carbon. The experiment was carried out on a Perkin-Elmer Lambda 12 UV-Vis spectrometer. Aliquots from the solution were extracted at different times and rapidly they measured to obtain their UV-Vis spectra.

2.4.2 Fourier Transform Infrared and Raman Spectroscopy

Raman spectra were recorded for all the carbon supports on a HORIBA Jobin Yvon LabRAM HR800 confocal microscope Raman spectrometer used a red laser with an excitation wavelength $\lambda=632.81$ nm to characterize the degree of graphitization of the carbon support materials. FT-IR was performed with a IR2 module FTIR spectrometer coupled to the confocal microscope Raman using an attenuated total reflection (ATR) accessory.

2.4.3 X-Ray Diffraction



Powder X-Ray Diffraction (XRD) analyses were carried out on a Rigaku Miniflex 600 diffractometer using a Cu K α : $\lambda=1.5406 \text{ \AA}$ radiation operated at 40 kV and 15 mA. Scans were measured in the range of 15-90° with a scan speed of 3 degrees/min and step width of 0.0100 deg. XRD patterns of all carbon supports and Pt catalyst supports were recorded.

2.4.4 Scanning Electron Microscopy

Scanning Electron Micrographs for all materials were obtained from a Zeiss HRSEM Auriga 3916 microscope equipped with a Schottky field emission GENIMI column working at 2 keV to examine the particle morphology. Elemental composition and mapping of the catalyst were measured by an Energy Dispersive X-Ray (EDX) detector attached to the microscope.

2.4.5 High Resolution Transmission Electron Microscopy

High Resolution Transmission Electron Micrographs for Pt supported catalyst were obtained from a Jeol JEM-ARM 200F microscope equipped with a Schottky field emission gun working at 200 keV to examine the particle morphology and the size distribution.

2.5 Electrochemical characterization

Electrochemical measures were carried out using a PARSTAT 2273 potentiostat/galvanostat coupled with a Rotating Disk Electrode system and using a three-electrode electrochemical cell. A Pt catalyst ink for each materials was prepared taking as reference the methodology reported by Garsany et al. [22] using a mixture of 2-Butanol, 2-Propanol and 5%w Nafion as dispersant media. 10 μl of the catalyst ink were deposited on the surface of a glassy carbon electrode, using as working electrode, with a geometric area of 0.196 cm^2 previously polished, rinsed and boiled with deionized water and dried in oven. The thin catalyst film formed had a Pt loading of 22.96 $\mu\text{g}/\text{cm}^2$. A fresh Hydrogen bubble electrode was used as reference electrode and a Pt mesh as counter electrode. 0.1M HClO₄ solution was employed as electrolyte. Firstly Cyclic Voltammetry was performed to activate the materials on a potential window of 0.05-1.2 V with a scan rate of 100 mV/s under a bubbling of N₂ flow. CO-stripping technique was performed on a potential windows of 0.05-1.2V with a scan rate of 20 mV/s with the purpose to determine the electrochemical surface area (ECSA). ORR sweep profiles were performed using the rotating electrode mode at 400, 900, 1600 and 2500 rpm under bubbling of O₂ flow. For this last measure, the potential window was 0.05-1.0V with a scan rate of 20 mV/s. A background profile was measure at the same conditions of the potential window for ORR measurement, but without electrode rotation and under N₂ flow. This was made with the purpose of subtract the background to the experimental ORR current and to eliminate any contribution of capacitive current [22]. The electrochemical characterization allows to determine the catalytic properties of the materials toward the oxygen reduction reaction.

3. Results and discussion

It knows experimentally that Sodium Citrate reduces the [PtCl₆]²⁻ species to Pt metallic (see eq. 1, 2) at elevated temperature [21], however with the purpose of accelerate the reaction it was added NaBH₄ as reducing agent. With this methodology the reduction process occurs very fast. Fig. 1 shows the UV-Vis spectra, with time dependence, for the absorption of the aqueous [PtCl₆]²⁻ species (Carbon free-contained) before and after to add the reducing solution. During the process it was evident the decrease of the



absorption band of the $[PtCl_6]^{2-}$ species at 264 nm, after 120 s the band practically disappears, this is result of the decrease of the precursor concentration to form Pt nanoparticles. Experimentally it observed a change of colour from pale yellow to a dark brown solution. The UV-Vis results are consistent with the found in the literature [23-25].

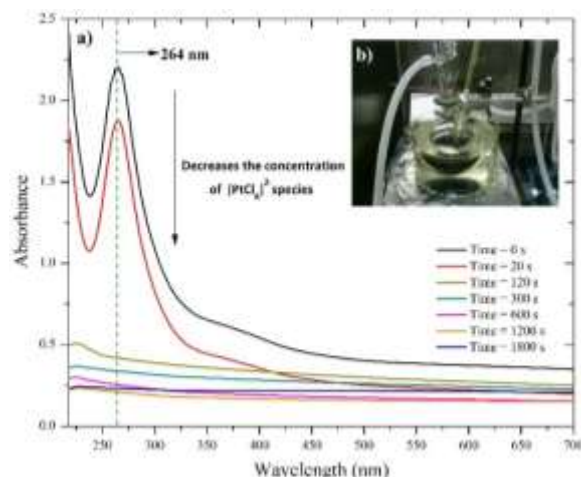
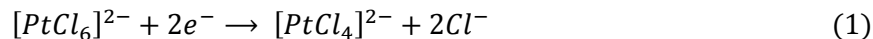


Fig. 1. a) Time dependent UV-Vis spectra for the reduction of $[PtCl_6]^{2-}$ species. b) Final dark brown colour obtained after one hour of reflux.

Raman spectroscopy is a powerful tool extensively used to distinguish the degree of ordering and disordering of carbonaceous materials [26]. Fig. 2a show the Raman spectra for all the carbon supports. The characteristic G band is appear at 1596 cm^{-1} and it is associated to all graphitic sp^2 carbon forms. Meanwhile the D band around at 1336 cm^{-1} is associated to the sp^3 hybridization of carbon atoms which indicates defects and disorder on a lightly graphitized material [27, 28]. The I_D/I_G (intensities) ratio is a qualitative measure of the disorder degree and number of the sp^2 domains [26]. In our case it appreciates that all the materials presents an amorphous behaviour because the 2D band practically is absent and the D and G bands are wide. Fig. 2a contains the values of the I_D/I_G ratio. Vulcan carbon has the higher value and is observed as the D band is higher than the G band, this suggests a possible dominance of a weak crystalline phase within the same amorphous carbon. It is necessary to take in count that this type of carbons in study belong to a class of materials called Carbon Blacks and they have a different form respect to diamond, graphite, charcoal, coke, among others. Carbon Blacks have a spherical or ellipsoidal form (which is possible see with HRSEM) and in their microstructure present both crystalline and amorphous substructures similar to a graphite layer with oriented planes [5]. For CC material the I_D/I_G ratio decreases compared with Vulcan carbon, this suggests the dominance of a more amorphous phase in this type of carbon. The subsequent treatments given to the CC slightly decrease the value but no results are relevant

for purposes of establishing a trend. In general, it can be suggested that the Vulcan carbon maintains a higher density of functionalized surface as evidenced by an increase in a high degree of defects in graphitic layers of the material compared to camphor carbons as suggested by changes in relationships I_D/I_G [27].

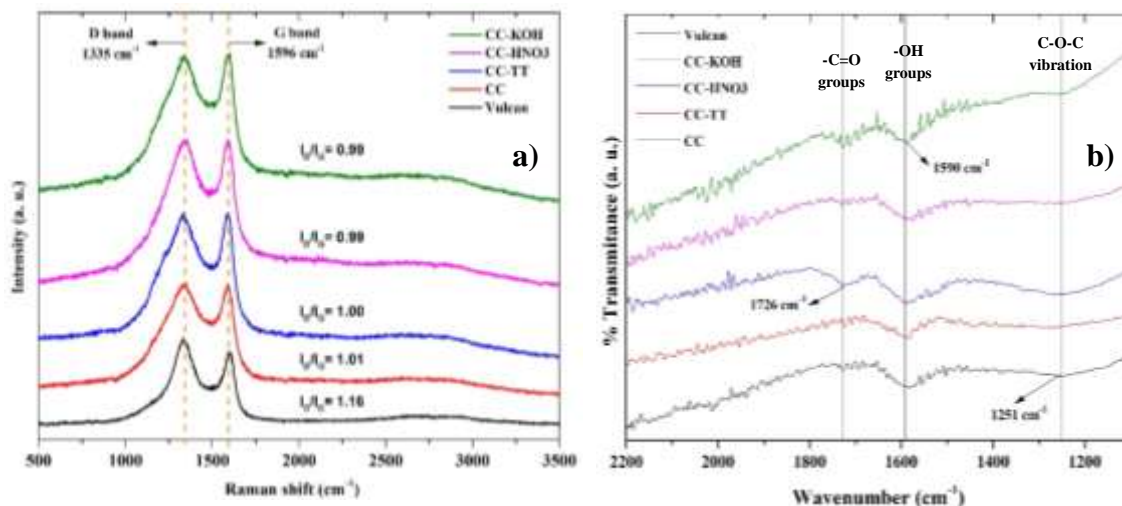


Fig. 2. a) Raman spectra and b) FT-IR spectra for carbon supports.

FT-IR spectra for carbon supports are showed in Fig. 2b. Three small characteristic bands were found in accordance to the literature [27, 29, 30]. The band at ~ 1726 cm⁻¹ found slightly more pronounced for Vulcan and CC-HNO3 and less pronounced for CC, and CC-KOH is associated to stretching mode of carbonyl groups. These groups were included on the surface of material after to the oxidative treatments with nitric acid given to Vulcan and CC-HNO3 carbons in accordance to the literature [8, 17, 27]. CC-TT material does not present this band possibly because the thermal treatment at 400°C eliminates this functional groups at this temperature interval. The wide band at ~ 1590 cm⁻¹ is assigned to bending vibration of the O-H group, evidence of the incorporation of -OH and -COOH groups which make more hydrophilic to the carbon. While CC material has this band originally, a slight increase in intensity after oxidative treatments is observed. This does not happen with the CC-TT in which the intensity decreases; so this is consistent with what previously said for the band at ~ 1726 cm⁻¹ due to the thermal treatment. The last less intense and wide band at ~ 1251 cm⁻¹ pronounced for all the materials, except CC-TT, can be assigned to the C-O-C vibration in ethers groups [27, 29, 30].

The X-Ray powder diffraction patterns for carbon supports and Pt/C are show in Fig. 3a and 3b respectively. For all the carbon supports (Fig. 3a) is evident a similar pattern which corresponds to an amorphous carbon with two diffraction maxima well defined according to the literature [28, 29], one broad (002) peak around at 24.47° and other less intense around at 43.33° which corresponds with the (100) reflection. It possible to appreciate a third peak around 80°, however this is much less intense and has not been found reported in the literature. If it takes the (002) diffraction maximum as comparative



reference for all carbons it is evident that CC-TT presents the most broad peak, which suggest a smaller crystallite size. When carbon are submitted to an oxidative chemical treatment it is possible that the microstructures may collapse and form a more amorphous carbon. Sharper (002) diffraction maximum around 26.38° corresponds to graphite phase, a shift of the (002) reflection to lower values below 26° is evidence, how occurs in our case, of the presence of an amorphous carbon [28].

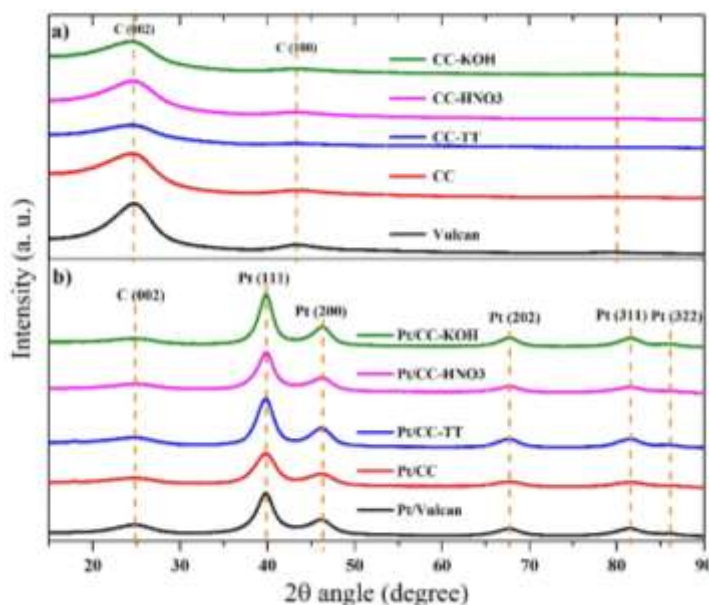


Fig 3. XRD patterns. a) Carbon supports. b) Pt/C catalysts.

Figure 3b shows the X-Ray powder diffraction maxima for Pt supported nanocatalyst. All patterns show clearly the characteristics reflections: (111) around at 40° , (200) around at 46° , (202) around at 67° , (311) around at 81° and (322) around at 85° correspond to a fcc lattice for pure bulk Pt metal [20]. Platinum crystallite size was calculated for (111) reflection using the Debye-Scherrer equation (eq. 3):

$$d = \frac{0.9 \lambda_{k\alpha 1}}{B_{2\theta} \cos \theta_{max}} \quad (3)$$

where $\lambda_{k\alpha 1}$ is the wavelength of X-ray (1.5406 \AA), $B_{2\theta}$ is the width half height (in rad) of the peak, and θ_{max} is the angle at the peak maximum [20, 28, 31]. Table 1 show the crystallite size for Pt/C catalysts, note that it exists a dependence of the Pt crystallite size respect the nature of each treated carbon. Pt-CC has the smaller crystallite size (2.9 nm) and all the treated carbons conducive an increase in the crystallite size. The chemical compositions were similar for all materials in accordance with theoretical expectations.

Scanning electron micrographs for Vulcan and CC supports are showed in Fig. 4a and 4b respectively. The morphology found for camphor carbon corresponds to particles like spheres and irregular ellipses

with an average size of 54 nm as shown in Table 2. Similar morphology was observed for Vulcan carbon with particle size of 53 nm, but there is a larger number of defects and smaller particles, possibly due to chemical attack with HNO_3 . This feature was also seen in the CC- HNO_3 material (micrograph not shown); however the damage is less compared with Vulcan. This might suggest that camphor carbon is more resistant to oxidative acid media; however keep in mind that the treatment given to Vulcan carbon was almost similar in concentration of HNO_3 but lasted four times higher (16 hours) compared with the treatment given to camphor carbon. Future studies BET surface area could clarify what hitherto found. The thermal treatment appear not to affect the morphology of carbon as is evidenced in the micrographs obtained (not shown); however the particle size decreased to 47 nm. Alkaline treatment apparently produces better rounded particles and increases the particle size (~60 nm).

Table 1. Properties for Pt/C catalysts obtained by XRD, EDAX-SEM and HRTEM.

Material	XRD crystallite size Pt(111) (nm)	XRD Semiquantitative Analysis		EDAX-SEM Quantitative Analysis		HRTEM Pt Particle size (nm)
		%C	%Pt	C (wt. %)	Pt (wt. %)	
Pt/Vulcan	3.5	80.0	20.0	83.5	16.6	2.51
Pt/CC	2.9	82.1	17.9	83.8	16.2	3.45
Pt/CC-TT	3.7	77.3	22.7	85.0	15.0	3.88
Pt/CC- HNO_3	3.8	76.2	23.8	86.9	13.0	2.74
Pt/CC-KOH	4.4	78.5	21.5	88.9	10.9	3.58

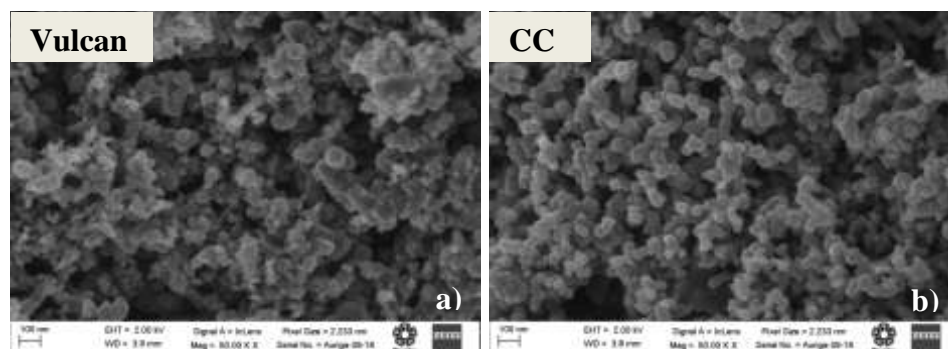


Fig. 4. SEM micrographs for: a) Vulcan carbon and b) Camphor carbon (CC).

Chemical composition for carbon supports are shown in Table 2. It can be seen that carbon with higher oxygen content is the CC- HNO_3 suggesting that oxidative treatment in effect incorporates new surface atoms and that the thermal and alkali treatment reduces the oxygen present. A prominent feature is that the camphor carbon do not contain sulphur.

The particle size of the catalysts of Pt supported was determined from the particle count of the HRTEM micrographs (Fig. 5a-d) as shown in Table 1. Is clearly observed that the treatment given to each carbon support influences in the Pt particle size. HNO_3 treatment allows a smaller particle size and thus a higher

surface area which have a positive effect on the catalytic activity for Pt/Vulcan. However the treatment with HNO₃ and KOH given to camphor carbon promotes agglomeration of particles of Pt, which is detrimental to the catalytic activity towards ORR and could explain the reduction of the elemental composition of Pt observed by EDAX (Table 1).

Table 2. Particle size and chemical composition for carbon supports.

Material	SEM Carbon particle size (nm)	C (atom %)	O (atom %)	N (atom %)	S (atom %)
Vulcan	53.0	94.58	2.71	2.57	0.14
CC	54.2	93.74	3.72	2.54	0.0
CC-TT	44.7	94.60	3.34	2.06	0.0
CC-HNO ₃	65.3	90.64	6.84	2.50	0.0
CC-KOH	59.6	94.65	3.10	2.25	0.0

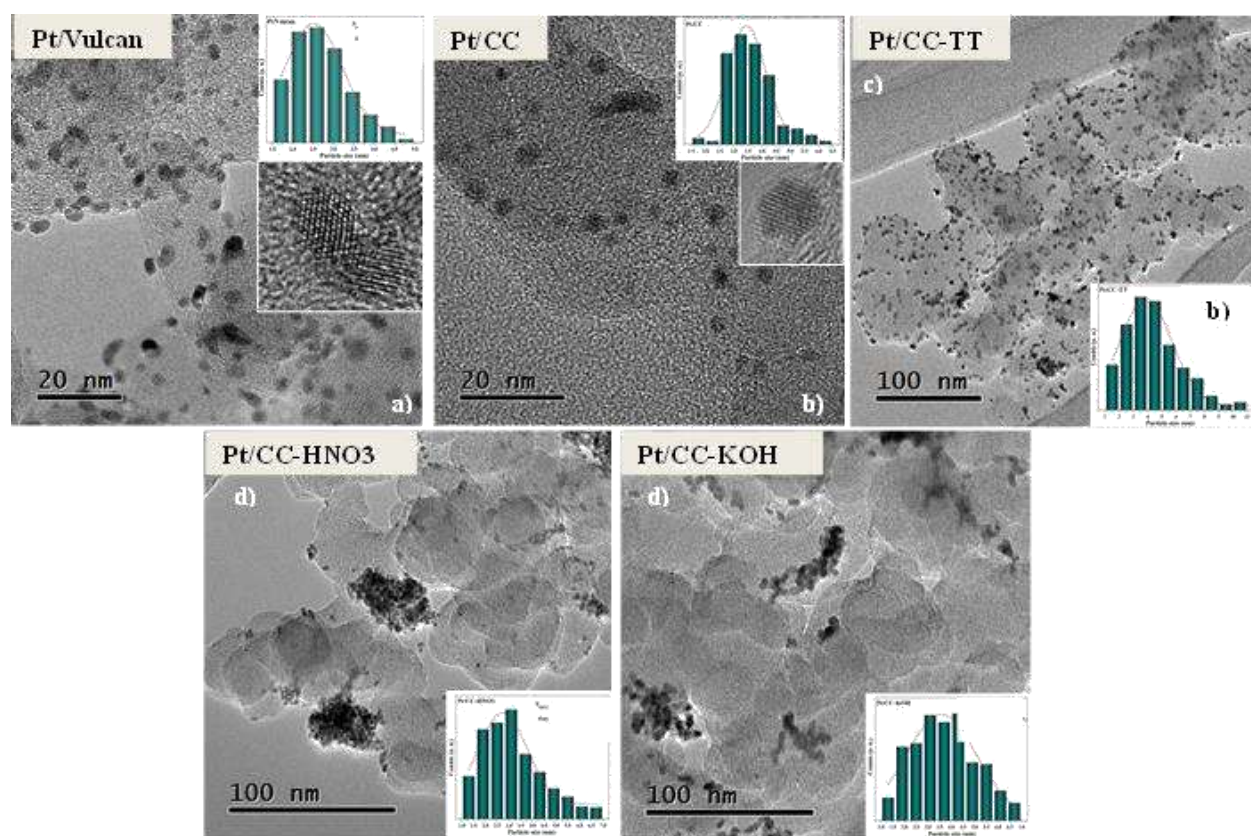


Fig. 5. HRTEM micrograph with size distribution for Pt/C catalysts.

Fig. 6 shows the cyclic voltammeteries for the Pt/C catalysts. It has essentially the characteristic response for Pt nanoparticle where the capacitance region is more pronounced for the Pt /Vulcan and Pt/CC-HNO₃

materials, which were treated with nitric acid. This feature suggests the presence of impurities in form of surface functional groups on the carbon which carried out oxidation-reduction process as a typical response of the quinone-hydroquinone equilibrium [32]. It is relevant to note that the Pt/CC-HNO₃ material exhibits a marked widening of voltammetric profile suggesting particle agglomeration problems which is indicated by HRTEM. Fig. 7a shows reduction curves for Pt/C catalysts with Tafel slopes corrected for mass transport (Fig. 7b). It is clear that materials with enhanced catalytic activity toward the ORR are in decreasing order: Pt/CC-KOH > Pt/CC-TT > Pt/CC > Pt/Vulcan > Pt/CC-HNO₃. This paradoxical behavior again is attributed to negative agglomeration effects seen in the micrographs despite having smaller Pt particles and contradicts the theory that a properly functionalized carbon promotes a better distribution of the metal nanoparticles on the surface. A better distribution leads to a more efficient use of the catalytic surface of the particles and if these are smaller, the material will have a greater active surface toward the ORR. In our study materials the best distribution was obtained for the Pt / CC-TT material even with the largest particle size obtained by HRTEM. Finally, Table 3 shows the numerical values for the specific activity and mass activity.

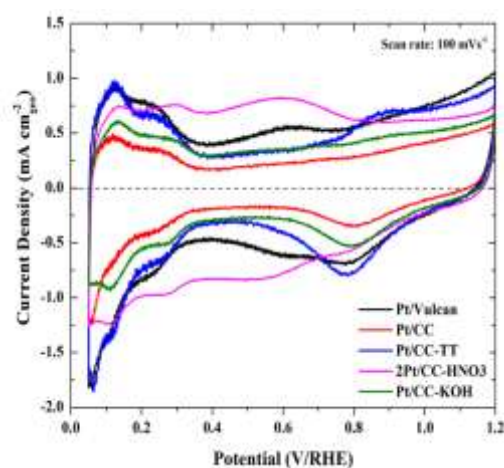


Fig. 6. Cyclic voltammeteries for Pt/C catalysts

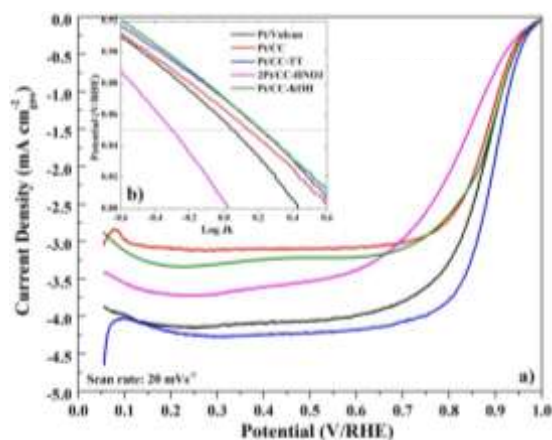


Fig. 7. a) ORR polarization curves. b) Tafel's slopes for Pt/C catalysts.

Table 3. Catalytic properties for Pt/C catalysts.

Material	Specify Activity ($\mu\text{A}/\text{cm}^2_{\text{Pt}}$)	Mass Activity ($\text{mA}/\text{mg}_{\text{Pt}}$)	ECSA (m^2/g)	Tafel Slope (mV dec^{-1})	BC_0 [$\text{mA cm}^{-2} \text{rpm}^{-1/2}$]
	\bar{a} 0.85 V	\bar{a} 0.85 V			
Pt/Vulcan	1290 ± 59	423 ± 21	26	97	0.1130
Pt/CC	1346 ± 62	315 ± 11	19	97	0.0831
Pt/CC-TT	1448 ± 95	465 ± 43	32	98	0.1097
Pt/CC-HNO ₃	883 ± 23	149 ± 9	17	136	0.1077
Pt/CC-KOH	1537 ± 129	303 ± 17	17	108	0.0823

4. Summary and perspectives

A new kind of carbon obtained from natural sources such as camphor can be used as support for nanoparticles catalysts toward the oxygen reduction reaction. The appropriate functionalization of the carbon surface has a significant effect on catalyst performance, and formation of metal nanoparticles. Oxidative treatments with acid chemical agents seem to promote agglomeration of particles with a considerable negative effect on catalytic activity. For this new type of carbon apparently it is enough just to carry out a thermal treatment to achieve satisfactory results.

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