



Universidad Autónoma
de Madrid

Biblos-e Archivo
Repositorio Institucional UAM

Repositorio Institucional de la Universidad Autónoma de Madrid

<https://repositorio.uam.es>

Esta es la **versión de autor** del artículo publicado en:

This is an **author produced version** of a paper published in:

Carbon 60 (2013): 76-83

DOI: <https://doi.org/10.1016/j.carbon.2013.03.058>

Copyright: © 2013 Elsevier B.V. This manuscript version is made available under the CC-BY-NC-ND 4.0 licence <http://creativecommons.org/licenses/by-nc-nd/4.0/>

El acceso a la versión del editor puede requerir la suscripción del recurso

Access to the published version may require subscription

The use of cyclic voltammetry to assess the activity of carbon materials for hydrogen peroxide decomposition

C. M. Domínguez^{1,*}, A. Quintanilla¹, P. Ocón², J. A. Casas¹ and J. J. Rodríguez¹.

¹Sección de Ingeniería Química, ²Departamento de Química-Física Aplicada, Universidad Autónoma de Madrid, Crta.de Colmenar km 15, 28049, Madrid, Spain

Abstract

It is known that carbon materials catalyze hydrogen peroxide decomposition in aqueous media. However, the catalytic activity of a particular carbon is dependent on various coupled structural, textural and chemical characteristics of the material, such that, formerly, the prediction of activity has not been possible. Here, the application of cyclic voltammetry (CV) is introduced as a rapid and conclusive technique in this respect. Three classes of carbon materials have been investigated: activated carbons, carbon blacks, and graphites, including some selected acid-washed samples which were used to examine the roles of mineral matter and surface oxygen. Characterization by electrochemical capacity measurements with CV, together with catalytic activity tests for hydrogen peroxide decomposition, reveal that the exchange current is directly proportional to the catalytic activity for hydrogen peroxide decomposition. That is, a linear dependence was found between this variable and the apparent first order catalytic decomposition rate constant. CV measurements with modified carbons also allow the elucidation of the effects of physicochemical characteristics of carbon materials on the rate of hydrogen peroxide decomposition.

*Corresponding author. Tel/Fax: +34 914975602/+34 914973516. E-mail address: carmenmaria.dominguez@uam.es (C.M. Domínguez).

1. Introduction

Hydrogen peroxide decomposition over carbon materials is of interest in the field of wastewater treatment because it leads to the formation of radicals ($\cdot\text{OH}$ and $\cdot\text{OOH}$), highly oxidizing species allowing the breakdown of organic pollutants in aqueous solution and/or adsorbed onto the carbon surface [1]. That decomposition reaction can take place due to the donor-acceptor properties of the carbon surface (C), through an electron-transfer mechanism similar to the Fenton reaction (Figure 1), acting C and C^+ as the reduced (1) and oxidized (2) carbon states, respectively [2-7]:

Figure 1. Hydrogen peroxide reduction (1) and oxidation (2) over carbon materials.

This redox cycle is highly dependent on the structural, textural and chemical characteristics of carbon materials [7, 8]. The most important features affecting the electron-transfer reactivity and, consequently, the carbon activity are the ash content [9-13], the microstructure and porosity [3, 7, 8] and chemical composition, specifically the quantity and nature of surface functional groups [1,4-10,12,14]. For this reason, the studies dealing with the application of carbon catalysts in hydrogen peroxide decomposition, or the processes in which this reaction is involved *viz.* wastewater treatments by wet peroxide oxidation [6,7,10,12,15], usually include a number of tedious, time-consuming and expensive characterization techniques (*e.g.* Raman spectra, Fourier transform infrared spectroscopy (FTIR), diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), temperature programmed desorption (TPD), X-ray photoelectron spectroscopy (XPS), thermal gravimetric analysis (TGA), elemental analysis (EA), X-ray diffraction (XRD), total reflection X-ray fluorescence (TXRF), induced coupled plasma (ICP), N_2 adsorption/desorption isotherms). In spite of this, achieving conclusive results about the characteristics of carbon materials, directly or indirectly related to the activity, is not always possible. The reason for this is that the

different issues cannot be analyzed independently, due to the difficulty of tailoring a single carbon characteristic upon the preparation process, without affecting the rest. Therefore, the occurrence of coupled effects is common and makes impracticable a reasonable prediction of the catalytic activity of carbon materials as a function of their structural and physico-chemical characteristics.

In this paper, we present cyclic voltammetry as a simple and direct technique which is able to provide conclusive information about the catalytic activity of carbon materials in hydrogen peroxide decomposition reaction. We demonstrate by using different types of carbon materials *viz.* activated carbons, carbon blacks and graphites, that the electrochemical behaviour of the carbon for some particular structural and physico-chemical characteristics given, governs the activity. This technique has occasionally been used to characterize metallic catalysts [16] and to predict their activity [17,18] but to the best of our knowledge it has not yet been reported for carbon materials.

2. Experimental

2.1. Carbon materials

Three types of commercial carbon materials with different structural, textural and chemical characteristics have been studied: two activated carbons (AC), supplied by Merck (AC-M, ref.: 102514) and Panreac (AC-P, ref.: 3108L); two carbon blacks (CB), supplied by Chemviron (CB-C, ref.: 2156090) and Vulcan (CB-V, ref.: CC72R) and two graphites (G), supplied by Sigma-Aldrich (G-S, ref.: 282863) and Fluka (G-F, ref.: 1249167). All samples were provided in powder form except for the AC-M, which was sieved to 80 - 100 μm before use.

In addition, the AC-M and G-S samples were treated with concentrated HCl (37%) solution, at room temperature for 4 h (2 g sample/25 mL HCl solution), and then

washed with distilled water until constant pH , filtered, and dried overnight at 60 °C. The resulting carbons were identified as AC-M-HCl and G-S-HCl, respectively. A similar treatment was performed on AC-P but using HNO₃ (65%) yielding the AC-P-HNO₃ sample. Table 1 summarizes the nomenclature of all the carbon materials tested.

2.2. Characterization

The structural parameters were determined by X-ray diffraction. XRD patterns were obtained using a Siemens Model D5000 X-ray diffractometer, Cu K α (8.04 keV) radiation, and a step of 0.02°/s for $2\theta=5^{\circ}$ – 100° . XRD data were analyzed with PDF 2000 (JCPDS-ICDD) software.

The BET surface area (S_{BET}) of the initial and modified carbons was obtained from the 77 K N₂ adsorption/desorption isotherms using Micromeritics Tristar apparatus, outgassing the samples overnight at 150 °C to a residual pressure of $<10^{-3}$ torr. The external or non-microporous surface area (A_{ext}) was calculated by the t -method.

Elemental analyses of the carbon materials were performed in a LECO Model CHNS-932 apparatus. The identification and quantification of the elements was determined by TXRF (Extra-II Rich & Seifert spectrometer).

The surface oxygen groups were analyzed by temperature-programmed desorption under N₂ (TPD). A 100 mg sample of carbon was placed in a quartz tube and heated at 10 °C/min from room temperature up to 900 °C under a continuous N₂ flow of 1 L/min. The CO₂ and CO evolved were measured in a gas analyzer (SIEMENS mod. Utrammat 22).

2.3. Cyclic voltammetry experiments

Electrochemical measurements were carried out in a conventional three-electrode

electrochemical cell, using a computerized potentiostat (Autolab PGSTAT 302, Eco Chemie) controlled by GPES software. A glassy carbon rotating disk electrode (3 mm diameter) was used as substrate for the carbon samples (working electrode). Prior to each test, the electrode was polished to 3 μm with alumina powder and rinsed with Milli-Q ultrapure water. A gold electrode was used as the counter electrode and a saturated Ag/AgCl, KCl electrode served as the reference. The electrochemical experiments were carried out at room temperature and ambient pressure using an HCl ($pH=3.5$) solution as the electrolyte.

The carbons under study were deposited on the working electrode as an ink. Typically, 6 mg of sample was dispersed in Milli-Q water (730 μL) with ultrasonic agitation (Hyelscher, UP50H), to obtain a homogeneous suspension; 10 μL of this suspension was carefully dropped on a glassy carbon electrode and allowed to dry at room temperature for 60 min to obtain a uniform film.

In a typical experiment, the working electrode was subjected to cyclic voltammetry (CV) measurements in a background solution (HCl, $pH=3.5$) at a sweep rate (v) of 100 mV/s and the potential range from -0.6 to 1.0 V. Once unchanging cyclic voltammograms were obtained for several cycles (variations in the coulombic charge lower than 2%), the sweep rate was reduced to a value of 10 mV/s, and data acquisition started. First, the coulombic charge (CC) for the carbon was calculated from the background voltammogram. Then, the precise volume of hydrogen peroxide (30%) was added to the electrolyte solution and the open circuit potential (E_{ocp}) registered. Finally, a new CV was recorded to determine the electrochemical behavior of the carbon materials in the presence of hydrogen peroxide. The absence of diffusion limitations in the interphase for the overall electrochemical process should be noted because identical results were obtained within the rotation velocity range from 0 to 3000 rpm, as was

expected for a surface-controlled process. All measurements were carried out under nitrogen atmosphere (Air Liquid) by bubbling 1 mL/min into the cell and all experiments were duplicated.

By comparing the CVs obtained in the absence and presence of hydrogen peroxide, the onset potential (E_{onset}) for first reduction and oxidation was obtained. Also, the *Tafel* slope for both processes, called as b , and the current exchange (i_o) were calculated from the overpotential ($E - E_{ocp}$) vs. $\log(I)$ plots for each test using the following equation:

$$(E - E_{ocp}) = m + 2.30 \cdot b \cdot \log(I)$$

2.4. Hydrogen peroxide decomposition with carbon catalysts

The reactions were carried out batch-wise in a magnetically stirred three-necked glass reactor equipped with a reflux condenser. The operating conditions were selected according to a previous work [19]. In a typical experiment, 45 mL of distilled water at $pH= 3.5$ (HCl, Sigma-Aldrich) was placed in the flask together with 0.125 g powdered catalyst. The content was heated to 80 °C (IKA RCT basic). Once this temperature had been reached, 5 mL of 250 g/L hydrogen peroxide (Sigma-Aldrich) was injected and the content stirred at 1200 rpm. After a reaction time of 2 h the heating was switched-off and the flask cooled to room temperature in cold water. Finally, the catalyst was separated by filtration (0.45 μm Nylon filter) and oven-dried at 60 °C.

3. Results and Discussion

3.1. Characterization study

Table 1 summarizes the structural characteristics of the carbons obtained from XRD, the BET and external surface area, ash and Fe content, and the amount of CO₂ and CO evolved upon TPD analysis.

The values of the structural parameters in Table 1, such as the interlayer spacing (d_{002}), average crystalline height (L_c), and average crystalline diameter (L_a), were calculated from the XRD patterns (shown in Figure S1 of the Supplementary Material). The calculated d_{002} values confirm the amorphous character of activated carbons, AC-M and AC-P. Conversely, the G-S and G-F samples, present a highly ordered structure as indicated by the d_{002} close to the value of graphite (3.354 Å). While the carbon blacks, CB-C and CB-V, exhibit intermediate values in the XRD parameters. The lower d_{002} and higher L_c and L_a values of CB-C indicate a more ordered structure compared with CB-V.

Table 1. Structural, textural and chemical characteristics of the carbon materials tested.

The S_{BET} values calculated from the N₂ adsorption/desorption isotherms at 77 K (Figure S2 of the Supplementary Material) demonstrate that activated carbons, AC-M and AC-P, present a highly developed porosity whereas the carbon blacks, CB-C and CB-V, and even more so, the graphites, G-S and G-F, show substantially lower values of surface area without microporosity contribution, except in the case of the CB-V carbon black. Differences in the distribution of porosity can be observed between the activated carbons, showing AC-P a substantially higher contribution of mesoporosity.

The ash content of the carbon materials tested is, in general, quite low, except in the case of the as-received activated carbon AC-M (4%). It is important to know the content of iron of the ashes because of its catalytic activity for hydrogen peroxide decomposition enhancing the ability of activated carbon in this reaction [3,10-13,20]. For this reason, the iron content was quantified (Table 1). Unexpectedly, G-S had the highest amount of Fe (0.44%) whereas the presence of this metal in the other materials was negligible. Regarding the surface composition, the amount of CO₂ and CO evolved,

as obtained from the integration of the TPD curves, (Figure S3 of the Supplementary Material) are shown in Table 1. As expected, the two activated carbons show the highest content of surface oxygen groups (SOG) as a result of the activation process.

Summarizing, three different types of carbons have been studied. Activated carbons, which are amorphous materials with a developed porous structure and significant amounts of surface oxygen groups; graphites, which have the opposite characteristics because they are almost crystalline materials, with a very low specific surface area and scarce surface oxygen groups; carbon blacks, with structural, textural and chemical features in between the two.

The effect of those characteristics on the catalytic behavior of activated carbons for hydrogen peroxide decomposition has been widely studied in the literature [1,4-6,8,10-14]. Some of these studies conclude that disordered structures with less developed graphitic layers have a higher concentration of electron-rich centers promoting hydrogen peroxide decomposition [3,7]. However, the more disordered the structure, the more surface oxygen groups. In general, acid SOG reduce the reactivity of the activated carbons due to their electron withdrawal capacity [1,5-7,12,14] whereas basic SOG are always beneficial [4,8]. On the one hand, the diffusion of the reagents toward the active sites is favored by the hydrophilic character of the carbon material, a feature controlled by the acid SOG [21], in the presence of a sufficiently developed mesoporosity [22]. By contrast, carbon materials with a highly ordered structure such as graphites have electronic and conductive properties which can favor the electron transfer between these materials and hydrogen peroxide [12].

In general, carbon materials have a wide diversity of characteristics which would hinder a predictive approach of their activity for hydrogen peroxide decomposition as coupled

effects frequently exist. In this context our proposal is that voltammetry measurements are a useful tool for the assessment of the activity of carbon materials in the aforementioned reaction. In that respect, the starting and modified carbon materials collected in Table 1 provide a series of widely different samples for testing.

3.2. Carbon voltammetry experiments

Figure 2 depicts the unchanging cyclic voltammograms in the background solution ($pH=3.5$, HCl) for each type of carbon. When the applied potential changes to a negative direction (reduction scan), a gradually increasing negative current was measured; in the same way, if the potential went in a positive direction, the positive current increases and the oxidation process takes place. None of the cyclic voltammograms recorded were totally symmetrical. This fact led us to believe that the carbon materials include not only purely capacitive, but also electro-active species (*viz.* surface oxygen groups, heteroatoms or ashes) with redox properties.

Figure 2. Cyclic voltammograms of carbon materials in the absence of hydrogen peroxide (background). Operating conditions: $v = 10 \text{ mV/s}$, $T = 25 \text{ }^{\circ}\text{C}$, $pH = 3.5$ (HCl).

The coulombic charge (CC), calculated from the background voltammograms, varied according to the specific surface area of the materials: $AC > CB > G$ and a linear relationship between this parameter (CC) and S_{BET} has been found as can be seen in Figure 3. The higher the surface area, the more active sites (electron-rich locations on the carbon surface), and so, an increased coulombic charge can be expected. Eventually, cyclic voltammetry could be used for specific surface determination of carbon materials.

Figure 3. Relationship between S_{BET} and coulombic charge. Operating conditions: $v = 10 \text{ mV/s}$, $T = 25 \text{ }^{\circ}\text{C}$, $pH = 3.5$ (HCl).

Additional cyclic voltammetry experiments were carried out in presence of hydrogen peroxide with the purpose of analyzing the electrochemical behavior of carbons when in contact with that electroactive reactant. The E_{ocp} values recorded before the potential application are given in Table 2 and the voltammograms are shown in Figure 4. The E_{ocp} values, ranged from 0.413 to 0.499 V, being within the thermodynamic reduction/oxidation potentials of hydrogen peroxide (-0.905 V and 1.566 V, respectively, Ag/AgCl) and correspond with a mixed potential. The oxidation and reduction current intensities measured in the presence of hydrogen peroxide (Figure 4) are clearly higher than those in the absence of it (Figure 2). The carbon that exhibits the maximum ability for the reduction step also shows the maximum for the oxidation step. It is noteworthy the crossover loops observed in the former. These hysteresis loops observed in both oxidation and reduction directions, indicate that the carbon surface is irreversibly modified upon cyclic voltammetry when hydrogen peroxide is in the media. At 1 V potential value, the carbon surface has been deeply oxidized by the effect of the going sweep and the created SOGs contribute to a more effective hydrogen peroxide oxidation upon the reverse scan. Then, currents registered are higher than those values measured in the going sweep, resulting in the first hysteresis loop. The irreversible oxidation of the carbon surface upon cyclic voltammetry also disfavors the reduction of hydrogen peroxide. As a consequence, a lower reduction current is obtained in the reverse scan, from -0.1 to -0.6 V, and the second hysteresis loop observed. Therefore, these findings suggest that the regeneration of the carbon active sites (step 2 in Figure 1) is expected to be the limiting reaction.

Figure 4. Cyclic voltammograms of carbon materials in presence of hydrogen peroxide.

Operating conditions: $\nu = 10$ mV/s, $T = 25$ °C, $pH = 3.5$ (HCl), $C_{H_2O_2} = 25$ g/L.

Several electrochemical parameters *viz.* E_{onset} , *Tafel* slopes and i_o were calculated from the voltammograms (see Experimental Section). The values are summarized in Table 2.

Table 2. Electrochemical properties of the carbon materials tested.

The E_{onset} values for hydrogen peroxide reduction were close to 0 mV for all the carbons tested, while for oxidation more variable values were obtained, ranging from 0.513 to 0.690 V. The *Tafel* slope values corresponding to hydrogen peroxide reduction were between -0.375 and -0.454 V/decade, while for oxidation, the range covered from 0.211 to 0.344 V/decade (Table 2). These relatively high values indicate that hydrogen peroxide decomposition over carbon materials is a complex process, which in addition to the charge transfer, other phenomena, like adsorption/desorption, must be involved. Furthermore, the fact that the *Tafel* slopes were quite similar for all the carbon materials tested, suggests that the reaction mechanism does not vary from one material to another.

According to the current exchange values, i_o (the most representative parameter in electrochemical reactions, Table 2), the activity of carbon materials in the cyclic voltammetry experiments follows the order: AC-M > G-S > AC-P > CB-V > CB-C > G-F. The lowest activity of G-F is consistent with the characterization results in Table 1 which show that this carbon material has the lowest surface area and no iron content. Nevertheless, the voltammetry results indicate that AC-M, and unexpectedly, G-S, are electrochemically more active than AC-P. In the case of G-S, the explanation could be that the effect of the iron content prevails over that of surface area (or its equivalent electrochemical parameter, the coulombic charge, according to Figure 3). To confirm the important effect of iron on the electrochemical carbon capacity, the cyclic voltammetry response of G-S-HCl sample was compared to that of G-S in Figure 5 (Fe content equal to 0.02 and 0.44 wt%, respectively, see Table 1). The decrease in the

reduction E_{onset} and the increase in the oxidation one of G-S-HCl with respect to the starting G-S (see values in Table 2) indicate a diminished electrochemical capacity of the former, supporting the initial hypothesis.

Figure 5. Effect of Fe content on the cyclic voltammetry response of G-S carbon.

Operating conditions: $\nu = 10$ mV/s, $T = 25$ °C, $pH = 3.5$ (HCl), $C_{H_2O_2} = 25$ g/L.

In the case of AC-M and AC-P, the iron content must have only a negligible effect because it is very low in both cases. However, other features such as the ash content and the amount of surface oxygen groups could explain their different electrochemical behavior. AC-M is the carbon tested with highest ash content by far (see Table 1). Among the elements identified by TXRF were Fe, Ti, Ca and Cu. The ash content was reduced by more than half after HCl treatment (see AC-M and AC-M-HCl in Table 1). The corresponding voltammogram obtained in presence of hydrogen peroxide is given in Figure 6 and the results (see i_o values in Table 2) show a decrease in the electrochemical capacity of AC-M after reduction of the ash content.

Figure 6. Effect of ash-content reduction on the cyclic voltammetry response of AC-M

carbon. Operating conditions: $\nu = 10$ mV/s, $T = 25$ °C, $pH = 3.5$ (HCl),

$C_{H_2O_2} = 25$ g/L.

To investigate the influence of surface oxygen groups, the AC-P carbon was oxidized with HNO_3 and a voltammogram of the resulting modified carbon (AC-P- HNO_3) obtained (Figure 7). HNO_3 oxidation substantially increased the amount of SOG (see Table 1) and the voltammetry results (Figure 7 and Table 2) indicate a decrease in the electrochemical capacity of the carbon. According to the shape of the voltammograms (Figure 7), the decline is more pronounced in the reduction reaction than in the oxidation reaction, because the former is more affected by the decrease of the electronic

density of the basal planes, caused by the presence of the acid oxygen groups.

Figure 7. Effect of surface oxygen groups content on the cyclic voltammetry response of AC-P carbon. Operating conditions: $\nu = 10 \text{ mV/s}$, $T = 25 \text{ }^\circ\text{C}$, $pH = 3.5$ (HCl), $C_{H_2O_2}=25 \text{ g/L}$.

In conclusion, AC-M showed a higher electrochemical activity than AC-P because of its higher ash content and lower amount of acid SOG.

3.3. Catalyst screening

The decomposition of hydrogen peroxide is assumed to follow pseudo-first-order kinetics [5,7,8,14]:

$$-\frac{dC_{H_2O_2}}{dt} = k_d \cdot C_{H_2O_2}$$

where k_d represents an apparent kinetic constant which includes several parameters such as temperature, catalyst concentration, and pH . Figure 8 shows the plot of $\ln(C_{H_2O_2})$ vs. reaction time for the carbon materials tested. The values of the apparent kinetic constant are given in Table 3 together with the corresponding correlation coefficients which confirm the validity of the simple rate equation used. According to these results, the activity of the carbons tested follows the same order as that previously found using voltammetry measurements. Also, the activity of the modified carbons is lower than those of their corresponding starting ones (Table 3).

Figure 8. First-order plots of hydrogen peroxide decomposition with the carbon materials. Operating conditions: $T = 80 \text{ }^\circ\text{C}$, $pH = 3.5$ (HCl), $C_{carbon}=5 \text{ g/L}$, $C_{H_2O_2,0}=25 \text{ g/L}$.

Table 3. Values of the apparent first-order rate constant for hydrogen peroxide

decomposition with the carbons tested.

A linear relationship has been found between the exchange current (i_o) (Table 2) and the decomposition rate constants (k_d) (Table 3) as shown in Figure 9. As can be seen, this relationship also applies to the modified carbons. Therefore, the electrochemical capacity of carbons, which is a measurable property in cyclic voltammetry, can be used to predict the activity of the carbon materials in hydrogen peroxide decomposition. According to these results, and further investigations being carried out in this laboratory, the outlook for the potential application of this technique to evaluate the activity of carbon materials in redox reactions in general is quite promising.

Figure 9. Relationship between the exchange current (i_o) and apparent first-order rate constant (k_d) for hydrogen peroxide decomposition with the carbons tested.

4. Conclusions

It has been proved that cyclic voltammetry provides a rapid, direct, and useful technique for predicting the catalytic activity of carbon materials for hydrogen peroxide decomposition. The exchange current, determined by the voltammograms, is an overall variable governing carbon activity. A linear dependence has been obtained between both.

Cyclic voltammetry also enables a greater insight into the catalytic behaviour because it becomes clear that the limiting step in hydrogen peroxide decomposition with carbon materials, is the regeneration of the active sites upon carbon reduction.

Applying the electrochemical characterization to a number of carbon materials of widely different physico-chemical characteristics provided an understanding of the

effects of those features on the catalytic activity for hydrogen peroxide decomposition. The results indicate that the most important factor in the catalytic activity is the content of metals, in particular iron, this is followed by the specific surface area and finally the content of surface oxygen groups.

Acknowledgments

The authors wish to thank the Spanish MICINN for the financial support for the projects CTQ2008-03988/PPQ, CTQ2010-14807 and S2009/AMB-1588. Our gratitude to the anonymous reviewer for his/her helpful comments and recommendations which have significantly contributed to improve the quality of the paper.

References

- [1] Gomes HT, Miranda SM, Sampaio MJ, Silva AMT, Faria JL. Activated carbons treated with sulphuric acid: Catalysts for catalytic wet peroxide oxidation. *Catal Today* 2010;151:153-58.
- [2] Kimura M, Miyamoto I. Discovery of the Activated-Carbon Radical AC^+ and the Novel Oxidation-Reactions Comprising the AC/AC^+ Cycle as a Catalyst in an Aqueous-Solution. *Bull Chem Soc Jpn* 1994;67:2357-60.
- [3] Lücking F, Köser H, Jank M, Ritter A. Iron powder, graphite and activated carbon as catalysts for the oxidation of 4-chlorophenol with hydrogen peroxide in aqueous solution. *Water Res* 1998;32:2607-14.
- [4] Oliveira LCA, Silva CN, Yoshida MI, Lago RM. The effect of H_2 treatment on the activity of activated carbon for the oxidation of organic contaminants in water and the H_2O_2 decomposition. *Carbon* 2004;42:2279-84.

- [5] Georgi A, Kopinke FD. Interaction of adsorption and catalytic reactions in water decontamination processes Part I. Oxidation of organic contaminants with hydrogen peroxide catalyzed by activated carbon. *Appl Catal B-Environ* 2005;58:9-18.
- [6] Santos VP, Pereira MFR, Faria PCC, Orfao JJM. Decolourisation of dye solutions by oxidation with H_2O_2 in the presence of modified activated carbons. *J Hazard Mater* 2009;162:736-42.
- [7] Rey A, Zazo JA, Casas JA, Bahamonde A, Rodriguez JJ. Influence of the structural and surface characteristics of activated carbon on the catalytic decomposition of hydrogen peroxide. *Appl Catal A-Gen* 2011;402:146-55.
- [8] Khalil LB, Girgis BS, Tawfik TAM. Decomposition of H_2O_2 on activated carbon obtained from olive stones. *J Chem Technol Biot* 2001;76:1132-40.
- [9] Pakula M, Biniak S, Swiatkowski A. Chemical and electrochemical studies of interactions between iron(III) ions and an activated carbon surface. *Langmuir* 1998;14:3082-89.
- [10] Rey A, Faraldos M, Bahamonde A, Casas JA, Zazo JA, Rodriguez JJ. Role of the Activated Carbon Surface on Catalytic Wet Peroxide Oxidation. *Ind Eng Chem Res* 2008;47:8166-74.
- [11] Aguinaco A, Pablo Pocostales J, Garcia-Araya JF, Beltran FJ. Decomposition of hydrogen peroxide in the presence of activated carbons with different characteristics. *J Chem Technol Biot* 2011;86:595-600.
- [12] Taran O, Polyanskaya E, Ogorodnikova O, Kuznetsov V, Parmon V, Besson M et al. Influence of the morphology and the surface chemistry of carbons on their catalytic

performances in the catalytic wet peroxide oxidation of organic contaminants. *Appl Catal A-Gen* 2010;387:55-66.

[13] Voitko KV, Whitby RLD, Gun'ko VM, Bakalinska OM, Kartel MT, Laszlo K et al. Morphological and chemical features of nano and macroscale carbons affecting hydrogen peroxide decomposition in aqueous media. *J Colloid Interf Sci* 2011;361:129-136.

[14] Huang HH, Lu MC, Chen JN, Lee CT. Catalytic decomposition of hydrogen peroxide and 4-chlorophenol in the presence of modified activated carbons. *Chemosphere* 2003;51:935-43.

[15] Quintanilla A, Casas JA, Rodriguez JJ. Hydrogen peroxide-promoted-CWAO of phenol with activated carbon. *Appl Catal B-Environ* 2010;93:339-45.

[16] Pozio A, De Francesco M, Cemmi A, Cardellini F, Giorgi L. Comparison of high surface Pt/C catalysts by cyclic voltammetry. *J Power Sources* 2002;105:13-19.

[17] Hutchings GJ, Carrettin S, McMorn P, Jenkins P, Attard GA, Johnston P et al. Cyclic voltammetry as a potential predictive method for supported nanocrystalline gold catalysts for oxidation in aqueous media. *Feedstocks for the Future: Renewables for the Production of Chemicals and Materials* 2006;921:82-98.

[18] Zhu J, Yang X, Xu X, Wei K. Cyclic voltammetry for predicting oxidation process in heterogeneous catalysis. *Z Phys Chem* 2006;220:1589-94.

[19] Quintanilla A, Garcia-Rodriguez S, Dominguez CM, Blasco S, Casas JA, Rodriguez JJ. Supported gold nanoparticle catalysts for wet peroxide oxidation. *Appl Catal B-Environ* 2012;111:81-89.

- [20] Zazo JA, Casas JA, Mohedano AF, Rodriguez JJ. Catalytic wet peroxide oxidation of phenol with a Fe/active carbon catalyst. *Appl Catal B-Environ* 2006;65:261-68.
- [21] Hernandez-Fernandez P, Baranton S, Rojas S, Ocon P, Leger J, Fierro JLG. Insights into the Effects of Functional Groups on Carbon Nanotubes for the Electrooxidation of Methanol. *Langmuir* 2011;27:9621-29.
- [22] Zazo JA, Bedia J, Fierro CM, Pliego G, Casas JA, Rodriguez JJ. Highly stable Fe on activated carbon catalysts for CWPO upon FeCl_3 activation of lignin from black liquors. *Catal Today* 2012;187:115-21.

Table 1. Structural, textural and chemical characteristics of the carbon materials tested.

Sample	d_{002} (Å)	L_c (Å)	L_a (Å)	S_{BET} (m ² /g)	A_{ext} (m ² /g)	Ashes (%)	Fe (%)	CO ₂ (μmol/g)	CO (μmol/g)
AC-M	3.614	17.7	38.0	1019	175	4.00	0.04	30	320
AC-M-HCl	-	-	-	843	128	1.38	0.03	74	562
AC-P	3.793	16.2	36.0	931	472	1.00	0.01	140	662
AC-P-HNO ₃	-	-	-	894	354	0.35	0.01	669	1866
CB-C	3.476	70.8	65.7	75	75	0.00	0.00	83	160
CB-V	3.618	38.7	38.9	233	110	1.00	0.00	148	106
G-S	3.383	440.9	487.0	12	12	0.50	0.44	105	36
G-S-HCl	-	-	-	11	11	0.08	0.02	-	-
G-F	3.367	466.3	488.7	7	5	0.20	0.00	128	79

Table 2. Electrochemical properties of the carbon materials tested.

Sample	Reduction process			Oxidation process		i_o (A/g)
	E_{ocp} (V)	E_{onset} (V)	b (V/decade)	E_{onset} (V)	b (V/decade)	
AC-M	0.460	0.094	-0.437	0.513	0.276	0.232
AC-M-HCl	0.489	0.022	-0.393	0.575	0.227	0.125
AC-P	0.413	0.057	-0.434	0.690	0.307	0.147
AC-P-HNO ₃	0.461	0.050	-0.443	0.686	0.294	0.121
CB-C	0.493	0.050	-0.398	0.559	0.219	0.060
CB-V	0.430	0.024	-0.426	0.679	0.344	0.137
G-S	0.492	0.086	-0.454	0.520	0.264	0.172
G-S-HCl	0.499	0.045	-0.342	0.629	0.261	0.099
G-F	0.420	0.009	-0.375	0.587	0.211	0.052

Table 3. Values of the **apparent** first-order rate **constant** for hydrogen peroxide decomposition with the carbons tested.

Sample	k_d (h⁻¹)	r^2
AC-M	1.005	0.993
AC-M-HCl	0.637	0.986
AC-P	0.571	0.983
AC-P-HNO ₃	0.370	0.995
CB-C	0.032	0.999
CB-V	0.424	0.978
G-S	0.869	0.997
G-S-HCl	0.203	0.995
G-F	0.049	0.966

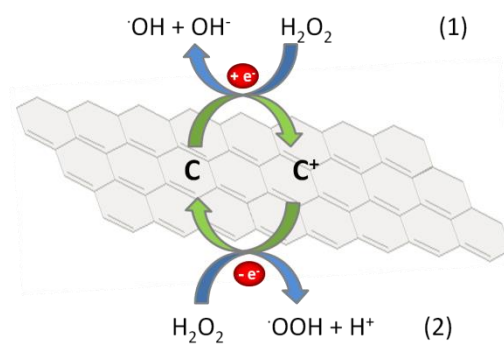


Figure 1. Hydrogen peroxide reduction (1) and oxidation (2) over carbon materials.

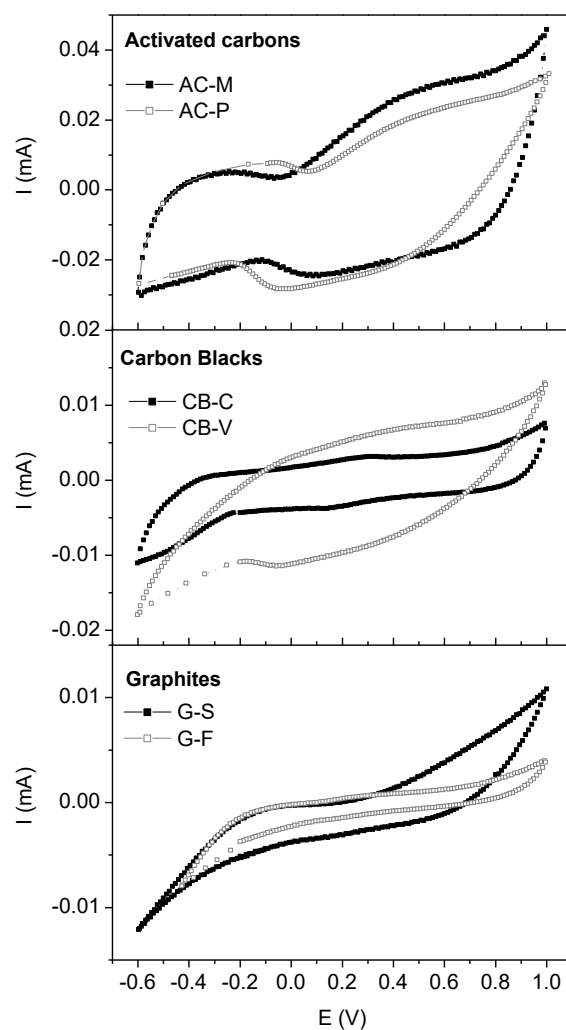


Figure 2. Cyclic voltammograms of carbon materials in the absence of hydrogen peroxide (background). Operating conditions: $v = 10 \text{ mV/s}$, $T = 25 \text{ }^{\circ}\text{C}$, $pH = 3.5$ (HCl).

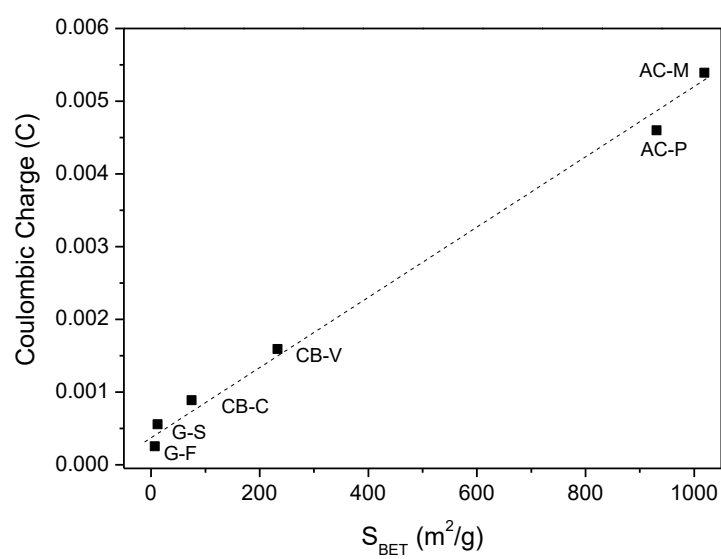


Figure 3. Relationship between S_{BET} and coulombic charge. Operating conditions: $\nu = 10$ mV/s, $T = 25$ °C, $pH = 3.5$ (HCl).

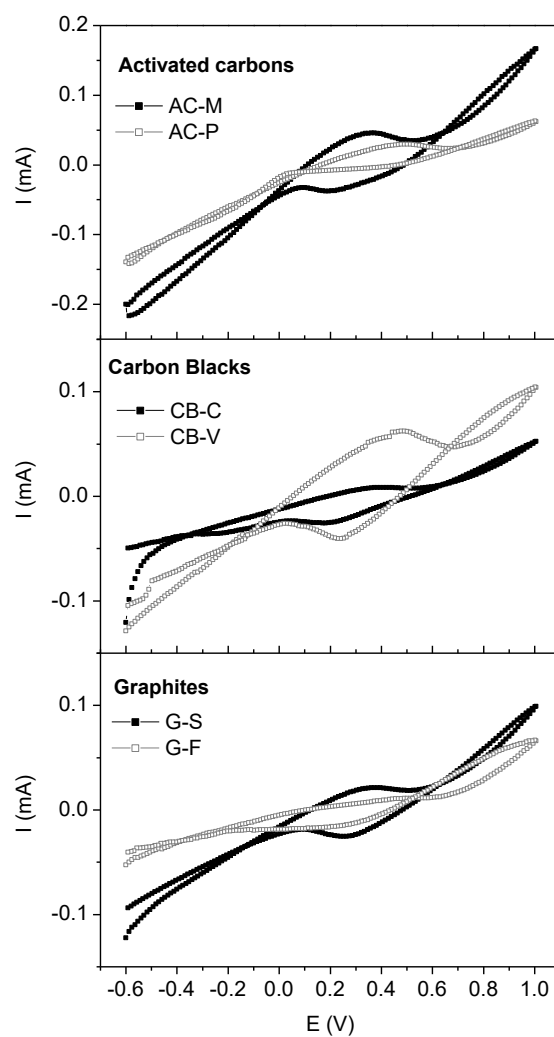


Figure 4. Cyclic voltammograms of carbon materials in presence of hydrogen peroxide.

Operating conditions: $\nu = 10$ mV/s, $T = 25$ °C, $pH = 3.5$ (HCl), $C_{H_2O_2} = 25$ g/L.

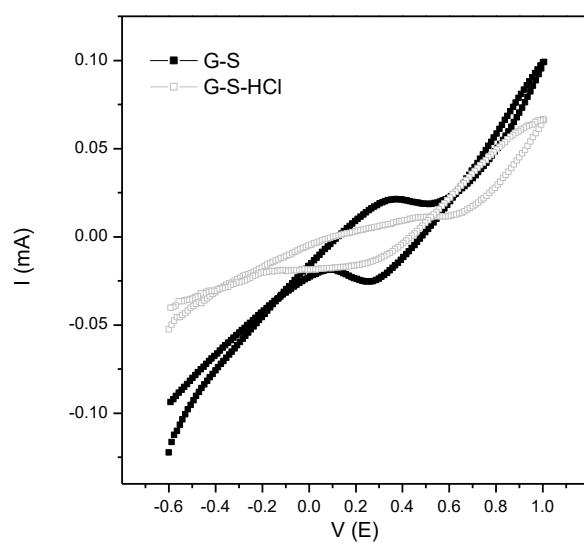


Figure 5. Effect of Fe content on the cyclic voltammetry response of G-S carbon.

Operating conditions: $\nu = 10$ mV/s, $T = 25$ °C, $pH = 3.5$ (HCl), $C_{H_2O_2} = 25$ g/L.

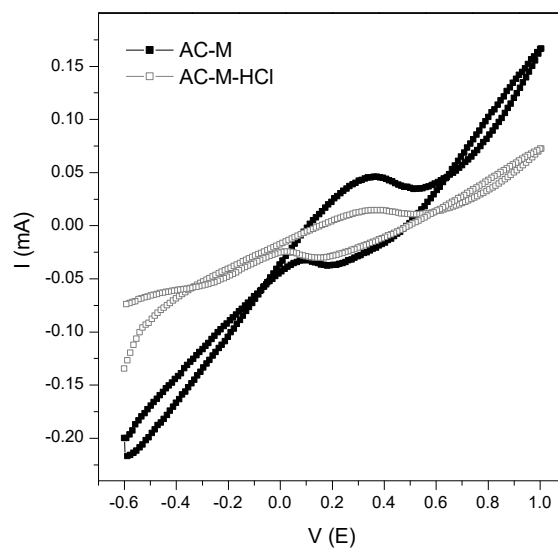


Figure 6. Effect of ash-content reduction on the cyclic voltammetry response of AC-M carbon. Operating conditions: $\nu = 10 \text{ mV/s}$, $T = 25 \text{ }^{\circ}\text{C}$, $pH = 3.5 \text{ (HCl)}$, $C_{H_2O_2} = 25 \text{ g/L}$.

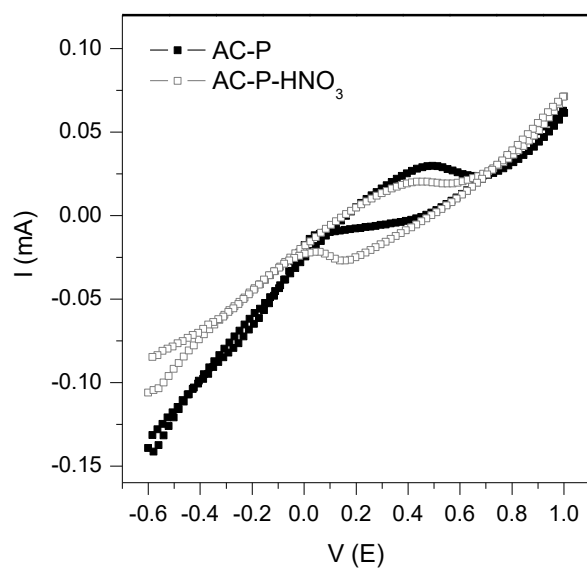


Figure 7. Effect of surface oxygen groups content on the cyclic voltammetry response of AC-P carbon. Operating conditions: $\nu = 10$ mV/s, $T = 25$ °C, $pH = 3.5$ (HCl), $C_{H_2O_2} = 25$ g/L.

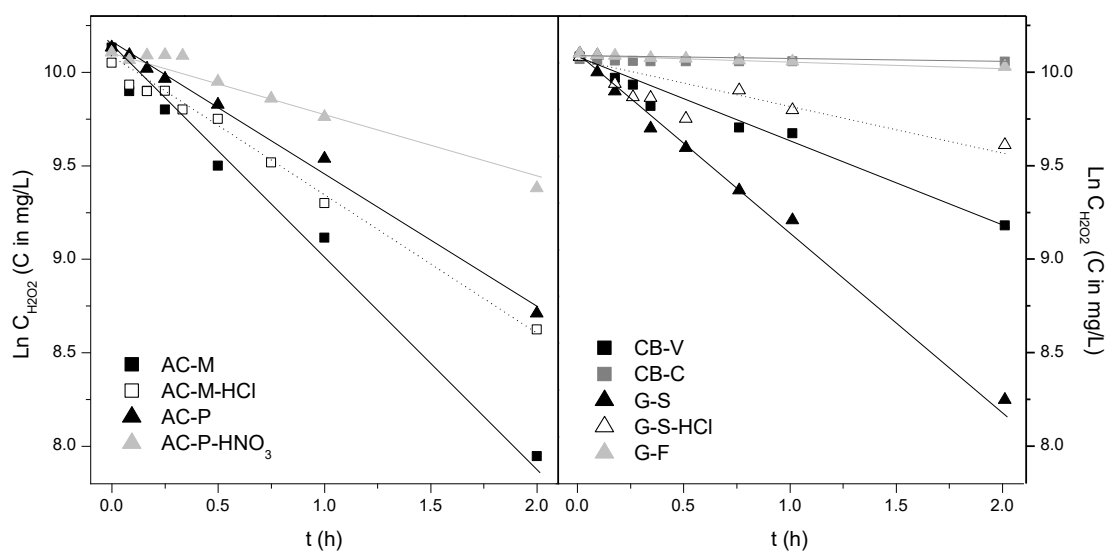


Figure 8. First-order plots of hydrogen peroxide decomposition with the carbon materials. Operating conditions: $T = 80\text{ }^{\circ}\text{C}$, $pH = 3.5$ (HCl), $C_{\text{carbon}}=5\text{ g/L}$, $C_{H_2O_2}^0=25\text{ g/L}$.

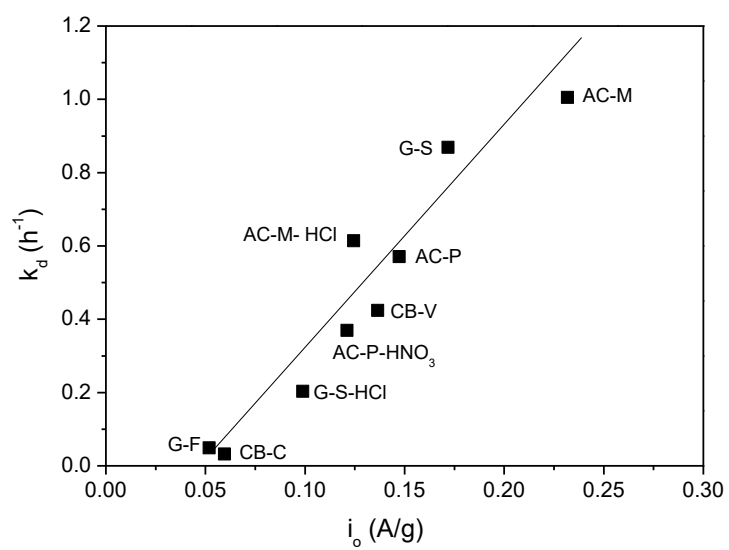


Figure 9. Relationship between the **exchange current** (i_o) and **apparent** first-order rate constant (k_d) for hydrogen peroxide decomposition with the carbons tested.

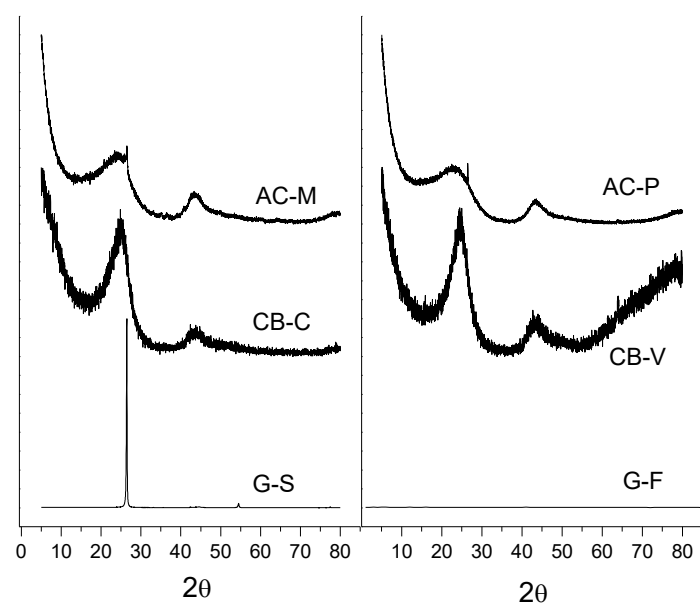


Figure S1. X-ray diffraction profiles of the carbon materials.

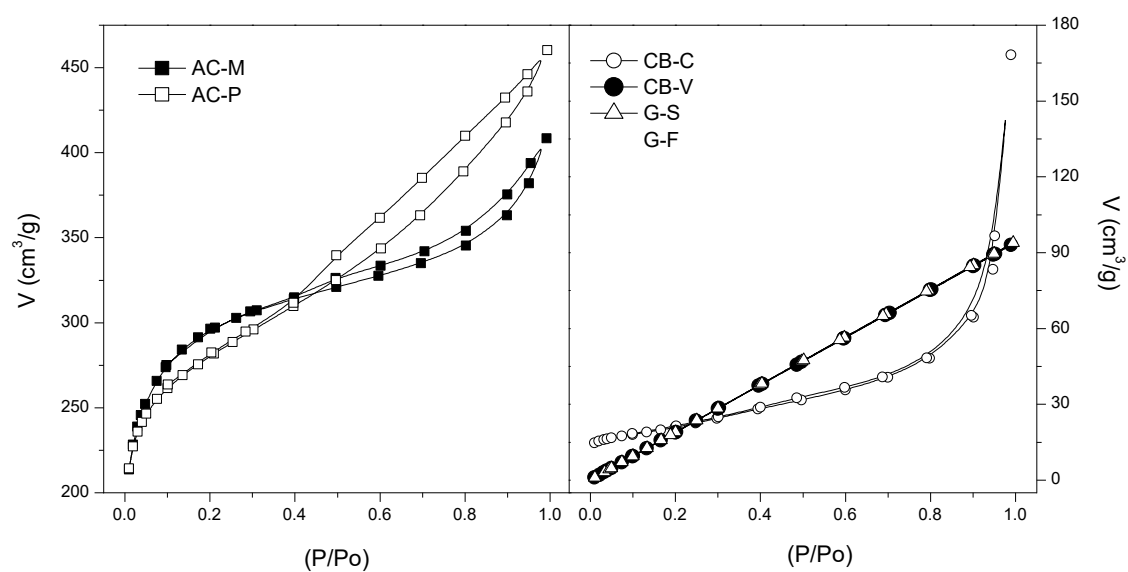


Figure S2. 77 K N_2 adsorption/desorption isotherms of the carbon materials.

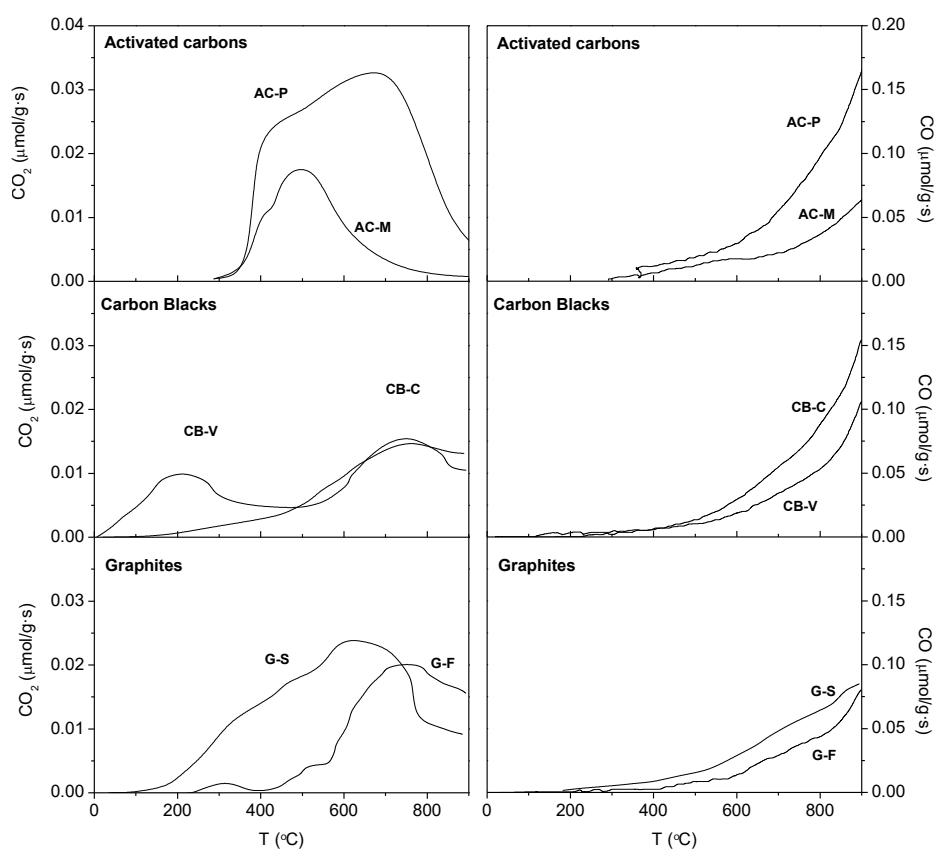


Figure S3. TPD profiles of the carbon materials.