Characterization of carbon pastes as matrices in composite electrodes for use in electrochemical capacitors

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Carbon paste electrodes (CPEs) were prepared from carbon black powder with different binders (Silicon Oil or Nujol). Cyclic voltammetry, chronoamperometry and chronopotentiometry techniques and different electrolytes (1M $HClO_4$ and 1M $LiClO_4$) were used to characterize the capacitive response and evaluate the capacitance (F/cm^2, F/g) of CPEs, with and without surface modification. The surface modification was carried out by applying a potential pulse (1.35 V vs. saturated calomel electrode, SCE) at a time of 300 s, where the growth of carbon-oxygen (C-O) species were induced on the surface of the electrode. The results show that modified electrodes enhanced the capacitance and the electrolytic system has an important influence in the stability and reactivity of electrodes. The modified electrodes shows an important pseudocapacitive behavior as result of a diffusion processes that involved an interfacial reaction between the C-O species formed during the electrochemical surface treatment and the protons present in the electrolyte.

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1. Introduction :

Due to relative low cost and versatile use, the carbon black recently has increased the interest as electrode material for different electrochemical applications such as electrocatalytic support in fuel cells, electrodes for lithium batteries; matrix base in modified composite electrodes, in conductor polymers or as a simple current collector [1-3]. The carbon black has on its surface carbon-oxygen compounds (active functional groups) whose nature and number depends of the synthesis or pre-treatment processes [4, 5]. These compounds are responsible of physicochemical and electric properties, finding specific applications such as charge storage, either in electrochemical capacitors of double layer (EDLC) or as electrochemical pseudocapacitors [6-9]. In spite of the economic advantages that carbon black offers, as material in energy storage devices, the good and efficient commercial development of EDLC requires considering other factors of practical use, such as the simple design of the devices and the easy preparation of the electrode material. In this study the carbon paste electrodes (CPE) are presented. These electrodes have been successfully used in electroanalytical applications [10-15]. Particularly, these electrodes are easily prepared, mixed intimately at room temperature the material of carbon powder with a hydrophobic binder who includes mineral oil, paraffin, silicon oil or the addition of polymeric components of low molecular weight. The CPE have the capacity to be molded in order to allows them to adapt at any geometric configuration of the current collectors. On the other hand, due to the hydrophobic surface - the area

involved in the interfacial processes is specifically defined, this allow it to be evaluated in an electrochemical way by electrochemical techniques. Other advantages are low cost of production, design and the easy renewal of their surface. Besides of the advantages of paste electrodes, not has been employed in energy storage devices [16-22]. In this work it is presented a systematic study of characterization and evaluation of the capacity to storage charge in CPE as alternative to matrix support by composite electrodes in store energy. The CPEs were prepared with carbon black powder and different binders. Cyclic voltammetry, chronoamperometry and chronopotentiometry, were used to describe the capacitive behavior in specific potential range. The quantity of charge storage was evaluated in two electrolytes: 1M $HClO_4$ and 1M $LiClO_4$ Was evaluated the influence of binder and surface conditions of electrodes with and without electrochemical modification.

2. Experimental :

The electrochemical characterization of the carbon paste electrodes was carried out in a typical three electrode cell, saturated calomel electrode (SCE) is used as a reference electrode. The potentials in this study are reported with regard to this electrode. The auxiliary electrode was a graphite bar with bigger area than the working electrode. It is important to mention here that the auxiliary and reference electrodes were kept in separate compartments inside the electrochemical cell. Different carbon paste electrodes were used as working electrodes prepared with powdered material of standard carbon black [CB, particle size ~ 390

nm, superficial area (BET) = 6.6 m^2/g, DBPA (adsorption DibutilFtalato) 42 ml/100 g, 0.35 % Sulfur, < 1 ppm lithium]. The pastes were prepared with silicon oil (S) or nujol (N). The composition of the CPE was a relation in weight of CB:S = 72 : 28 or CB:N = 73 : 27, in all the studied electrodes. The paste (0.06 g) was supported in a 4 - mm thickness Teflon ring (0.50 cm^2) with stainless steel as the back contact.

In order to determine the reproducibility of the electrochemical response of the CPE, a system of reference of well-known response was used (i.e. 10^{-2} M Fe $(CN)_6^{-3}$, 10^{-2} M Fe $(CN)_6^{-4}$, 1M KCl). The electroactive areas of the paste electrodes were evaluated by chronopotentiometry technique, applying different potential pulses during 100 s, in the system of 10^{-2} M Fe $(CN)_6^{-4}$ / 1M KCl. The characterization and evaluation the storage charge process was carried out in 1M HClO$_4$ and 1M LiClO$_4$. in pastes electrodes where the surface area was previously modified.

The surface area of CPE were modified applying a potential pulse of 1.35 V vs. SCE to a time of 300 s in 1M HClO$_4$ and 1M LiClO$_4$ from an independent and previous way to their characterization. Thus four different electrodes are evaluated: CB:S, CB:N, CB:Sm and CB:Nm, where m indicates that they have been modified. With the purpose of assuring the same interfacial conditions and good reproducibility in the electrochemical response, new paste was used for each test. The working potential range was determined by cyclic voltammetry in each electrolytic system (1M HClO$_4$ and 1M LiClO$_4$). The charge of the double layer was evaluated with voltammetry applied different scan rates within potential range of ± 50 mV respect to the rest potential ($E_{i=0}$) of each system. The chronopotentiometry technique (pulse of constant current) was used to evaluate the charge and discharge capacity. Electrochemical measurements were carried out with IF 1287 Electrochemical Interface / Solartron equipment connected to a personal computer.

3. Results and Discussion :
3.1. Evaluation of the electrochemical response of CPE in 10^{-2} M Fe $(CN)_6^{-3}$, 10^{-2} M Fe $(CN)_6^{-4}$, 1M KCl :

The preparation of CPE, simple mixture of the components (carbon black powder and the binder) is an important step that can be affect the physical-chemical properties of the electrode material, such as the consistency and adherence that directly affect the conductivity of the pastes. Furthermore as a result of their synthesis methods, the carbon black has impurities in an intrinsic way that limits its use as electrode material; these impurities can influence the electrochemical response of the electrodes. The CEPs were evaluated in the reference system: 10^{-2}M Fe$(CN)_6^{-3}$/10^{-2}M Fe$(CN)_6^{-4}$, 1M KCl, whose voltammetric response is widely known for a conductive electrode, such as platinum [23, 24].

Figure (1a) shows the voltammetric response corresponding to the CPE in 10^{-2} M Fe $(CN)_6^{-3}$, 10^{-2} M Fe $(CN)_6^{-4}$, 1M KCl at 50 mV/s. Scan initiating in the negative direction from the rest potential ($E_{i=0}$= 0.22V vs. SCE). Each response shown in this figure correspond to paste electrodes CB:S prepared with different mixing time ($t_1 < t_2$

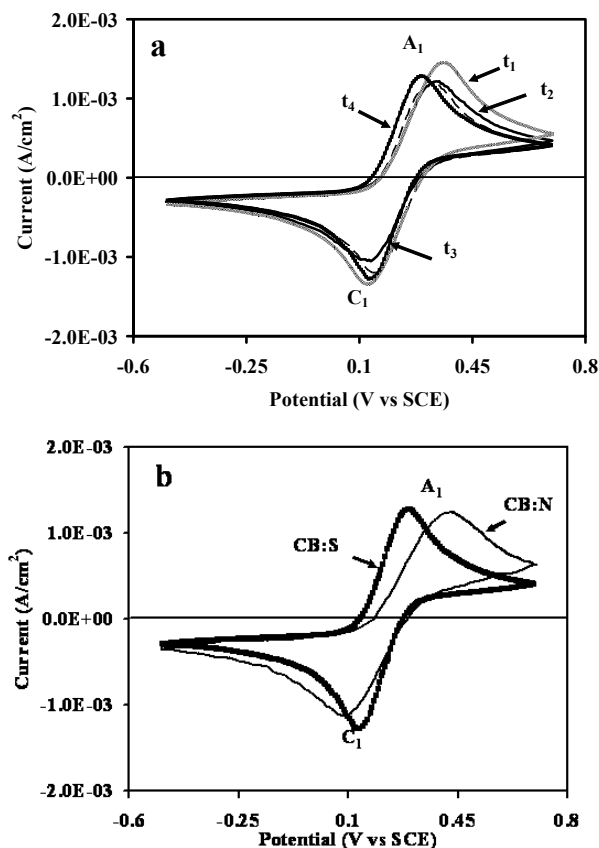$<t_3 < t_4$). Typical voltammetric response of the Ferro/Ferricyanide

Figure (1) : Typical voltammograms corresponding to the reference system, 10^{-2}M Fe $(CN)_6^{-3}$, 10^{-2}M Fe $(CN)_6^{-4}$, 1M KCl, in the range -0.5 to 0.7 V vs. SCE at 50 mV/s. (a) Electrode CB:S with different mixed time $t_1 < t_2 < t_3 < t_4$ = 20 min, (b) Electrodes CB:S and CB:N, these responses correspond to the greatest mixed time (20 min) of each electrode.

redox couple is observed, C$_1$ corresponds to the reduction of ferricyanide ion and A$_1$ is associated to the oxidation of the ferrocyanide, and another type of contributions at the response does not present. On the other hand, the Figure (1a) show a variation weak in current peak magnitude (Ip) and the potential peak (Ep) for the corresponding redox process A$_1$ and C$_1$. Although the CPEs have the same composition, these differences show the effect of the mixing time. In the practice, it is quite difficult to controlling the way to mix the components; this depends on the experimenter. Thus in this case, a criterion of reproducibility was established: the magnitudes of peak potentials (Epc, Epa), currents peak (Ipc, Ipa) and the difference of peak potentials (ΔEp) obtained from voltammetric response by paste electrode with more mixing time (t_4 = 20 min). In this study, new pastes were been prepared and evaluated in the reference system and the voltammetric responses for each electrode fulfill the criterion of reproducibility established by voltammetric parameters. On the other hand in Figure (1b) show the

voltammetric responses obtained in the reference system correspond to CPE elaborated with silicon oil and nujol.

3.2. Evaluation of the electroactive area of CPEs in the system 10^{-2}M Fe $(CN)_6^{-4}$, 1M KCl :

The electroactive area of the unmodified and modified CPEs was determined by chronoamperometry technique, to applied a potential pulse of different magnitude during 100 s where current/time response is describe by Cottrell equation [23, 24] :

$$I = \frac{nFD^{1/2}C_0A}{\pi^{1/2}t^{1/2}} \qquad (1)$$

n is the number of transferred electrons, F = Faraday Constant (96485 coulomb/mol), D = diffusion coefficient (cm^2/s), A = electroactive area (cm^2) Co = solution concentration (mol/cm^3). From equation (1), I vs. $t^{-1/2}$ keep a lineal relationship and the slope b is defined :

$$b = \frac{nFD^{1/2}C_0 A}{\pi^{1/2}} \qquad (2)$$

and the electroactive area A is evaluated. To use the equation 2, it is important to know the diffusion coefficient of the electro active species, in the case of the ferrocyanide ion D=6.3x10^{-6} cm^2/s and C_0=1x10^{-5} mol/cm^3.

Due to the hydrophobic state of the surface of the CPEs, the surface area is defined in a specific way thus is possible to consider a lineal diffusion and it allows used the Cottrell equation [see Figure (2a-b)]. On the other hand, considering the value of BET (6.6 m^2/g) of this material and the values of the evaluated electroactive area, the mass associated to this area was estimated and presented in table I.

Table (I) : Values of electroactive surface area, mass and C_{dl} of the carbon paste electrodes unmodified and modified in different electrolytic systems.

CPE/ Electrolytic system	Electroactive area* / cm^2	Mass in surface area**/mg	C_{dl} $\mu F/cm^2$
C:Sm/HClO$_4$	**6.19**	**0.094**	**37.26**
C:S/HClO$_4$	0.98	0.015	14.09
C:Sm/LiClO$_4$	**1.29**	**0.020**	**17.96**
C:S/LiClO$_4$	0.89	0.013	8.51
C:Nm/HClO$_4$	**1.82**	**0.028**	**12.36**
C:N/HClO$_4$	1.64	0.025	2.13
C:N/LiClO$_4$	**1.69**	**0.026**	**8.16**
C:N/HClO$_4$	1.41	0.021	4.28

** Mass evaluated considering BET area = 6.6 m^2/g and the electroactive area *

3.3. Evaluation of the capacitive response of CPEs by voltammetry in 1M HClO$_4$ and 1M LiClO$_4$:

The capacitive response influenced by the impurities present in an intrinsic way in the surface of carbon black materials (functional groups with carbon -oxygen) has been studied and it is controversial. In some cases the presence of these compounds has shown its contribution to the total capacitance due to the pseudocapacitance of the

corresponding redox couple [9]. Contrarily, it has been reported that these compounds do not play an important roll due to their instability and it is assumed that the capacitance
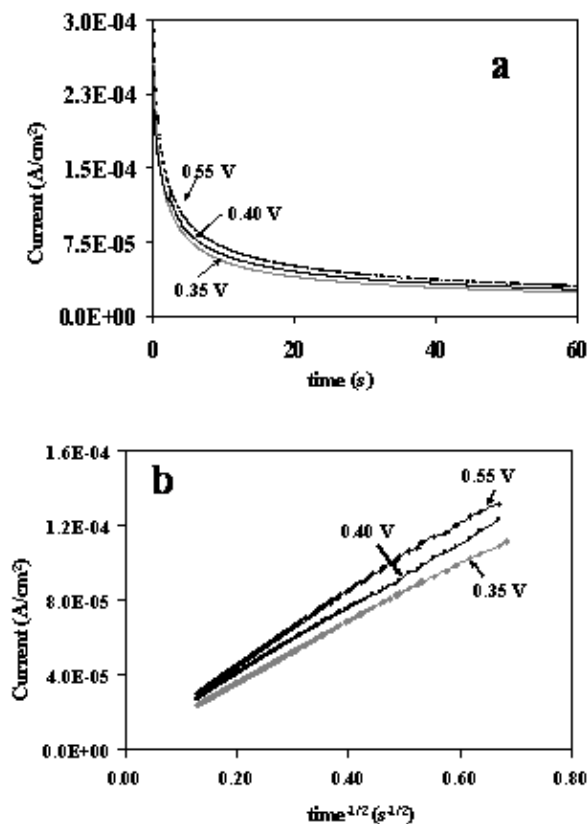

Figure (2) : (a) Response current-time correspond to a carbon paste electrodes CB:Sm (modified previously in 1M LiClO$_4$) obtained applying different pulse potential in 10^{-2}M Fe $(CN)_6^{-4}$, 1M KCl, (b) Lineal relationship of I vs. $t^{-1/2}$ for evaluated electroactive area from the slope defined by Equation (2).

of the double layer only depends of surface area of the electrode material [25-27]. In order to evaluated the influence of chemical surface conditions in the capacitive behavior of the CPE; in this study the surface of the CPE was electrochemically oxidized applying a potential pulse of 1.35 V vs. vs. SCE during 300 s, in the electrolytic systems either 1M HClO$_4$ or 1M LiClO$_4$. Figure (3) compared the voltammetric response corresponding to paste electrodes unmodified and modified previously in 1M HClO$_4$ [CB:S Figure (3a); CB:N Figure (3b)]. The sweep potential start in negative direction from the rest potential of each electrode at 10 mV/s (see direction of the arrows). The electrode CB:S without treatment [Figure (3a) thick line and insert] show small capacitive currents in potential range -0.2 to 1.0 V vs SCE, as well a slightly reduction process C_1, and in reversed direction, an oxidation peak A_1 is observed. Following with the scan a current plateau B is observed in E =1.1 V vs. SCE and the potential limit E = 1.3 V vs. SCE the current is increase. The processes in C_1 and A_1 are associated to reduction and oxidation of some intrinsic superficial oxide of the carbon black [16, 20]. In other hand, the currents response in B and E= 1.3 V are associated to the surface oxidation of carbon pastes electrodes or the electrolytic system.
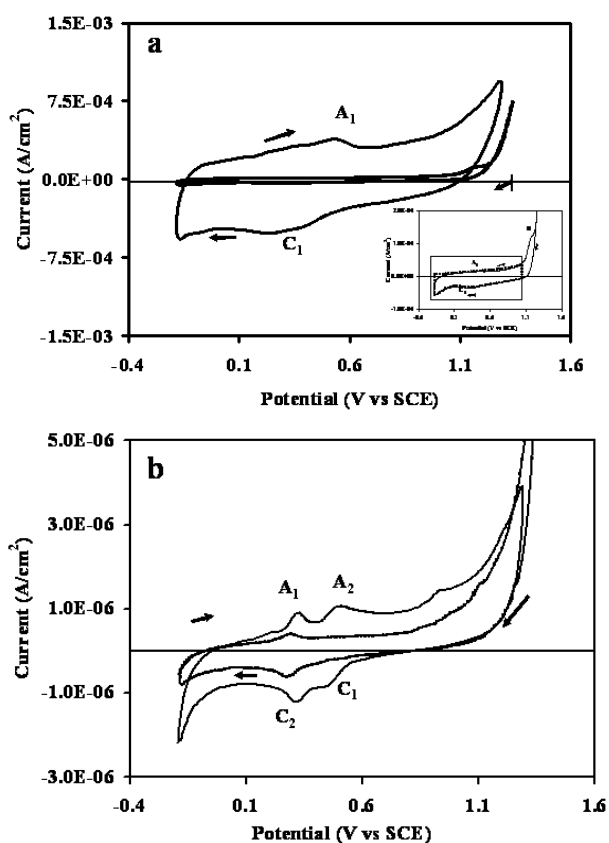
Figure (3) : Comparison of the voltammetric responses obtained in 1M $HClO_4$ in the potential range between -0.2 to 1.35 V vs. SCE at 10 mV/s, corresponding to different CPE unmodified (thick line) and previously modified (thin line) in independent way in the same system : (a) electrode CB:S and (b) electrode CB:N.

For the case of the electrochemically modified electrode CB:Sm [Figure (3a) thin line], the current response is typically capacitive and with higher magnitude than the electrode CB:S without treatment, also the processes C_1 and A_1 mentioned previously are described. Figure (3b) corresponds to unmodified (thick line) and modified (thin line) CPEs prepared with Nujol (CB:N). The voltammetric responses show important differences respect to Figure (3a). The reduction C_1 and oxidation A_1 processes are associated to the native oxides of the material of carbon described previously, and the processes C_2 and A_2 are related with an electroactive redox couple formed as product by electrochemical treatment. It is important to observe that the current is smaller than electrodes CB:S. Finally the Figure (4) shows the responses of electrode CB:S in 1M $LiClO_4$ unmodified (thin line) and modified (thick line) previously in same electrolyte. The voltammetric response is typically capacitive in a wide potential range (marked in the figure). in the positive limit potential the current increase possibly to oxidation of the electrolyte. Likewise it is important to observe that for this case redox processes are not defined as previous Figures (3), this is possibly due to that in 1M $LiClO_4$ the products formed on the surface are not electroactive; however they contribute to the capacitive response. Considering the

previous discussion, it is clear that the electrochemical treatment induces the formation of carbonyl functional groups on electrode surface and it influences directly the response of capacitive current of the paste electrodes in a potential range defined. Likewise the influence of binders is shown in Figure (3) and the influence of the electrolyte in the electrochemical modification of the electrodes is show in Figure (4).
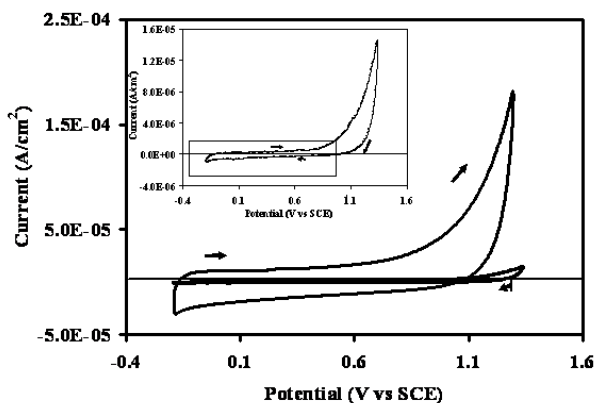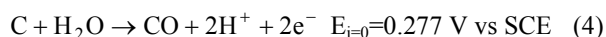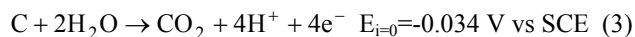

Figure (4) : Comparison of the voltammetric responses obtained in 1M $LiClO_4$ in the potential range between -0.2 to 1.35 V vs. SCE at 10 mV/s., correspond to carbon paste electrode CB:S, unmodified (thick line) and previously modified (thin line) in independent way in 1M $LiClO_4$ system.

Although the characterization and chemical identity of the products formed after the electrochemical treatment is outside of the scope of this study, is important to consider the literature, where the reactions (3) and (4) describe the electrochemical oxidation of the Carbon Black in aqueous solutions (acid or basic):

$$C + 2H_2O \rightarrow CO_2 + 4H^+ + 4e^- \quad E_{i=0}\text{=-0.034 V vs SCE} \quad (3)$$

$$C + H_2O \rightarrow CO + 2H^+ + 2e^- \quad E_{i=0}\text{=0.277 V vs SCE} \quad (4)$$

Here the carbon monoxide is thermodynamically unstable with regard to the CO_2, and the reaction of CO to CO_2 is:

$$CO + H_2O \rightarrow CO_2 + 2H^+ + 2e^- \quad E_{i=0}\text{=-0.344 V vs SCE} \quad (5)$$
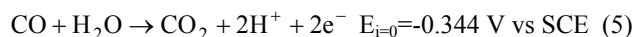
The previous reactions represent the final oxidation products, but there are intermediate processes, where surface oxides associated to different functional groups can be presented [25-29]. There are not thermodynamics reactions that can be easily described the formation of surface functional groups, nevertheless this electrochemical oxidation is represented by :

$$\text{Carbon} \rightarrow \text{surface oxide} \rightarrow CO_2 \qquad (6)$$
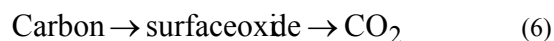
Possibly, the processes (C_2, and A_2) described in the voltammetric responses show in Figure (3), are associated with this electrochemical oxidation. Furthermore the oxidation of the water (reaction 7) in 1.0 V vs. SCE

contributes to the current measure in the positive potential of each response of Figure (3) [23].

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \quad E_{i=0} = 0.988 \text{ V vs SCE} \quad (7)$$
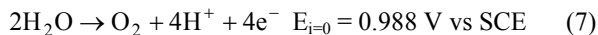
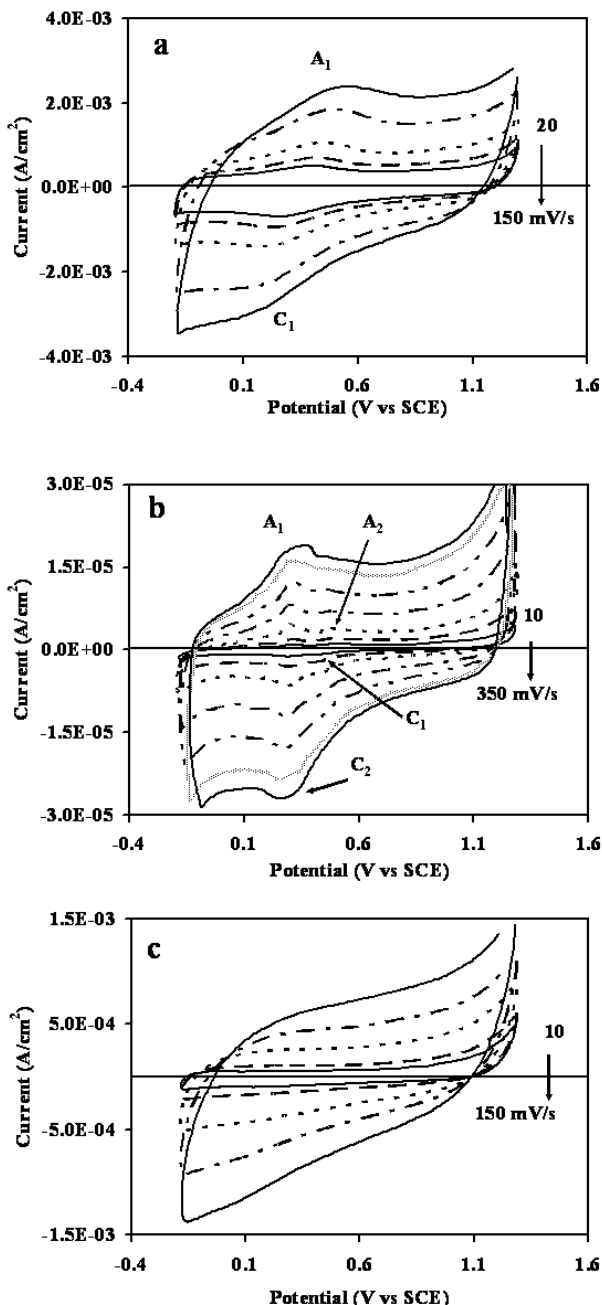### 3.4. Electroactivity of the carbon-oxygen compounds in the capacitive response of the modified CPE :

Figure (5) : Cyclic voltammograms obtained at different scan rate v, corresponding to CPE modified and evaluated in the system that it is indicated : (a) CB:Sm/1M HClO₄, (b) CB:Nm/1M HClO₄, (c) CB:Sm/1M LiClO₄.

In order to evaluate the pseudocapacitive contribution of the carbon-oxygen compounds formed on surface carbon

paste electrode during the electrochemical treatment was carried out a Voltammetric study applying different scan rates.

The Figure (5) show these responses corresponding to CPE previously modified either in 1M HClO₄ or in 1M LiClO₄, it is observed that the current response increase with scan rate and shown that the processes C_1 and A_1 have influence with the scan rate. For the electrode CB:Sm in the system 1M LiClO₄, shows a typically capacitive response [Figure (5c)]. In general similar responses with the scan rates were obtained for the other CPEs studied. The capacitive current (I_C) has a lineal relationship with the scan rate (v), while the faradic current (I_F) for controlled processes by diffusion, shows a lineal relationship with $v^{1⁄2}$. [24]. Considering that the total current (I_T) of voltammetric response, has the contributions of the current I_F and current I_C, such as :

$$I_T = I_F - I_C \quad (8)$$

The current I_C was evaluated by graphic method reported in [23, 24] and show in Figure (6). After of corrected the capacitive current I_C of the total current I_T (equation 8) for each voltammetric response obtained at different scan rates [Figure (5)], the voltammetric response corresponding to faradic current I_F is shows in Figure (7).

Figure (8) shows the relationship of Ip vs $v^{1⁄2}$ by C_1 and A_1 processes, the lineal relationship by C_1 indicates that this process is controlled by the diffusion of any electroactive specie, while A_1 is practically independent of $v^{1⁄2}$, A_1 is possibly an absorbed species on the surface of the electrode.
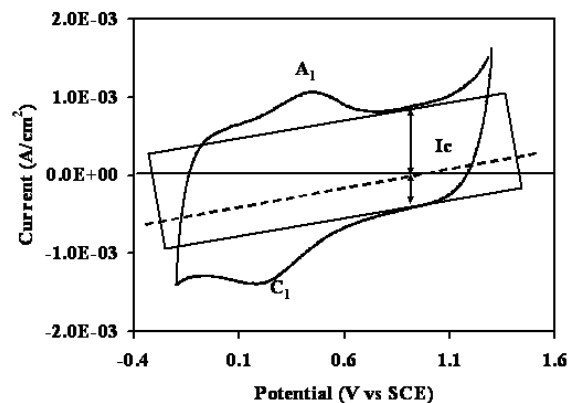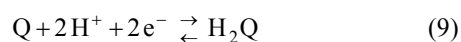

Figure (6) : Capacitive current (I_C) evaluated from cyclic voltammetry response. This response correspond to CB:Sm /1M HClO₄.

The quinone group is reported as product of surface modification and in acid medium the reaction (9) represent the equilibrium that take place and involves the couple quinone/hydroquinone and ion H^+ [3, 4].

$$Q + 2H^+ + 2e^- \rightleftarrows H_2Q \quad (9)$$

The ion H^+ diffuses from the bulk of solution towards surface electrode and carried out the interfacial reaction (9),

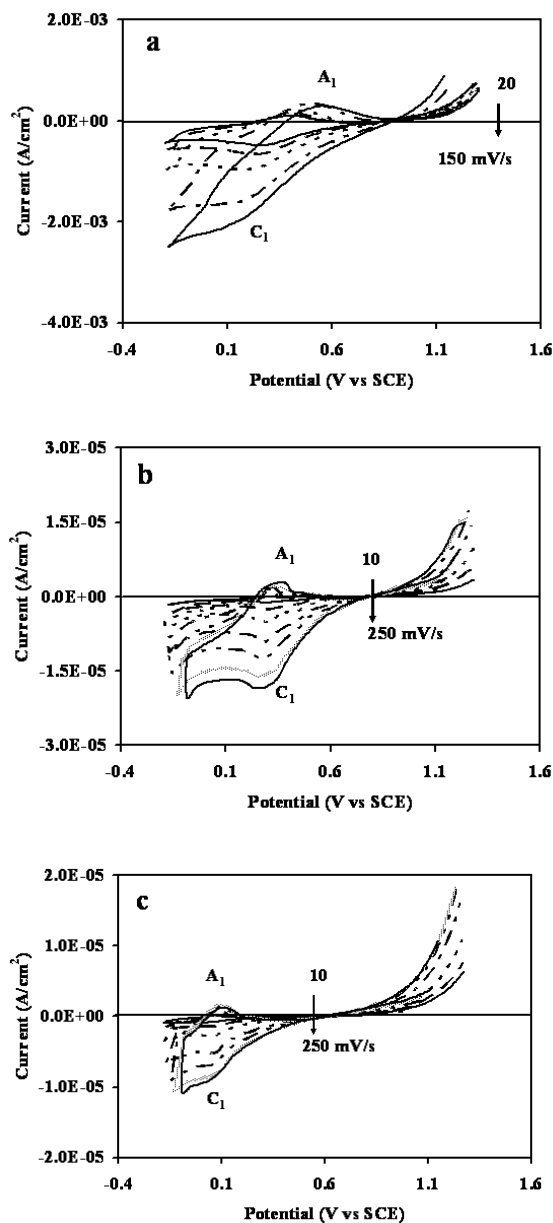this mechanism is in according to results shown in the Figures (7-8).

Figure (7) : Voltammetric response corresponding to faradaic current (I_F), evaluated from the responses shown in the Figure (5), (a) CB:Sm/1M $HClO_4$, (b) CB:Nm/1M $HClO_4$ respectively, and (c) CB:Nm/1M $LiClO_4$.
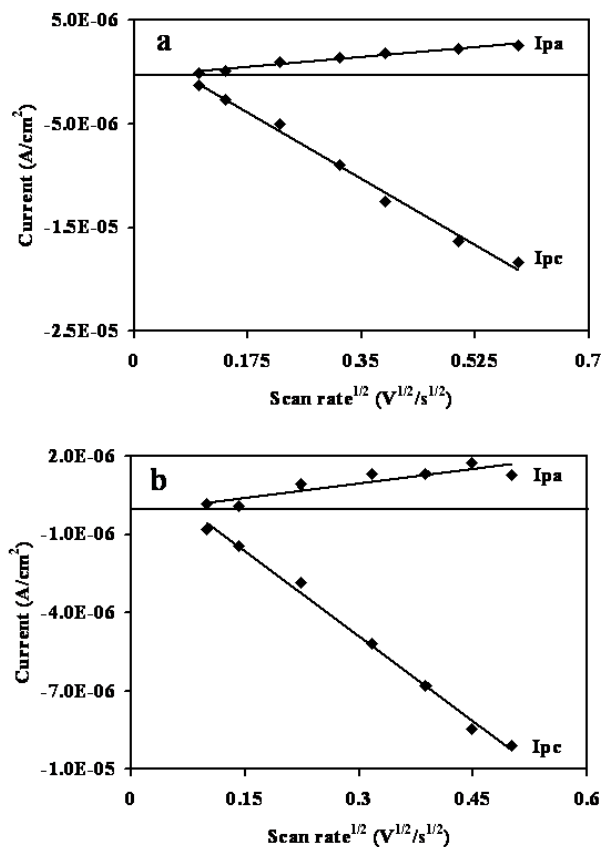

Figure (8) : Relation of the current peaks (Ip) vs. $v^{1/2}$ corresponding to results shown in Figure (7) for paste electrodes CB:N in different electrolytes : (a) CB:Nm/1M $HClO_4$, (b) CB:Nm/1M $LiClO_4$.

3.5. Evaluation of the stability of modified CPE by voltammetry in the electrolytic system 1M $HClO_4$ and 1M $LiClO_4$:

In order to evaluated the stability of modified electrodes, the Figure (9a-c), shows the voltammetric responses corresponding to 100 successive sweep cycles obtained in previously modified electrodes, at 10 mV/s in the potential range of 1.3 to -0.2 V vs SCE. It is observed, in Figure (9a) (CB:Nm/ 1 M $HClO_4$) that the voltammetric response is independent from the number of cycles, two reduction processes are presented (C_1 and C_2) and two processes of oxidation (A_1, A_2) previously described in Figure (3b), this behavior reflects the stability of the electrode. For the case of Figure (9b), corresponding to CB:Sm /1 M $HClO_4$, it is observed from the first cycles that the current increases according to number of cycles, also the presence of the reduction C_1 and oxidation A_1 processes already described in the Figure (3a). Finally the voltammetric response corresponding to the electrode CB:Nm/1M $LiClO_4$ [Figure 9c] it is observed that the current/potential response is independent from the number of applied cycles.
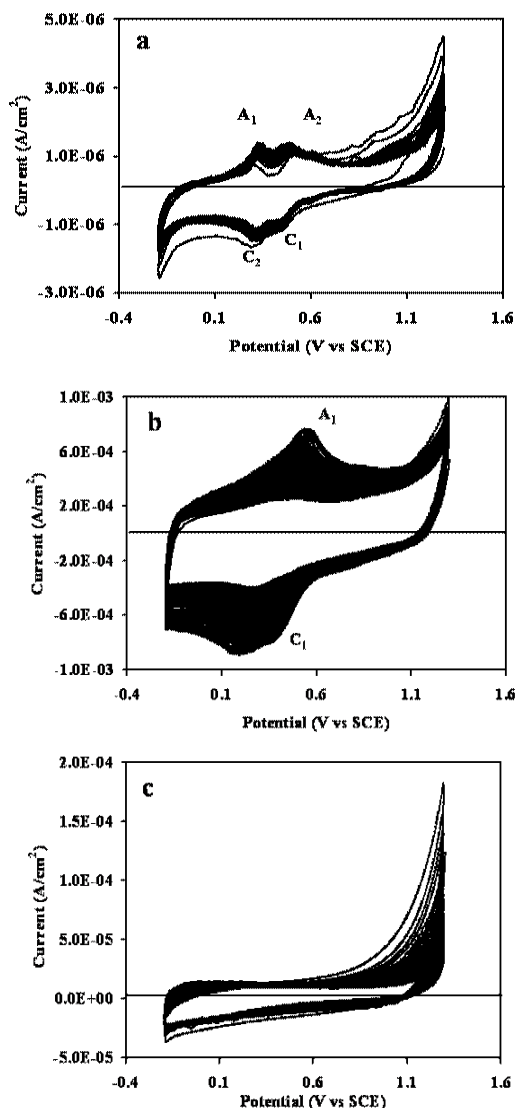
Figure (9) : Cyclic voltammograms obtained during 100 successive cycles on CPEs modified and evaluated in different electrolytes : (a) CB:Nm/1M HClO$_4$, (b) CB:Sm/1M HClO$_4$, (c) CB:Sm/1M LiClO$_4$.
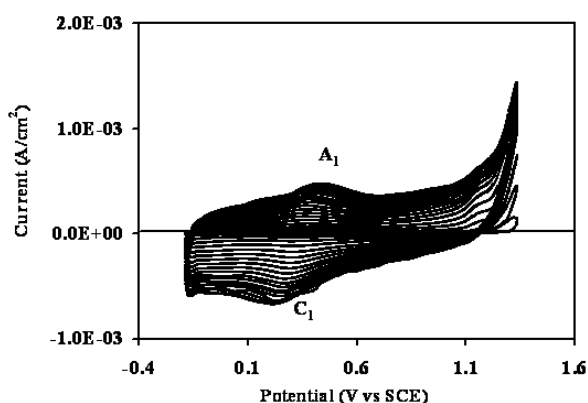

Figure (10) : Voltammetric response obtained in the system 1M HClO$_4$ at 10 mV/s for carbon paste electrode CB:S unmodified applying 20 successive cycles.

Considering the voltammetric responses in Figure (9), only the electrode CB:Sm in 1M HClO$_4$ [Figure (9b)] shows influence with the number of applied cycles, furthermore this electrode has electroactive area biggest than other electrodes (see table I).

This can be possibly due to an effect of removal of the material with the cycling, that is to say that the electrolyte diffused into the bulk of the paste and in this case the area increases constantly, another possibility could be that the oil silicon interacts with the electrolyte. In order to described the effect, the Figure (10) shows the voltammetric response at 10 mV/s, corresponding to a paste electrode CB:S without modified applying successive sweep cycles. It is observed that the current response increases successively with the number of cycles. Comparing Figures (9b and 10), it would seem that the current response is independent of surface state of the paste electrode, this indicates that an effect of material removal can exist with the cycling. However it is important to point out that in the other responses (Figures 9a and 9c) they do not present this effect when applying the same number of cycles. On the other hand considering Figures (9a-b), in the positive limit potential (1.1 to 1.3 V) a constant increment of the current is observed. This behavior is associate of the couple quinone/hydroquinone formed in the electrode surface in each cycle [3, 4], and possibly, it is dissolved in silicon oil and diffuse into the bulk of the paste it may cause an increase of the electroactive area [response in Figure (9b)]. This behavior is not observed in the electrode that contains Nujol contains [Figure (9a)]. In the literature, it has been reported for CPEs with silicon oil the dissolution and diffusion of different electroactive species, as ferrocene [12, 15].

3.6. Evaluation of the charge/discharge capacity of the electrodes CPE by means of current pulses :
Before evaluating the charge/discharge capacity of the electrodes CPE, the capacitance of the double layer was evaluated by cyclic voltammetry technique at different scan rates in a potential interval of ± 50 mV from the potential of null current of each system, following the relationship given by the equation 10 [23].

$$\Delta i = Ia - Ic \text{ vs. } (dE/dt) \qquad (10)$$

Where Δi is the difference between the intensity of the anodic current (I_a) and the cathodic current (I_c), dE/dt is taken from the scan rate. The capacitance of the double layer is obtained from the slope of a graph of Δi vs dE/dt (v). The values obtained within this determination are presented in table I. These values are similar to those reported for carbon materials with and without chemical species of carbon–oxygen [4, 5, 8].

The charge/discharge capacity was evaluated by chronopotentiometry technique, applying a double pulse of current during 50 successive cycles in the CPEs CB:S and CB:N without treatment and modified. The magnitude of the current was selected considering the voltammetric response of Figure (3) and (4). As an example it is shown in Figure (11a), the response obtained for an electrode modified CB:Sm and evaluated in the system 1M HClO$_4$

36

and in Figure (11b) show the response correspond to modified electrode CB:S and evaluated in the system 1M LiClO$_4$.
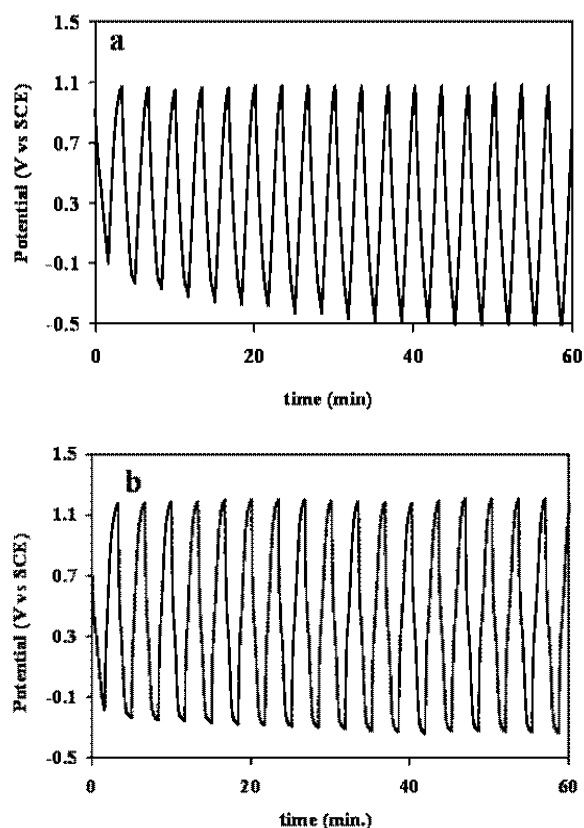

Figure (11) : Response potential-time obtained when applying a double pulse of current of different magnitude that depends of the system. It shown 18 first cycles from 50 consecutive cycles : (a) CB:Sm/1M HClO$_4$ ± 5x10^{-4} A, (b) CB:Sm/ 1M LiClO$_4$ ± 5x10^{-5} A.

The capacitance of charge and discharge in function of the number of cycles was evaluated following the method reported in [23] considering the following equation :

$$C = \frac{(\tau * I)}{\Delta E} \qquad (11)$$

where τ is the time of transition of each process, I is the current imposed and ΔE is the difference of potential associated to the time of pulse. The table 2 shown the charge and discharge values evaluated of potential-time response for the different electrodes CPE. Comparing the capacitance values reported in the literature corresponding to materials of activated carbon and activated fibers with BET areas much bigger that that of the carbon black used in this study [8, 27], it is observed that modified electrodes CPE show values of very similar capacitance to those reported. It gets the attention that the electrode CB:Sm characterized in 1M HClO$_4$ shows a magnitude of C (F/g) which is very above from the reported values. It is important to remember that the electrode CB:Sm presented an important interaction with the species generated in the electrochemical and the Silicon Oil treatment [Figure (9)

and (10)], which allowed the electrolyte to diffuse to the bulk of the material enhancing the charge capacity.

Table (2) : Values of specific capacities correspond to 50 cycles of charge/discharge [Figure (11)] of the carbon paste electrodes electrochemically modified in different electrolytic systems.

CPE/ Electrolytic system	Specific Capacity (F/cm^2)	Specific Capacity (F/g)
C:Sm/HClO$_4$	0.034	2265.91
C:Sm/LiClO$_4$	0.002	153.56
C:Nm/HClO$_4$	0.005	348.29

The BET area, the geometric area and the total mass used to prepare the electrode material are parameters used to evaluate the capacitance in F/cm^2 or F/g. In this work, was evaluated the electroactive area and the associate mass (table I) the magnitude of these parameters shown that not all the geometric area (0.50 cm^2) neither the used mass (0.06 g) participate in the process of charge accumulation, which indicates that there are active sites that are directly involved in the process. The BET area is a parameter referred to the adsorption of N$_2$ in materials of carbon in powder form, it is assumed that the micro and mesoporos accessible for N$_2$, are also accessible for the electrolyte, consideration that is not always been worth [30, 31] because the interfacial conditions between the electrolyte and the electrode are very different. The process of charge storage is of electrochemical nature, it is necessary to implement a methodology, by means of electrochemical techniques to evaluate electroactive areas and masses that can help us to obtain reliable values of the real capacitance of the material. Although in this study, a methodology to evaluate the electroactive area was proposed, this is enough and is necessary employed other techniques such as electrochemical impedance to describe the accessibility in the micropores of the carbon paste electrodes and with this to evaluate the real electro active area of these materials.

4. Conclusions :

In the charge/discharge process, the presence of different electroactive species on paste electrode surface, formed during the electrochemical pretreatment, have an important influences in the pseudocapacitive behavior, which enhancement the charge accumulation. The contributions to the total current of these electroactive species as well as their stability were evaluated and it was demonstrated that they are influenced by electrolytic system. Important interaction of the silicon oil with the products formed in the electrochemical treatment of the carbon black paste electrodes in the system of 1M HClO$_4$ was shown. The fact that this electrode shows the best results of charge storage is due to the conjugation of two situations; one of them is the presence of redox couple quinone/hydroquinone and seconds the important influence of oil silicon in the diffusion process of this couple toward the bulk of the paste. Finally is important to say that electroactive area and the associated mass evaluate in this work, shown that not all the geometric area (0.50 cm^2) and total mass in electrode (0.06 g) participate in the process of

charge storage, which indicates that there are active side accessible that are directly involved in the process. Facts that evidence the necessity to implement methodologies to evaluate electroactive areas and masses that help us to obtain reliable values of the real capacitance of the material.

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