

**9th International Symposium on New Materials and Nano-Materials for  
Electrochemical Systems  
XII International Congress of the Mexican Hydrogen Society  
Merida, Mexico, 2012**

**Effect of Carbon Porosity on the Electrochemical Properties of Carbon/Polyaniline Supercapacitor Electrodes**

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**ABSTRACT**

Electrochemical supercapacitors have attracted great attention in power source applications, due to their high power density, high charge/discharge rate, good reversibility and long life. Activated carbons are the most frequently used electrode material, due to their high accessibility, non-toxicity, high chemical stability, good electrical conductivity, high surface area and low cost, but in practice the capacitance values are limited by the material microstructure. Several methods have been reported to increase the capacitance, such as the incorporation of functional groups at the surface, the development of nanostructured carbons and the synthesis of hybrid composites of carbon with conducting polymers or metal oxides. In this work we report on the synthesis and electrochemical characterization of carbon/polyaniline composites, synthesized by in-situ chemical oxidative polymerization in acid media of aniline monomer on the surface of two commercial activated carbons having different textural properties, and the effect of the carbon porosity on the electrochemical properties of the electrodes. Results obtained indicate that the BET specific surface of the composites decreases sharply due to the collapse of the porous structure (mainly the micropores) of the carbon by the polyaniline chains. Regarding capacitance values,  $C_{sp}$  increases on increasing polyaniline loading in the composite, however high polymer concentration lead to a decrease on capacitance when high current were applied, probably due to diffusion restrictions of the electrolyte to the carbon surface.

## 1. Introduction

Electrochemical capacitor devices, often called supercapacitors or ultracapacitors, have received significant attention in recent times due to their wide range of potential applications in hybrid electric vehicles, fuel cells, cellular phones, PDAs, etc [1-4]. Two types of mechanisms are associated with energy storage in a this kind of devices: one is the electric double-layer capacitor (EDLC), in which stored energy is accumulated by the separation of electronic and ionic charges at the interface between a high surface area electrode and an electrolyte solution; the other is the pseudocapacitor, in which the active species can be fast and reversibly oxidized and reduced at characteristic potentials. Carbon materials such as activated carbon fibers and powders, carbon aerogels, carbon nanotubes [5-8] etc, are commonly used as electrode materials for EDLC, displaying good stability, but the capacitance values are limited by the microstructures in the materials. Conducting polymers such as polyanilines (PANI's), polypyrroles (PPY's), polythiophenes (PT's), etc [9-11] and transition metal oxides such as  $\text{RuO}_2$ ,  $\text{NiO}$ ,  $\text{MnO}_2$ , etc [12-14], have been used for redox capacitors. These devices generally display high capacitance, however conducting polymer based devices usually exhibit poor stabilities during the charge/discharge process while the high price of metal oxide restricts their commercial use.

Composites of carbons having different morphologies and conducting polymers can fully combine advantages of double-layer capacitance of carbon materials and pseudo-capacitance of conducting polymer, providing materials with high specific capacitance and working voltage, but also excellent cycle stability [32-36]. In this work we report on the synthesis and electrochemical characterization of carbon/polyaniline composites, synthesized by in-situ chemical oxidative polymerization in acid media of aniline monomer on the surface of two commercial activated carbons having different textural properties, and the effect of the carbon porosity on the electrochemical properties of the electrodes.

## 2. Experimental

Two commercial activated carbons, mesoporous-rich (Monarch 1400C) and microporous-rich (BP2000) both obtained from Cabot, hereafter labeled as Meso-C and Micro-C were tested. Aniline monomer (Aldrich) was distilled prior to use and stored at 278K. Carbon/polyaniline composites were prepared by adsorption of aniline on the carbon surface followed by chemical polymerization. In a typical reaction, 2 g of carbon was added to 30 ml of an aqueous 1M HCl solution containing 0.5 g (5.37 mmol) of aniline. After stirring for 30 min, 30 ml of an aqueous 1 M HCl solution containing 1.227 g (5.37 mmol) of ammonium peroxodisulfate (Aldrich) was added dropwise at 273 K and stirring continued for 3 h. The resulting composites were filtered and washed with deionized water up to neutral pH, then dried at 313 K over  $\text{P}_2\text{O}_5$  for 72h. The mass loading of PANI in the composite was evaluated by microanalysis (LECO CHNS- 932).

Porosity of the composites was analyzed by  $\text{N}_2$  adsorption at 77K (Micromeritics ASAP 2010). The apparent specific surface area was determined from the  $\text{N}_2$ -adsorption isotherm using the BET equation [15]. The pore volume ( $V_{\text{total}}$ ) was calculated by applying the Dubinin–Radushkevich (DR) equation to the  $\text{N}_2$ -adsorption isotherms [16]. The



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microporous surface area was obtained from the equation:  $S_{\text{mic}} (\text{m}^2 \cdot \text{g}^{-1}) = 2000V_{\text{N}_2} (\text{cm}^3 \text{g}^{-1})/L_0 (\text{nm})$ , where  $L_0$  represents the average micropore width [17]. Additionally, the analysis of the adsorption isotherm by a classical comparison plot based on the reference  $\text{N}_2$  adsorption for a non-porous carbon (Vulcan 3G carbon) provided information on the mesopore area  $S_{\text{meso}}$ . Pore size distribution was calculated by means of the Kruk–Jaroniec–Sayari method [19] applied to the adsorption branch. The electrochemical performance of the composites was analyzed in symmetric two-electrode Swagelok™-type cells by both cyclic voltammetry and constant current galvanostatic charge–discharge using a Solartron 1480 multichannel potentiostat–galvanostat equipment. The electrodes (12 mm in diameter and ca. 1 mm height), were obtaining by pressing (500 Kg) a homogeneous mixture of the composite (70 wt.%), polyvinylidene fluoride binder (20 wt.%) and carbon black (Super P, 10 wt.%). Glassy microfibre paper discs (Whatman BS45) were used as separator and aqueous 2 M  $\text{H}_2\text{SO}_4$  solution as electrolyte. Two stainless steel (A20 alloy) rods acted as current collectors.

### 3. Results and discussion

Table 1 shows composite composition obtained from microanalysis tests (N determination, average of three measurements). A small decrease on the PANI content in the composites regarding to the theoretical one was detected in all cases.

Table 1. Carbon/PANI composites composition

Sample	PANI Nominal content	PANI Real content
	wt%	wt%
Meso-C/PANI1	20.0	18.6
Meso-C/PANI2	33.3	25.7
Meso-C/PANI3	50	39.0
Meso-C/PANI4	60	46.0
Micro-C/PANI1	20	16.1
Micro-C/PANI2	33.3	24.3
Micro-C/PANI3	50	35.1
Micro-C/PANI4	60	43.1

Figures 1 show the  $\text{N}_2$  adsorption–desorption isotherms corresponding to both carbons, polyaniline and the synthesized carbon/PANI composites. In terms of shape, the isotherm of both carbons can be classified as type IV according to the IUPAC, a hysteresis loop being observed on both isotherms in the range of ca. 0.6–1.0  $P/P_0$  for the Meso-C sample and 0.85–1.0 for the Micro-C carbon.

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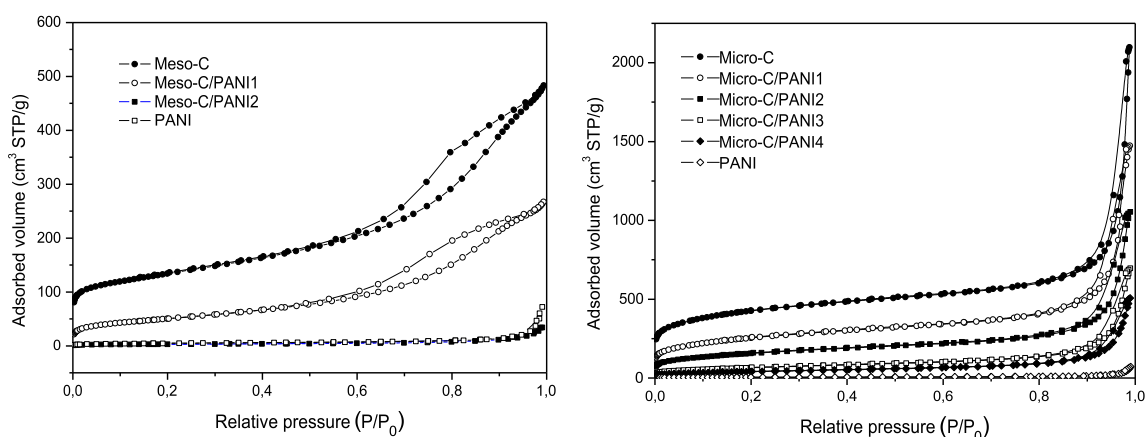


Figure 1. Nitrogen adsorption isotherms of carbon/PANI composites.

The textural characteristics of the samples calculated from nitrogen adsorption–desorption isotherms are listed in Table 2. Results indicate that the pore structure of the composites depends strongly on PANI concentration, the BET surface area decreasing from 471 m<sup>2</sup>g<sup>-1</sup> calculated for the Meso-C to 4.7 m<sup>2</sup>g<sup>-1</sup> for the composite with a 46 wt% PANI loading, due to the partial covering or filling of the pore structure of the carbon by the polymer, the mesoporous structure of the carbon was maintained after PANI loading up to 20 wt%. The total pore volume also decreases when increasing PANI concentration, mesopore and micropore structure being practically disappear for high PANI loadings.

Table 2. Textural properties of carbon/PANI composites

Sample	$S_{BET}$ (m <sup>2</sup> g <sup>-1</sup> )	$V_{total}$ (cm <sup>3</sup> g <sup>-1</sup> )	$V_{mic}$ (cm <sup>3</sup> g <sup>-1</sup> )	$V_{mes}$ (cm <sup>3</sup> g <sup>-1</sup> )	$S_{mic}$ (m <sup>2</sup> g <sup>-1</sup> )
Meso-C	471	0,75	0,18	0,57	254
MESO-C/PANI1	183	0,41	0,07	0,31	28,9
MESO-C/PANI2	20,2	0,08	0,01	0,01	1,77
MESO-C/PANI3	12,2	0,04	-	-	1,80
MESO-C/PANI4	4,7	0,02	-	-	1,04
Micro-C	1510	3,24	0,57	2,68	700
Micro-C/PANI1	930	2,28	0,32	1,96	320
Micro-C/PANI2	566	1,63	0,20	1,43	171
Micro-C/PANI3	237	1,08	0,08	0,99	47,3
Micro-C/PANI4	145	0,78	0,05	0,73	24,0
PANI	16,7	0,10	0,01	0,09	0,03



Similar effect was observed for Micro-C/PANI samples, but in this case the hysteresis, associated to the mesoporous pore structure was detected in all cases, independently of PANI concentration in the composite. Pore-size distribution of the samples, calculated by applying the Kruk-Jaroniec-Sayari to the adsorption branch of the isotherms, is shown in Figure 2. Meso-C carbon has a broad pore size distribution, with a maximum centered at 11.8 nm. Regarding the composites, the sample with the lower loading of PANI shows a profile similar to that of the carbon, with a maximum centered at 11.2 nm; increasing PANI loadings lead to a decrease in the pore size to 7.3 nm for the Meso-C/PANI2 sample, no pore being detected for higher PANI concentration. Regarding Micro-C-based composites, the pore size distribution graph indicates the presence of macropores (pore diameter >50 nm) in all samples, the volume decreases on increasing PANI concentration in the composite.

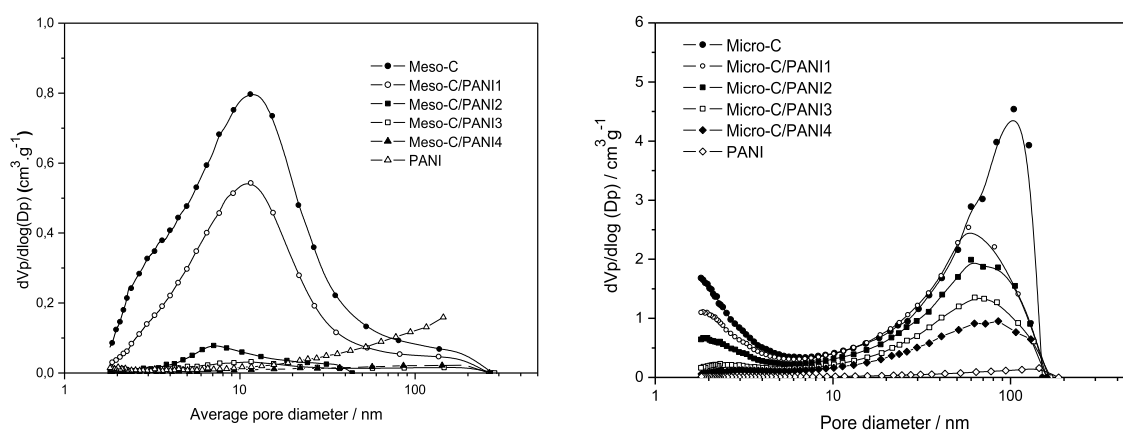


Figure 2. Pore-size distribution calculated for carbon/PANI composites.

Figure 3 shows the cyclic voltammograms of symmetric supercapacitors based on the Meso and Micro-C/PANI composites under study recorded at a scan rate of  $10 \text{ mV} \cdot \text{s}^{-1}$ . Carbon-based devices cyclic voltammograms show the expected rectangular shape associated to EDLC behaviour, while deviations from this behaviour were detected for all composites, where two redox oxidation and reduction peaks were observed, associated to the pseudocapacitive contribution of the polymer.

Figure 4 shows the variation of the specific capacitance, calculated from constant current galvanostatic charge/discharge test vs. the applied current density. The larger values of  $C_{sp}$  were obtained for the PANI device, but the value decreases sharply on increasing the applied current due to restrictions on the diffusion of the electrolyte. Carbon/PANI composites show specific capacitance values that, at low applied current, are higher than that of the pristine carbon, but again due to electrolyte diffusion restrictions decrease on increasing the applied current density up to being lower than the carbon. This effect was observed in both Meso and Micro-C derived composites.

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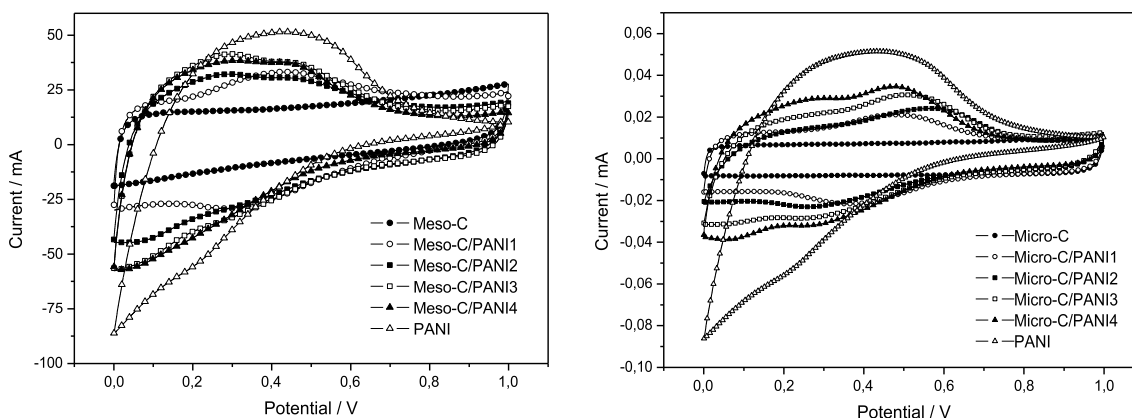


Figure 3. CV's of symmetric supercapacitors based on Meso and Micro-C/PANI composites measured at a scan rate of  $10 \text{ mV.s}^{-1}$ . Potential window 0-1 V.

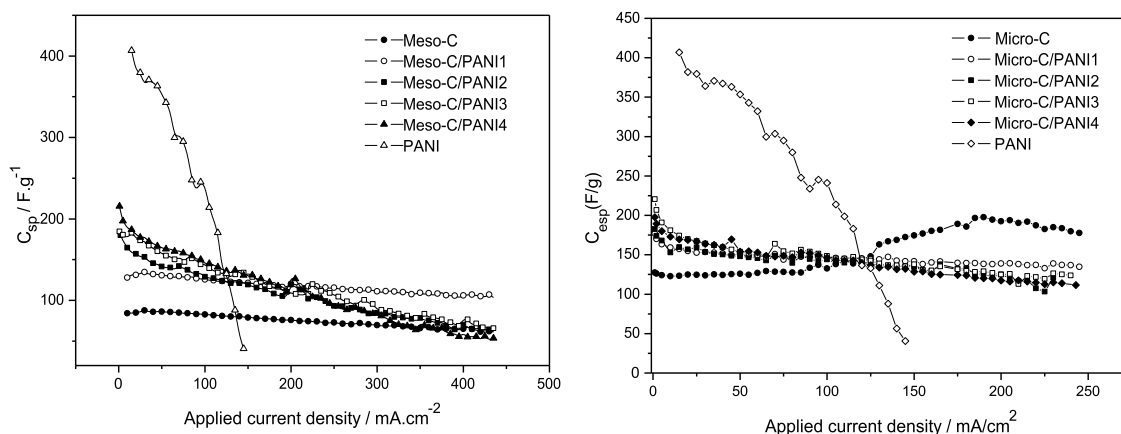


Figure 3. Discharge specific capacitance vs. applied current density of Meso C and Micro-C/PANI based symmetric supercapacitors. Potential window 0-1 V.

The best results were obtained for the Meso-C/PANI composite with the lower polyaniline loading (20 wt %), where the specific capacitance is 70% higher than that of the Meso-C carbon through all the range of applied current densities tested. Looking at the results obtained can be postulated that for carbon/PANI composites, the best electrochemical properties, in terms of specific capacitance, will be obtained when using carbons with a mesoporous structure and low polyaniline loadings. The diffusion of the electrolyte to the carbon surface, and so the EDLC contribution to the energy storage mechanism, is restricted in the presence of micropores, that can be easily collapsed by the polymer, or when using high polymer loadings in the composite.



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#### 4. Conclusions

Meso and microporous carbon/polyaniline composites have been synthesized by the in-situ oxidative polymerization of aniline monomer on the surface of the carbon particles. Textural analysis indicate that composites porous structure depends strongly on the PANI content,  $S_{\text{BET}}$  and pore volume decreasing on increasing PANI concentration. Regarding supercapacitor performance, the best results, in terms of specific capacitance, were obtained for the Meso-C/PANI composite, the specific capacitance been 70% higher than that of the Meso-C carbon through all the range of applied current densities tested. The results obtained suggest that, for carbon/PANI composites, the best specific capacitance will be obtained when using carbons with a mesoporous structure and low polyaniline loadings. The diffusion of the electrolyte to the carbon surface, and do, the EDLC contribution to the energy storage mechanism, is restricted in the presence of micropores that can be easily collapse by the polymer or when using high polymer loadings in the composite.

#### 5. Acknowledgements

Financial support by the Spanish Ministry of Science and Innovation Project ENE2007-62791/ALT is gratefully acknowledged. M.A. Torre thanks for a contract associated with that project.

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