ELECTROCHEMICAL METHODS TO ENHANCE THE CAPACITANCE IN ACTIVATED CARBON/ POLYANILINE COMPOSITES

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Abstract

Activated carbon/polyaniline composites have been prepared using different electrochemical methods: potentiostatic step, multiple potentiostatic steps and potentiodynamic polymerization using two final potentials (0.75V and 1V vs. Ag/AgCl). The so-prepared samples were characterized by cyclic voltammetry, galvanostatic charge-discharge, electrochemical impedance spectroscopy and FTIR spectroscopy. The preparation conditions turned out to be very important in the electrochemical behaviour of the samples. The best results in terms of capacitance were obtained for the potentiostatic polymerization methods. On the other hand, potentiodynamic methods provide better conductivities. As a general trend, activated carbon/polyaniline composites present synergic effects; that is, the capacitance of the composite is higher than the sum of the capacitance of the independent components and the resistance decreases.

Introduction

In recent years, the growth of energy requirements has strongly promoted the research in the field of energy storage devices. Among them, electrochemical capacitors have received special attention because they provide high power and present high cyclability. The electrode materials often used in supercapacitors are porous carbons, conducting polymers and hydrous ruthenium oxide (Conway 1999). The latter, despite presenting high capacitance values (Barbieri 2006; Chang 2006; Hu 2004a; Kim 2006), is too expensive for mass production. Porous carbons and conducting polymers, not so costly, appear as a very suitable choice for this application.

Porous carbons have been widely studied as supercapacitor electrode materials. From all this research, it can be concluded that the porosity is the main controlling parameter of the capacitance through its double layer contribution (Conway 1999). Recently, the contribution of the surface chemistry by faradic processes has been proven to be important (Bleda-Martinez 2005; Bleda-Martinez 2006; Lozano-Castello 2003). In any case, since the porosity development in porous carbons has a limit, the double layer capacitance of those materials cannot be improved indefinitely. Thus, the only way to enhance capacitance of porous carbons is taking advantage of the pseudocapacitive behaviour (redox contribution) of chemical species bonded or added to the carbon material.

Conducting polymers show this pseudocapacitive performance as they present a continuous range of oxidation states with increasing electrode potential (Conway 1999). Among them, polyaniline has aroused interest due to its easy polymerisation in aqueous media, good stability in air, easiness in doping/dedoping, low-cost production and relatively high conductivity (Gupta 2005; Hu 2002; Ko 2004; Ryu 2002). Additionally, for this polymer when thin films were grown, capacitance values in the range of 700-800 F/g have been reported (Prasad 2002; Ryu 2002; Zhou 2005). However, it is very difficult to obtain a large amount of polyaniline with these excellent properties. When the thickness of the film increases, worse performances are obtained (in terms of lower capacitance and higher resistance) (Zhou 2005). Moreover, the morphology of polyaniline affects the redox behaviour of the material, since it influences the specific surface area and the ions diffusion (Fusalba 2001; Mondal 2005; Zhou 2005). Taking into account these facts, deposition of polyaniline over a support with high surface area looks a promising method to obtain improved supercapacitors.

In this sense, successful attempts have been done using carbon materials as supports for polyaniline (Bleda-Martinez 2007; Chen 2003; Dalmolin 2005; Hu 2004b; Ko 2004; Lin 2003; Mondal 2007; Talbi 2003; Wu 2005). In these studies, it is remarkable the cooperative effect between the carbon material and the polymer, since the former provides better mechanical properties (Dalmolin 2005) and a high surface area where the latter can grow as a thin film with better redox kinetics (Ko 2004).

However, we have not found a systematic study of the influence of the electrochemical preparation method on the carbon/polyaniline composites properties. In this work, we have prepared these composites by using one activated carbon with a very high surface area and different electrochemical methods to polymerize polyaniline: potentiostatic step, multiple potentiostatic steps and potentiodynamic using two final potentials. The advantages and disadvantages of each one have been discussed.

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Experimental

Activated carbon preparation and its porous texture characterization

An anthracite was chemically activated using KOH as activating agent. The activating agent/carbon ratio employed was 3:1. The activation temperature (750ºC) was kept for 1 hour in inert atmosphere (800 ml/min N_2). Details of the activation process are available elsewhere (Lozano-Castello 2001). The porous texture of the sample was determined by physical adsorption (N_2 at 77 K and CO_2 at 273 K) using an automatic adsorption system (Autosorb-6, Quantrachrome) after sample out-gassing at 523 K under vacuum for 4 h. The total micropore volume (pore size smaller than 2 nm) was calculated from the application of the Dubinin-Radushkevich equation to the N_2 adsorption at 77K. The narrow micropore volume (pore size smaller than around 0.7 nm) was assessed from CO_2 adsorption at 273 K using the DR equation (Cazorla-Amoros 1998). The densities of the adsorbed phase used for the calculations were 0.808 and 1.023 g/ml for N_2 and CO_2 (Cazorla-Amoros 1998), respectively. The apparent surface area was calculated by the BET equation.

Electrochemical system

All electrochemical measurements were carried out with a potentiostat/galvanostat (Autolab model PGSTAT30 or EG&G model 273 controlled by software ECHEM M270) using a standard three-electrode cell configuration. Ag/AgCl electrode was used as reference and a graphite bar was employed as a counter electrode. 1M HCl + 0.5M KCl solution, prepared with Merck p.a. chemicals, was used as aqueous electrolyte in all experiments, including polymerization ones.

Electrodes preparation

Carbon/polyaniline composites were prepared by electrochemical polymerization over the carbon material. A graphite bar was used as a current collector. A paste consisting of the porous carbon and binder (PTFE) (80%-20% wt.), was deposited onto the graphite bar. No acetylene black or other conductivity promoters were used. The polymerization solution was 0.15M aniline + 1M HCl + 0.5M KCl aqueous solution prepared with Merck p.a. chemicals. The electrode was then subjected to three different electrochemical polymerizations, including i) potentiostatic step from 0.3 V to either 0.75V or 1V until the total electrical charge passed was 2C, ii) potentiodynamic polymerization at 75 mV/s from 0V to either 0.75V or 1V during 30 cycles and iii) multiple potentiostatic steps from 0.3V to either 0.75V or 1V during 200 pulses of 4 seconds at each potential. The nomenclature of the samples is exposed in Table 1.

Table 1. Nomenclature and polymerization conditions of the Carbon/PANI samples:

Sample	Type	Method	Potential
A	Activated carbon	_	_
AP1	Composite	Potentiostatic step	1V
AP75	Composite	Potentiostatic step	0.75V
AD1	Composite	Potentiodynamic	From 0V up to1V
AD75	Composite	Potentiodynamic	From 0V up to 0.75V
AS1	Composite	Multiple Potentiostatic Steps	0.3V to 1V
AS75	Composite	Multiple Potentiostatic Steps	0.3V to 0.75V

Additionally, we have prepared on the graphite support some polyaniline films at the same experimental conditions and following these methods, for comparison purposes.
The weight of the samples was determined with a microbalance (Sartorius Supermicro Model S4), with an accuracy of 1 μg.

Electrochemical characterization.

The galvanostatic method (at 0.5, 1 and 5 mA), was used to measure the capacitance. The capacitance values were calculated from the discharge time from 0.6V to 0V. The coulombic efficiency was also calculated. The results are expressed in F/g taking into account the weight of the active part of the composite, that is, carbon and polyaniline (excluding binder). Cyclic voltammograms were also obtained in order to assess the redox behaviour of the samples. The scan rate was 10 mV/s. The Autolab model PGSTAT30 was employed for these measurements. Electrochemical impedance spectroscopy was also applied on these samples in order to study the resistive behaviour of the composites. These analyses were carried out in a FRD-100 Frequency Response Detector module connected to the EG&G model 273 potentionstat/galvanostat.

Infrared spectroscopy characterization.

The pristine activated carbon material, the activated carbon/polyaniline composites and polyaniline films were analyzed by FTIR spectroscopy. A Nicolet Continuμm FT-IR microscope attached to a Nicolet 5700 FT-IR spectrometer, equipped with a liquid nitrogen-cooled MCT detector, was used. The spectra were acquired in ATR mode using a Germanium crystal. The resolution employed was 16 cm^{-1}. Additional FTIR spectra were collected in the transmission mode.

Results and discussion

Porous texture characterization of the carbon material

The pristine carbon material presents a type I isotherm for N_2 adsorption (not shown), which is typical of microporous solids. Table 2 contains the BET surface area and the micropore volumes calculated from N_2 adsorption data at 77 K [$V_{DR}(N_2)$] and CO_2 adsorption data at 273 K [$V_{DR}(CO_2)$] for the carbon sample**.**

Table 2. Porous texture characterization of the pristine carbon material

Sample	BET (m^2/g)	V_{DR} N_2 (cm^3/g)	V_{DR} CO_2 (cm^3/g)
A	2584	1.20	0.55

Polymerization process

Potentiostatic step method

The current vs. time curves (not shown) present two zones: an exponential decrease of current, followed by an increase. The first stage is usually related to double layer charge and the nucleation process and the subsequent increase of current is attributed to the linear growth of polymer chains (Mandic 1997). The polymerization at 0.75 V is slower than at 1V. Additionally, the increase of the current after the exponential decay is more important in the case of the polymerisation at 0.75V rather than at 1V. As it has been said before, this increase in current is due to the one-dimensional chain growth by means of a direct monomer-unit incorporation into the existing polyaniline film (Mandic 1997). This mechanism is favoured when the potential is not too high. It is also remarkable that the polymerization is faster when it is carried out over the carbon material than directly over the bare graphite support, for both potentials. This can be a consequence of the increase in the surface area in the presence of activated carbon

Potentiodynamic method

As expected, a higher polymerization rate is obtained when the upper potential is 1V (plot not shown), since more aniline molecules can be oxidized and incorporated into the polymer chain. As in the previous method, the porous carbon material increases the polymerization current as consequence of the increase in the surface area.

Multiple Potentiostatic steps method

In this method the pristine carbon material was subjected to 200 alternative potentiostatic pulses from 0.3V to either 0.75V or 1V for 4 seconds at each potential. The current vs. time was registered (not shown). When the pulses are carried out at 1V, the amount of deposited polyaniline is larger, as expected.

Characterization by chronopotentiometry

The activated carbon/polyaniline composites were characterized by chronopotentiometry. The samples were subjected to charge-discharge cycles at 0.5, 1 and 5 between 0 and 0.6V. The capacitance of all the samples was determined from the discharge process and the coulombic efficiency was additionally calculated. As a general trend, this efficiency was between 95-100%, except for sample AD75 whose efficiency was about 65%. This low coulombic efficiency can be due to additional polymerization occurring during the charging process at 0.5 mA.

The capacitance values as a function of the applied current for all the activated carbon/polyaniline composites and the pristine activated carbon are shown in Figure 1.
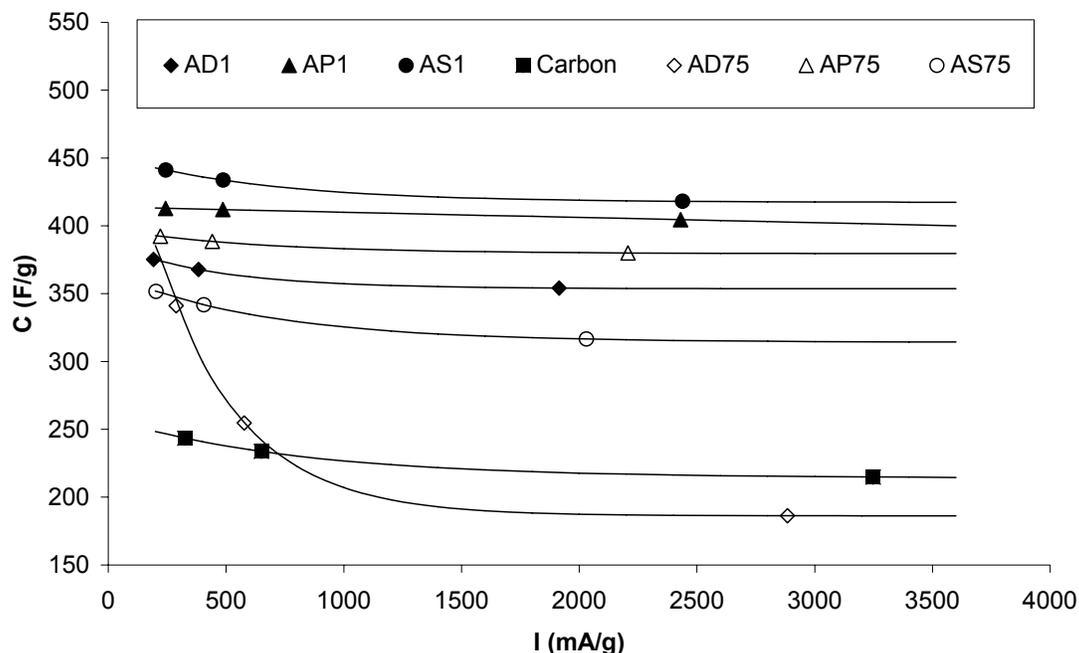
Figure 1. Capacitance values determined by chronopotentiometry vs. current.

It can be observed that samples prepared at higher potentials (closed symbols) present higher values of capacitance and, in all cases, higher values than the pristine activated carbon. Table 3 shows the loss of capacitance for each sample when the applied current increases from 0 to 3600 mA/g. The data at 0 mA/g have been obtained by extrapolation from each curve in Figure 6.

Table 3. Capacitance loss and resistance for each composite

Sample	Capacitance loss	Resistance (Ω)
A	17%	23.44
AP1	3%	14.12
AP75	5%	11.32
AD1	9%	14.70
AD75	91%	25.71
AS1	8%	11.19
AS75	14%	15.07

It can be observed that in all cases, except for sample AD75, the capacitance loss is lower for the composites than for the pristine activated carbon. Moreover, if we compare samples prepared by the same method, this loss is lower in composites prepared at higher potentials. Additionally, comparing different polymerization methods, the performance of composites at high current is better for samples prepared using a potentiostatic method. The behaviour at high power is determined by the porosity of the material, that is, the easiness to reach the available surface area. When the composites are prepared potentiodynamically, the growth rate of the polymer is slow. The resulting polymer possesses then high porosity with entrapped electrolyte within the pores (Mondal 2005). However, when the polymerization takes place potentiostatically, the polymer growth takes place continuously, faster and developing a compact film. Composites prepared by the multiple potentiostatic steps method present an intermediate behaviour. All these observations allow us to conclude that the slower the polymerization rate, the higher the porosity development in the films. Consequently, samples prepared at lower potentials or by means of potentiodynamic polymerization methods, that is, with slow polymerization rate, present rougher morphology and higher loss of capacitance with increasing current.

Dealing with the relationship between capacitive performance and polyaniline content in the composite, Figure 2 shows the capacitance of each composite vs. the wt % of polyaniline at 400 mA/g (interpolating from Figure 1). For comparison purposes, the results for some pure polyaniline films have been included, which were prepared by the potentiodynamic method because it is well known that the obtained polyaniline presents better quality (Mondal 2005). We can see that, as a general trend, the composites present a similar or better capacitance than the result of the combination of the independent components, using the mixtures rule. Moreover, it is interesting to remark that this comparison is done with a very thin film

of polyaniline of high quality. Since the weight of the composites is about 2 mg, if we compare the results with polyaniline films of similar weight, we observe that the composites present a much better behaviour. As it has been pointed out before (Talbi 2003), a cooperative effect of the π-conjugated system of the polymer and the porous carbon material can give larger specific capacitance than just the porous system or the conducting polymer alone.
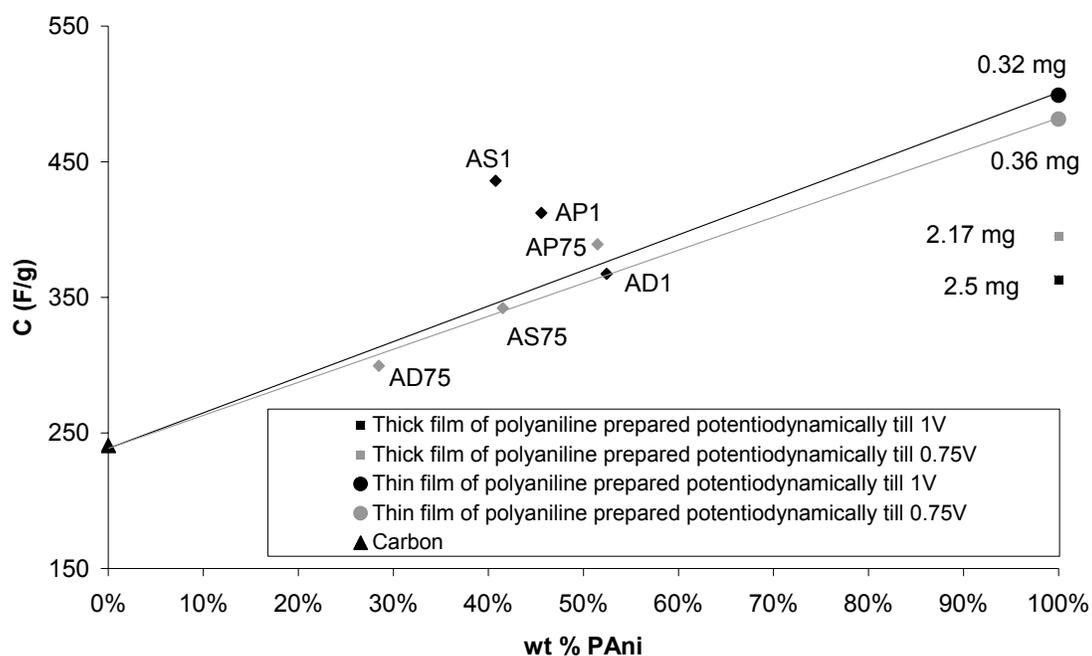

Figure 2. Capacitance values of the composites vs. the polyaniline content.

On the other hand, charge-discharge experiments can also give information about the resistance of the composite. From the ohmic drop of the chronopotentiograms, the values of resistance have been calculated. These values are shown in Table 3. It can be concluded that, as a general trend, the resistance of the composite decreases in relation to the pristine activated carbon, that is to say, the conducting polymer improves the conductivity of the pristine material.

Characterization by cyclic voltammetry

Figures 3 and 4 present the cyclic voltammograms at a slow scan rate (10 mV/s) of the composites compared with the activated carbon. The carbon material presents a quasi-rectangular shape, indicating that the main contribution to capacitance is the charge and discharge of the double layer. However, the composites present several overlapped peaks, indicating the contribution of redox processes. Comparing both figures, it is interesting to note that the cyclic voltammograms in Figure 3 (polymerization until 0.75V) present less pronounced peaks than in the case of Figure 4 (polymerization until 1V). That is, the response of the composites prepared at lower potentials has a more capacitive behaviour. Comparing different methods, it can be observed that the potentiodynamic polymerization is the one presenting a more rectangular performance and lower ionic resistance. However, the total area in the voltammograms is larger for potentiostatic methods; thus, the capacitance value is higher.

Regarding the voltammetric peaks, an anodic one between 0.2 and 0.3V, related to the oxidation of the leucoemeraldine state to emeraldine state of polyaniline, can be distinguished as well as a second peak between 0.5 and 0.6V, associated to the benzoquinone-hydroquinone redox couple (Santiago 1998). The latter process appears when the polyaniline is oxidized at potentials higher than 0.7V vs. SCE in acidic solutions (Aoki 2005) and it is known to be produced by the degradation products of polyaniline. This process shortens the polymer chains, leaving a more resistive skeleton (Aoki 2005). When degradation takes place, the polyaniline produced has poorer quality, since its conductivity decreases. However, when we prepare the carbon/polyaniline composites as charge storage devices, it is important to look for a compromise between capacitance and resistance. The polyaniline degradation produces shorter chains (lower conductivity) but, at the same time, generates benzoquinone groups in the material, which are positive to enhance capacitance by provision of extra faradic current (Bleda-Martinez 2005; Bleda-Martinez 2006). Then depending on the application and the features demanded for it, different electrochemical methods should be used.
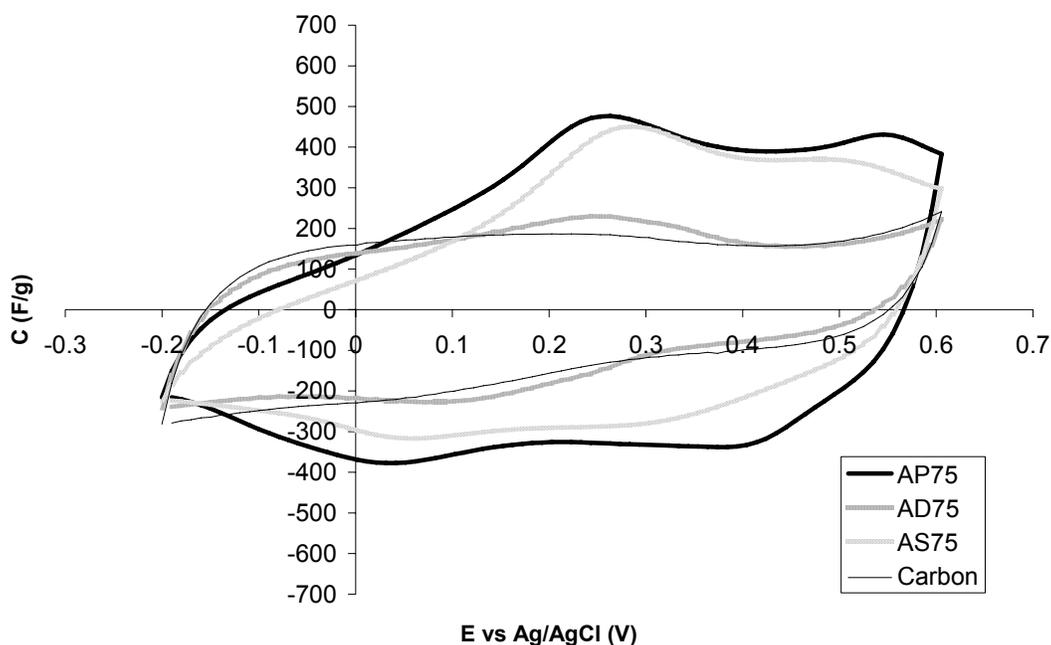
Figure 3. Steady state voltammograms at 10 mV/s. 1M HCl + 0.5M KCl solution Polymerization methods at 0.75V.
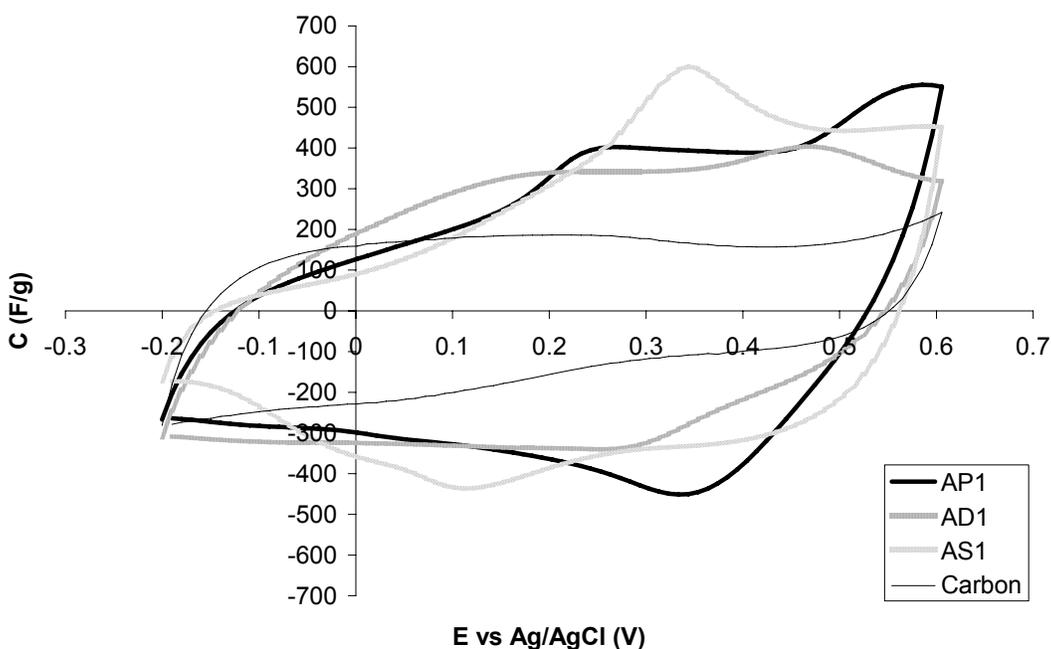

Figure 4. Steady state voltammograms at 10 mV/s. 1M HCl + 0.5M KCl solution Polymerization methods at 1V.

Characterization by electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy provides information about the capacitive and resistive behaviour of the samples studied depending on the frequency, that is to say, the rate of the process. This technique has been used in this study from 10kHz to 4mHz at 0.3V. As an example of the results obtained, the corresponding Nyquist plot for the composite prepared potentiostatically at 0.75V is shown in Figure 5. The rest of the samples present a similar behaviour. In the graphic, the corresponding plot for the pristine carbon before the polymerization and a pure polyaniline film prepared at the same conditions has also been included for comparison purposes.
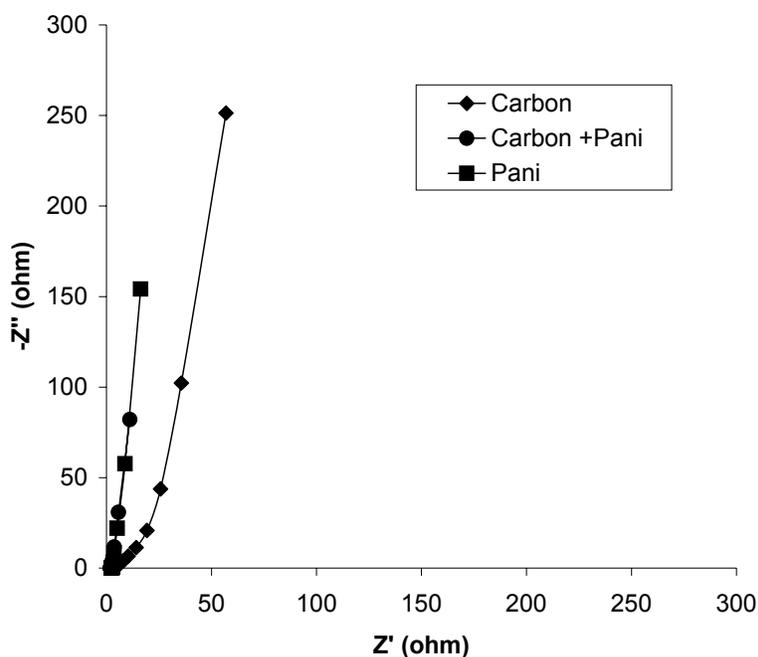
Figure 5. Nyquist plot for the composites prepared by potentiostatic step at 0.75V, Q=2C. The pristine carbon and a pure polyaniline film are also included. 1M HCl + 0.5M KCl solution

The resistive behaviour of the samples can be assessed taking into account the real part of the impedance. That is, the closer to the Y axis the plot is located, the lower the resistance. In this sense, it can be concluded that the pure polyaniline presents better conductivity than the pristine carbon material and that the composite improves this feature, presenting a lower resistance than the carbon material and very close to the behaviour of pure polyaniline.

Regarding the capacitive performance, the capacitance value is usually calculated from the last value (lower frequency) of $Z"$, taking into account that $Z" = \dfrac{1}{2\pi f C}$. In potentiostatic experiments, it is reasonable to assume that the same amount of polyaniline is formed over the carbon material compared to the amount formed directly over the bare graphite electrode if the final charge is the same. So, we can compare directly the values obtained from the Nyquist plots without using the weight of the samples. Table 4 shows the capacitance values for the pristine activated carbon, pure polyaniline films and composites obtained by the potentiostatic method at both potentials. Additionally, the theoretical capacitance of the composite by simple addition of the capacitance of the pure carbon and the polyaniline has been included.

Table 4. Capacitance obtained by electrochemical impedance spectroscopy

Polymerization potential (V)	Carbon capacitance (F)	Polyaniline capacitance (F)	Composite capacitance (F)	Theoretical capacitance (F)	% Improvement
0.75	0.17	0.28	0.52	0.45	16%
1	0.25	0.31	0.60	0.56	7%

It can be observed that the capacitance of the composite is higher than the sum of the capacitance of the independent components. As we mentioned before, in the analysis of the chronopotentiometric data, a synergic or cooperative effect between carbon and polyaniline is observed.

Characterization by infrared spectroscopy

We have obtained the infrared spectra for all the composites prepared and the polyaniline films grown by the same methods but on the bare graphite. As we cited in the experimental section, the spectra were acquired in ATR mode.

Polyaniline shows five characteristic absorption bands at 1592, 1497, 1302, 1165 and 828 cm^{-1} (see as an example the FTIR spectra for sample D1, that is, polyaniline potentiodynamically grown until 1V on graphite). The band at 1497 cm^{-1} corresponds to the stretching of C=C in benzenoid units related to the reduced state of the polymer, while the band at 1592 cm^{-1} corresponds to the C=N stretching of the quinonimine units produced when PANI is oxidized (Socrates 2001). The band at 1302 cm^{-1} can be associated to the C-H stretching vibration, the bands at 1165 cm^{-1} and 828 cm^{-1} to the C-H aromatic

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bending in-plane and out-plane respectively (Singh 1997; Socrates 2001; Yang 2007). The band at 1165 cm^{-1} is used as an indicator of the degree of electron delocalization on polyaniline chain (Chiang 1986). Additionally, an increase in the intensity of the band at 828 cm^{-1} suggests an increase in the 1,4-para-disubstitution character, that is to say, the linear structure predominates over the branched one (Yang 2007). Table 5 includes the intensities of the 1592, 1165 and 828 cm^{-1} bands related to the 1497 cm^{-1} band (benzenoid ring), for polyaniline films grown on the graphite by the different methods used in this study. That is, these samples were prepared with the same polymerization methods but without using the activated carbon.

Table 5. Relative intensities of the different band related to the benzenoid band in the infrared spectra of PANI films.

Polyaniline film	Relative intensity to band at 1497 cm^{-1}		
	band at 1592 cm^{-1}	band at 1165 cm^{-1}	band at 828 cm^{-1}
P1	0.72	0.51	0.41
D1	0.81	0.44	0.40
S1	0.74	0.60	0.39
P75	0.85	0.86	0.50
S75	1.04	0.87	0.78

It can be observed that the faster the polymerization process is (higher potentials), the smaller the intensities of the bands at 1165 cm^{-1} and 828 cm^{-1}. As expected, when the polymerization rate is large, the polyaniline obtained is of worse quality: the electron delocalization is lower and the branching of the polyaniline is larger. Both facts produce less conducting polyaniline.
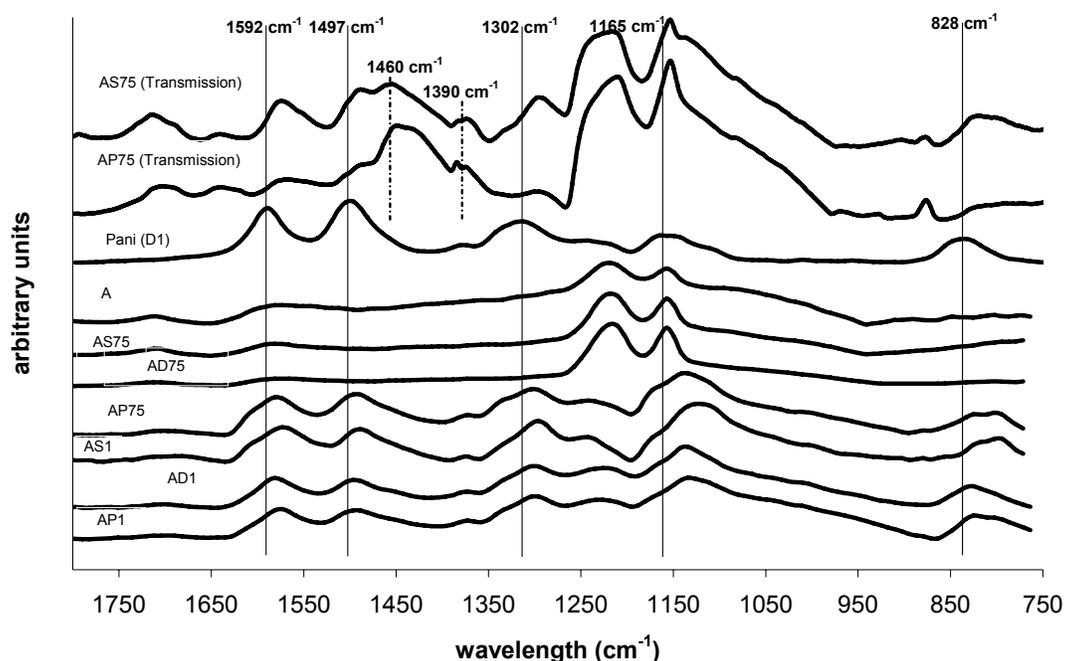

Figure 6. FTIR spectra for all composites, one polyaniline film (D1, potentiodynamically polymerized till 1V) and the pristine carbon (A), in ATR mode. Additionally, samples AD75 and AS75 are shown in transmission mode.

Figure 6 shows the FTIR spectra for the composites, the pristine carbon material and one of the pure polyaniline films for comparison purposes. It is difficult to observe differences between the composites since the presence of the carbon material affects the spectrum. However, a slight shift towards lower wavenumbers, with respect to the bands in pure polyaniline, can be found. It is also important to note that samples AD75 and AS75 present a completely different spectrum from the rest of composites. The spectra for these samples (AD75 and AS75) are similar to the pristine carbon one, with the bands at 1160 and 1230 cm^{-1} corresponding to PTFE (binder). However, we have evidence of the presence of polymer in these composites (electrochemical analysis). Thus, the infrared spectra were also obtained for them in transmission mode (diluting the sample with KBr) (see Figure 12). Now, the bands corresponding to polyaniline can be observed, although again shifted towards lower wavenumbers with respect to the bands in the pure polymer film. Moreover, additional bands can be observed in these spectra at 1460 cm^{-1} and 1390 cm^{-1}, associated to the formation of imines and C-N bonds with intermediate order, which are

characteristic of the conducting form of polyaniline and related materials (Cotarelo 2006). Thus, it can be concluded that, in these composites (prepared with the slowest polymerization methods), the polymer is located in the inner parts of the porous structure, what is an interesting difference compared to the other composites and that is a consequence of the slower polymerization rate.

Conclusions

Carbon/polyaniline composites have been prepared by different electrochemical methods in order to study their performance as electrochemical capacitors. It has been shown that the combination of these two materials for this application is very effective, since they present synergic contributions. The capacitance of the composites is larger than the theoretical one deduced from the contribution of the independent components. Moreover, the resistance of the composite is lower than the resistance of the pristine carbon material, indicating the beneficial effect of the polymer in improving the conductivity. Additionally, the polymerization of aniline is faster over the carbon material since it presents a high surface area.

Potentiostatic methods provide composites with larger capacitance values and better performances in the high power regime. Potentiodynamically methods provide composites with better quality polyaniline and higher conductivities. The multiple potentiostatic steps method presents an intermediate behaviour. According to the requirements of concrete applications, the preparation method of the composite should be chosen.

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