Polyaniline and polyaniline-carbon black nanostructures as electrochemical capacitor electrode materials

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1. Introduction

Energy consumption/production that relies on the combustion of fossil fuels is having a severe worldwide impact on economics and ecology. The electrochemical energy production is under consideration as an alternative energy/power source, as long as this energy consumption is designed to be more sustainable and environmentally friendly. Operative systems for electrochemical energy storage and conversion include batteries, fuel cells, and electrochemical capacitors or supercapacitors [1]. The electrochemical capacitors differ from the conventional dielectric capacitors in their special energy storage mode. These systems store electrical energy through double-layer charging steps, faradaic processes or a combination of both ways. The main interest of these devices is their capability to deliver high specific peak power, associated with a good specific energy [2,3]. The process is completely reversible and the charge-discharge cycles can be repeated over and over again, virtually without limit. The electrochemical capacitors are robust devices that can improve the effectiveness of battery-based systems by decreasing the number of required batteries and by reducing the frequency of their replacement. The carbon family offers a...
number of components to be applied as electrode super-
capacitors materials; they are, among others, activated carbon,
carbon black (CB), carbon nanotubes (CNT) and graphene [4–6].
In particular, CB is considered as a promising material due to its
particular ordered nanostructure, low density, large surface
area, high thermal stability, good electrical conductivity, lower
cost, corrosion resistance, less material requirement for
percolation, and ease of processing into host polymers [7–9].

A route to enhance the capacitance of a material is syn-
thetizing composites through the proper combination of
substances, among others ruthenium oxide and conductive
copolymers [6,10,11].

Polyaniline (PANI) is one of the most extensively studied
conducting polymers, because it can be obtained through not
expensive ways, it is stable at room temperature and is an
ionic-electronic conductor in a wide potential range [12–14].
There are different chemical and electrochemical methods of
synthesis producing easily a large amount of substance or
obtaining high purity polymer samples, respectively. The
polymeric nanostructures present unique characteristics
derived from their nanoscale size; among others, high elec-
trical conductivity, large specific surface, a mixed ionic-
electronic conductivity mechanism and a high discharge ca-
pacity to mass ratio. Methods of hard and soft templates are
used to obtain conducting polymer nanostructures, being the
microemulsions technique the most promising route [15].

Conducting polymers and carbon materials can be com-
bined properly forming composite materials with properties
that can be used adequately in practical systems [16–19].

This paper reports the synthesis by in-situ oxidative poly-
merization of polyaniline nanotubes and polyaniline - carbon
black nanocomposites, and their behavior related to super-
capacitors properties are scrutinized. The initial synthesis
mixture consists in an acid solution of aniline with a surfactant
agent, without additions and with the incorporation of carbon
black particles (Vulcan XC-72R), both as-received and pre-
treated ones. The structure and morphology of the obtained
nanostructures were analyzed by SEM, TEM, EDS, RDX, FTIR
and UV–Vis. The electrochemical capacitance performances
of the developed and characterized nanostructures were
investigated in acid solution showing an outstanding behavior.

2. Experimental

2.1. Synthesis of nanostructures of PANI and PANI-CB

The synthesis solution was prepared mixing 0.045 g of aniline,
0.30 mL of 0.25 M HCl and 0.005 g of sodium dodecyl sulfate
(SDS) in 18 mL of distilled water under constant magnetic
stirring, at room temperature (25 °C) for 20 min. Then, 2 mL of
0.24 M ammonium persulfate (APS) were added to the initial
mixture and the resulting dispersion was stirred vigorously
for half a minute. Afterwards, it was left for 24 h at 25 °C
without agitation to progress with the polymerization. A resi-
due is obtained after filtering and washing repeatedly the
obtained precipitate. Finally, it was dried for 24 h at 60 °C.

PANI-CB nanostructures were synthetized applying the
procedure just described, but with the addition of 0.1 mg mL⁻¹
of CB particles to the initial aqueous dispersion. Carbon black
(Vulcan XC-72R) was used either as received (CBnf) or pre-
treated (CBf) ones.

The applied pre-treatment consisted in adding CB particles
to 2.2 M nitric acid at room temperature. After stirring the
preparation with an ultrasonic bath, it was kept at room
temperature for 20 h, then filtered and washed to achieve
neutral pH in the filtrate solution. Finally, the residue con-
sisting in CBf particles was dried at 37 °C for 2 h [20].

2.2. Characterization methods

The synthetized nanostructures were characterized through
various physicochemical techniques. Energy diffraction
spectroscopy (EDS) and Scanning Electron Microscopy (SEM)
were performed with an EDAX Genesis XM4 – Sys 60 analyzer
coupled to scanning electron microscope Jeol JSM-6460LV; and
the Transmission Electron Microscopy (TEM) micrographs
with a JEOL model 100CX operated at 100 KV. The TEM images
were processed with Image J to determine the particle size.

FTIR spectra were recorded between 4000 and 400 cm⁻¹ using
a Nicolet, Magna 500 (250–4000 cm⁻¹) equipment with CsI optics.

UV–Vis spectra were obtained for the different samples in
aqueous solution, using a spectrophotometer UV-1800 PC
MAPADA in the 250–900 nm range.

The X-ray diffraction (XRD) patterns of samples were
recorded using an X-ray diffractometer (Philips PW 3710) and
Cu Kα line (λ = 1.5451 nm) with cooper anode.

2.3. Preparation of electrodes and electrochemical
measurements

The working electrodes were assembled through the following
routine. Firstly, PANI or PANI-CB nanostructures were
dispersed in pure isopropanol and a suitable amount of Nafion
solution was added in order not to exceed 5%. The dispersion
was stirred using an ultrasonic bath for 5 min. Finally, the
suspension was settled on a mirror-polished glassy-carbon
electrode using a micropipette, being the amount of PANI or
PANI-CB nanostructures of 0.2 mg cm⁻².

Typical electrochemical techniques such as cyclic volt-
ammetry and galvanostatic charge/discharge measurements
were used to study the capacitive behavior of the synthetized
materials. Runs were carried out in the 0.0–1.0 V (vs. RHE)
oltage range in 0.5 M H₂SO₄. I/V profiles were registered
varying the scan rates from 10 to 100 mV s⁻¹. The charge/
discharge curves were recorded at various current density
values in the 2–100 A g⁻¹ range.

All electrochemical experiments were performed in a
three-electrode cell thermostated at 25 °C, using a large Pt
sheet and a Ag/AgCl (sat.) electrode as counter and reference
electrodes, respectively. The connected potentiostat/galva-
nostat was EG&G PAR Model 362.

3. Results and discussion

3.1. SEM and TEM characterization

Fig. 1 shows SEM and TEM micrographs of different PANI and
PANI-CB nanostructures. PANI nanotubes of ca. 15 μm length
and an outer diameter of 95 nm (Fig. 1a and b) are obtained when synthesizing aniline solution without additions. The incorporation of CB particles to the initial solution promotes the formation of different morphologies, depending on the added CB.

The addition of CBf particles promotes the development of nanostructures with different shapes such as nanobelts and nanotubes (Fig. 1c and d). PANI-CBf nanobelts have a thickness of ca. 100 nm, a wide of 2 µm and 12–15 µm in length. PANI-CBf nanotubes have a mean outside diameter of ca. 95 nm and 15 µm in length. On the other hand, when adding CBnf particles, the development of various nanostructures is evident: nanotubes (diameter: 95 nm, length: 5–8 microns), nanoparticles (diameter: 85–90 nm) nanobelts (length: 10–12 microns, width: 1 micron and thickness: 100 nm) and nanosheets (length: 0.5 microns, width: 0.3 microns and thickness: 95–100 nm) (Fig. 1e and f).

According to other researchers [21, 22], the type of nanostructures is determined by variables such as the concentration ratio between aniline and APS ([aniline]/[APS]), the acid and dispersant concentrations in the reaction mixture, and the temperature. Common synthesis process starts at a pH of ~ 7.5 and in 24 h the pH drops to ~ 1.0 and different nanostructures are formed as a function of pH, from nanoflakes to fibrillar nanostructures [22].

When adding CBf, the structure of the developed PANI composites adopts nanobelt and nanotubes morphologies. To sustain this fact, it must be taken into account that in the PANI synthesis mechanism, anilinium cations are formed in the first step of the polymerization process [15]. The oxidizing chemical pretreatment done to the CB particles provokes the formation of carboxyl, hydroxyl and carbonyl surface groups [23]. Thus, when adding CBf to the polymerization mixture, the negatively charged functional groups of the CBf interact with the anilinium cations, favoring the adsorption of the CBf and promoting the growth of polymer chains from them. The same type of interaction was reported when using oxidized carbon black and graphene oxide for the synthesis of various polyaniline nanocomposites [18–24].

In the case of adding CBnf, the synthesized product is not morphologically homogeneous. It has been pointed out that the formation of self-assembled PANI nanotubes depends on...
molecular interactions such as hydrogen bondings, van der Waals forces and π-π stacking [22]. A two-step mechanism has been proposed for the formation of nanofibers or nanotubes. The first step comprises the formation of nanosheets in the first stage of the oxidative polymerization process, at higher pH. These nanosheets tend to decrease their surface energy by two ways. Through stacking, relatively thick (~30–100 nm) nanoflakes are built and by rolling or curling, oligomeric nanotubes are developed. The second step occurs at lower pH when polyaniline polymerizes either on the oligomeric nanotube walls making their walls thicker or as grains on the walls of the smooth nanotubes, giving the final form of the nanotubes or nanorods [22].

3.2. Energy dispersive spectroscopy X-ray (EDS)

Fig. 2 shows the EDS spectra of synthetized nanomaterials, stating the presence of C, N and O. It was found a significant amount of S, indicating a doped PANI structure as a result of using APS and SDS during the synthesis [25]. The S percentage is higher in PANI-CBf and PANI-CBnf nanocomposites.

3.3. X-ray diffraction

Fig. 3 shows the X-ray diffraction patterns of the PANI and PANI-CB nanocomposites. The main diffraction peaks are at 2θ values of 12.2°, 15.2°, 18.4°, 22.4°, 24.6°, 28.3° and 29.2°. These peaks are characteristic of polyaniline in its doped emeraldine salt form. The peaks are superimposed on a broad background, which suggests the presence of an amorphous phase. The peaks at 18.4° and 24.6° are usually assigned to the periodicity parallel and perpendicular to the polymer chain,
respectively. The peaks at 22.4° and 28.3° (corresponding to spacing of 3.1 and 3.8Å) could be due to a periodicity caused by π–π stacking of rigid phenazine-like structures [22,26].

3.4. FTIR spectra

In Fig. 4, FTIR spectra are presented showing several bands that appear in all the PANI nanostructures spectra [21,25]. The position of the common bands and the corresponding assignment are stated as follows: 1142 cm⁻¹ (assigned as −N=quinoid=−N−), 1305 cm⁻¹ (CN stretching with aromatic conjugation), 1498 and 1585 cm⁻¹ (C=C stretching in benzoza rings and quinoid rings respectively), 2847 and 2916 cm⁻¹ (CH stretching of −CH₃ and −CH₂−), respectively, which shows the presence of SDS in the synthesized products. As reported by Zhou [21], the anionic surfactant added in the polymerization solution contributes doping the PANI chain establishing electrostatic interactions with the anilinium cation at the beginning of the reaction and then, building a supramolecular structure [25].

In the nanostructures spectra, a distinguishable band is present at 1042 cm⁻¹; it is attributed to the substitution of S=O groups in the 1,2,4-aromatic rings, indicating a doped PANI structure as a result of using APS during the synthesis. These results agree with the EDS results, where the presence of S was determined. Another band located at 3250 cm⁻¹ is assigned to NH-stretching associated to different of intra- and inter-molecular hydrogen bonds in secondary amines. In the presence of a sulfonate group, a hydrogen bond such as the NH…O type can be proposed. The presence of hydrogen bonds is indicative of a self-organization process of PANI chains in supramolecular assemblies and can be associated to the stabilization of the nanotubes [21,25]. These results are consistent with those found in the analysis by UV–Vis spectroscopy, confirming the presence of groups that tend to form hydrogen bonds.

Furthermore, other bands must be indicated as contributions to the final formation of the nanostructures, including the ones located at 825 cm⁻¹ (CH deformation out of plane in benzoides rings), at 692 cm⁻¹ (CC out of plane deformation of rings monosubstituted aromatic), at 1242 cm⁻¹ (CN–strectching of secondary aromatic amines) and at 1446 cm⁻¹ (presence of branched structures such as phenazine) [22,24].

3.5. UV–Vis spectra

UV–Vis spectra of PANI nanotubes and PANI-CB nanostructures are shown in Fig. 5. PANI and PANI-CB nanostructures present two adsorption zones. One of these bands is located in the 300–450 nm region (possibly overlapping), related to PANI chain protonation. The other band between 600 and 850 nm is attributed to the π–π* polaron transition [26,27,21].

The nanostructures spectra has three peaks at 300, 360 and 440 nm, which is due to the superposition of bands corresponding to the π–π* transition of para-substituted benzoides segments and a weak adsorption n–π*. This is consistent with the presence of substituted quinone (strong π–π* peak centered at 250–314 nm, a medium π–π* peak centered at 308–398 nm, and in some cases, a weak n–π* band centered at 424–525 nm) and oligomer-type structures superimposed leucoemeraldine [22]. Substituted quinones are present in hydrolytic reactions at high pH in the presence of a strong oxidizing agent and it is attributed to polyaniline chain protonation.

Moreover, the emeraldine base form of polyaniline usually absorbs strongly in two areas, with maxima at 320–330 and 600–660 nm. The first band is assigned to π–π* transition of the para-substituted benzenoid segment (−B–NH–B−NH), whereas the other is associated with the excitation of the quinoid segment (−N=Q=N−) [27].

3.6. Cyclic voltametric studies

Voltamperometric runs of the prepared nanostructures are carried out between 0.0 V and 1.0 V at various scan rates in order to evaluate their electrochemical characteristics. The typical voltammograms of the nanocomposites are shown in Fig. 6. The anodic and cathodic current peaks assigned to PANI leucoemeraldine/emeraldine pair at ca. 0.4 V are clearly distinguished [13]. At all scan rates, pronounced reversible redox waves are observed in the profiles of PANI-CBf and PANI-CBnf nanocomposite electrodes, indicating their better
capacitive behavior in comparison to PANI electrode. This fact may be due to the combined contributions from both PANI and CB structures. However, it can be observed a resistive behavior due mainly to internal resistance.

3.7. Galvanostatic charge/discharge experiments

Galvanostatic charge/discharge measurements at different current densities are performed in order to understand the behavior of PANI, PANI-CBf and PANI-CBnf nanostructures for supercapacitor applications. Typical potential versus time profiles for a constant current density of 2 A g\(^{-1}\) are shown in Fig. 7. Other supercapacitor materials such as activated carbon, metal oxides, carbon nanotubes and carbon blacks exhibit the observed behavior that corresponds to the ideally triangular shaped charging/discharging pattern\([10,28,29]\). In the present case, the curves are not straight lines indicating the occurrence of a faradaic reaction among the electrode materials. In addition, an initial potential drop caused by internal resistance can be observed\([27]\).

The electrical parameters of the capacitor, namely, specific capacitance (\(C_m\)), specific energy (\(E_s\)) and specific power (\(P_s\)) are calculated using Eqs. (1)–(3).

\[
C_m = \frac{C}{m} = \frac{I\Delta t}{\Delta V m} \quad (1) \\
E_s = \frac{I\Delta V\Delta t}{m} \quad (2) \\
P_s = \frac{I\Delta V}{m} \quad (3)
\]

where \(C_m\) is the specific capacitance, \(I\) is the charge/discharge current, \(\Delta t\) is the discharge time, \(\Delta V\) is the potential range and \(m\) is the mass of active material\([6,27,30]\).

The formation of PANI and PANI-CBs structures is attained using the self-organization chemical method where the total mass and volume are included in the charge storage. The values of specific capacitance, \(SC\), measured at different current densities are presented in Table 1. Notably high capacitance values of ca. 1490 F g\(^{-1}\), 370 F g\(^{-1}\) and 310 F g\(^{-1}\) were obtained for PANI-CBf, PANI-CBnf and PANI nanostructures, respectively. PANI-CBf nanocomposites have specific capacitance values very high even evaluated at 40 A g\(^{-1}\)\([27,31]\).

Several factors can be considered as responsible for the performance of the PANI-CBf nanocomposites, among others the presence of charge carriers in these arrays and the functionalization after the chemical treatment of the CB particles. It was reported that the charge carriers can either move along the chains within the polymer structure or jump from chain to chain by hopping\([32]\). Moreover, ab-initio calculations established that the quinoid structures have great affinity for charges that acquire high mobility due to the delocalized polaron\([33]\). On the other hand, the incorporated CB particles contribute to the SC values providing faradaic pseudocapacitance generated on the superficial oxygenated groups developed during the acid pretreatment. The porous structures have also an important contribution because they operate through both their internal and external interfaces facilitating the electrolyte access.

The stability of the electrodes was evaluated through charge–discharge cycling tests. The specific discharge capacitances of the different electrode materials as a function of the number of cycles are presented in Fig. 8, from runs conducted for 500 cycles at 2 A g\(^{-1}\). The capacitance of PANI-CBf composites is greater than the values corresponding to PANI

![Cyclic voltammograms of the nanostructured composite electrodes at 20 mV s\(^{-1}\) in 0.5 M H\(_2\)SO\(_4\).](image_url)

![Galvanostatic charge–discharge curves of the nanostructured composite electrodes for a current density of 2 A g\(^{-1}\) in 0.5 M H\(_2\)SO\(_4\).](image_url)

| Table 1 – Specific capacitances of the synthetized nanomaterials. |
|------------------------|----------------|----------------|
| Nanomaterial | PANI | PANI-CBf | PANI-CBnf |
| I (A g\(^{-1}\)) | C\(_m\) (F g\(^{-1}\)) | C\(_m\) (F g\(^{-1}\)) | C\(_m\) (F g\(^{-1}\)) |
| 2          | 314  | 1486    | 370          |
| 4          | 134  | 552     | 200          |
| 10         | 72   | 500     | 171          |
| 20         | 58   | 470     | 120          |
| 40         | 42   | 200     | 120          |
and PANI-CBnf nanostructures. The loss of capacitance during the charge/discharge cycles is lower than 18% for the three checked materials, being the highest value the corresponding to the PANI nanostructure without additions. These results reveal that the stability of the material can be improved remarkably when introducing CB in the PANI nanostructures.

In Fig. 9, the relationship between the specific power density and specific energy density in the so-called Ragone plot [34] for PANI, PANI-CBF and PANI-CBnf nanostructures is shown. PANI-CBF composites show higher specific power and specific energy values than PANI and PANI-CBnf nanostructures. For PANI-CBF composites, a specific power of 40 kW kg\(^{-1}\) and a specific energy of 412 W h kg\(^{-1}\) are obtained. It is to point out that for the same specific power value, the specific energy of PANI-CBF composite electrodes is five times larger than the value corresponding to PANI electrodes. Other authors reported SC values of ca. 500 F g\(^{-1}\) [16,31].

For the prepared nanocomposites, the synthesized morphology and the developed porous structure add synergistically to their behavior as possible supercapacitors materials, as both the charge transport and the occurrence of faradaic processes are lightened and a facile access to the electrolyte is provided by the novel structure.

4. Conclusions

Polyaniline nanotubes and PANI-CB nanocomposites were synthesized using a simple method of self-organization. Taking into account their likely application as supercapacitor electrode materials, the electrochemical properties were scrutinized. Firstly, different types of nanostructures were developed during the polymerization process. Nanotubes of polyaniline with an outer diameter of ca. 95 nm and ca.12 \(\mu\)m length were obtained from acid solutions of aniline. When incorporating unfunctionalized or functionalized CB particles, nanobelts and nanotubes were obtained in the former case and nanoparticles, nanobelts, nanotubes and nanosheets when adding CBf.

The formation of the different nanostructures is ascribed to the own chemical polymerization process that provoked a doped PANI state and generated hydrogen links which stabilized the new structures. The electrochemical characterization of the synthesized nanostructures has been carried out applying voltamperometric and charge/discharge runs.

The developed morphologies influenced the capacitance, specific power and energy values. PANI-CBF nanocomposites displayed improved capacitive properties in H\(_2\)SO\(_4\) solutions, namely 1486 F g\(^{-1}\) at 2 A g\(^{-1}\). The charge–discharge tests indicated that the loss of capacitance during the charge/discharge cycles was lower than 18% for the synthesized materials and that the introduction of CB particles in the PANI nanostructure improved remarkably their electrochemical behavior.

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