THE ELECTROCHEMICAL BEHAVIOUR OF SOME COMPOSITE COATINGS WITH DIFFERENT ADDITIVES OBTAINED BY ELECTRODEPOSITION ON METALLIC SUBSTRATE

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Nanocomposite films of polyaniline and functionalized carbon nanotubes (FCNTs) with different additives have been electrochemical deposition from synthesis solutions such that constituents were deposited simultaneously onto metallic substrate. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) techniques established that these composite films had electrochemical like respond rates to pure polymeric films however a reduced resistance and much improved mechanical integrity. The morphology of composite films has been investigated by scanning electron microscopy (SEM). The negatively charged functionalized carbon nanotubes (CNTsF) and additives utilized as anionic dopant through the electropolymerization to obtain polymer/CNTsF composite films. The electrochemical and physical properties like specific electrochemical capacitance of the composite films is a meaningful bigger value than that for pure polymer films obtained likewise. The additives substances used were : cetyl benzyl dimethyl ammonium chloride (CBDACl) and KClO3. Using these composite films, the modified electrodes with enhanced characteristics were achieved.

INTRODUCTION

Many researches have investigated to combine carbon nanotubes and conducting polymers for application as modified electrodes in various practices through conductive and high-strength composites, energy storage and energy conversion devices, batteries, capacitors, corrosion protection coatings, sensor applications, field emission displays and radiation sources, hydrogen storage media etc.1-5 Conducting polymers can be doped and de-doped rapidly to high charge density and as a result are potential active materials for use in various electrochemical applications. Conducting polymers are also intriguing molecular structures because their ability to dramatically change properties when stimulated by an electric signal. These materials offer exciting prospects for a wide range of new devices as membranes, artificial muscles, solar cells, batteries, capacitors, corrosion protection coatings or sensor applications.4-9 Thus an important application is the fabrication of modified electrodes. For this consideration, the nanocomposite materials based on the functionalized carbon nanotubes, conducting polymers and different anionic dopants were grown electrochemically onto a platinum substrate from a synthesis solution.

Carbon nanotubes (CNTs), as one of the most important carbon materials, have attracted a great interest over the recent years, as an effect of their

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special properties and wide domain of applications. Their very high mechanical resilience, nanometer size, high accessibility surface area, high electrical conductivity, chemical and mechanical characteristics are especially significant for various practice such as in nanoelectronics, biosensors, supercapacitors and so on. All the obtained composites showed improved mechanical integrity, higher electronic and ionic conductivity and exhibited larger electrode specific capacitance than the polymer alone. The negatively charged FCNTs served as anionic dopant during the electropolymerization to synthesize CP/FCNTs composite films. The intensive interaction between the most delocalized $\pi$ electron of CNTs and the $\pi$ electron corresponded with the structure of the polymers framework increases the electron / orifice assignment between CNTs and conducting polymers.

This research is a continuation of previous work on the synthesis and electrochemical characterized of the composite films doped with some functionalized single-walled carbon nanotubes and some additives that have been deposited on the platinum substrate by electrochemical method.

In this paper we presented an electrochemical synthesis of nanocomposite films from conducting polymers aniline, functionalized carbon nanotubes (SWCNTsF with carboxylic acid) and different additives; cetyl benzyl dimethyl ammonium chloride (CBDACl) and KClO$_3$. The electrochemical characterization of these nanocomposites has been done by cyclic voltammetry, electrochemical impedance spectroscopy and scanning electron microscopy. The synthetic, morphological and electrochemical properties of nanocomposite materials type CP/FCNTs/dopants were compared.

**EXPERIMENTAL**

The electrochemical polymerization and characterization were realized by using a single-compartment cell with the conventional three electrodes set up at room temperature. The electrochemical cell was connected to a VoltaLab potentiostat coupled to a PC running VoltaMaster software. A saturated calomel electrode (SCE) was used as the reference electrode and a platinum plate as an auxiliary electrode. The working electrode was a platinum disk with a surface area of 0.5 cm$^2$. All chemicals were reagent grade and used as received without further purification. In this paper were used aniline (99.5% Fluka), H$_2$SO$_4$ (96% Merck), cetyl benzyl dimethyl ammonium chloride (CBDACl) and KClO$_3$ (96% Fluka) and single-walled carbon nanotubes functionalized with carboxylic acid (FSWCNTs) were the commercial product from Sigma-Aldrich with the following characteristics: 80-90% carbon basis, $D \times L$ 2-10 nm $\times$ 0.5-2 µm, bundle dimensions. All the solutions were prepared with double distilled water.

**Preparation of modified electrode**

Prior each electrochemical experiment the surface of the platinum electrode has been polished with 0.3, 0.01 and 0.05 µm alumina powders and rinsed in double distilled water and ethanol. The prepared electrodes were dried and used for modification. Experimental methods were described previously. Nanocomposite films of CPs/FSWCNTs have been obtained by electrochemical polymerization from a synthesis solution containing the functionalized carbon nanotubes (FSWCNTs) and the corresponding monomer (aniline). FSWCNTs were used in this paper namely: single wall carbon nanotubes (SWCNTs) functionalized with carbolic acid. The negatively charged SWCNTs-COOH in solution acted as sole supporting electrolyte and additives for the PANI depositions. For this fact CNTsF are enveloped in polymers during the electropolymerization process in the form of counter ions or dopants.

Thus, PANI/FSWCNTF/additives composite films were obtained from an synthesis solution containing 0.2 mol/L aniline + 0.25 mol/L H$_2$SO$_4$ + 0.5 mg/SCNTsF and 0.2 M various additives (cetyl benzyl dimethyl ammonium chloride (CBDACl) and KClO$_3$) by cyclic voltammetry in the potential scanning range of -250 to +900 mV at a sweep rate of 10 mV/s and for a cycles number of 10. The pure PANI films were prepared from an aqueous solution of 0.2 mol/L aniline + 0.25 mol/L H$_2$SO$_4$, without adding CNTsF and additives.

**Characterization of the modified electrodes**

Cyclic voltammetry and electrochemical impedance spectroscopy have been utilized to investigate the physical and electrochemical properties of the composite films.

The electrochemical characterization of the PANI-CNTsF-additives composite films has been performed in 0.25 mol/L H$_2$SO$_4$ aqueous solution by cyclic voltammetry in the potential scanning domain of -250 to +900 mV at a sweep rate of 50mV/s and for a cycles number of 50. The electrochemical impedance spectroscopy experiments were realized using a VoltaLab 40 potentiostat/galvanostat with EIS dynamic in the frequency range of 100 kHz + 1 mHz with an AC wave of 5 mV (peak-to-peak) overlaid on a DC bias potential and the impedance data were obtained at a rate of 10 points per decade change in frequency. All tests have been performed at 25°C under atmospheric oxygen without agitation.

**RESULTS AND DISCUSSION**

In the first stage, the PANI/Pt coating has been also electrodeposited onto electrode surface (platinum) by electrochemical polymerization from a synthesis solutions containing 0.2 mol/L aniline and 0.25 M H$_2$SO$_4$ as supporting electrolyte (see figure 1 Inset). The obtained the PANI/Pt /Pt film was presented in previous work. It can be said that polyaniline can exist in three different oxidation states such as leucoemeraldine (fully reduced form $y = 1$), emeraldine (partially oxidized form $y = 0.5$) and pernigraniline (fully oxidized form $y = 0$) as shown in the following scheme:
Fig. 1 – Polymerization cyclovoltammograms of aniline + SWCNTs-COOH in 0.25 M H₂SO₄ aqueous solution. Inset electropolymerization PANI/Pt at 25°C.

Fig. 2 – Polymerization cyclovoltammograms of a) PANI/KClO₃/Pt; b) PANI/KClO₃/SWCNTs-COOH/Pt; c) PANI/cetyl benzyl dimethyl ammonium chloride/Pt; d) PANI/cetyl benzyl dimethyl ammonium chloride/SWCNTs-COOH/Pt in 0.25 M H₂SO₄ aqueous at 25°C.
The three polyaniline oxidation forms are indicated to the three anodic oxidation peaks while the three polyaniline (PANI) reduction states are shown by the three reduction peaks from the cathodic branch of cyclovoltammograms (figure 1-inset). These states of polyaniline are influenced on the applied potential.

Composite films of polyaniline-and functionalized, single-walled carbon nanotubes with polycarboxilic acid (PANI/SWCNTs-COOH) were fabricated by a simple oxidative electropolymerization method. These composite films were electrodeposited on a platinum working electrode using a classical system with three electrodes. The obtained cyclovoltammograms for PANI/SWCNTs-COOH /Pt are given in Figure 1 and have the same shapes with those obtained for PANI/Pt modified electrode cycled in the same conditions, but in this case the anodic peaks are much higher and in the main the anodic and cathodic currents are much greater than those for PANI film. From figure 1 and table 1 it can be observed that the current is increasing upon continuous cycling, being indicative for a conductive film formation. This situation can be assigned considering that, FSWCNTs (in our case SWCNTs-COOH) are negatively charged and they can function as doped anions and consequently, the conductivity of PANI/FSWCNTs composite film increases.

The PANI/SWCNTs-COOH/dopant films were achieved on the platinum substrate in a synthesis solution of 0.2 mol/PANI + 0.5 mg/L SWCNTs-COOH + 0.2 mol/L dopant substance in 0.25 M H2SO4 by cyclic voltammetry in the scanning potential range of -250 to +900 mV at a scan rate of 10 mV/s and for 10 cycles. The additives substances used were: cetyl benzyl dimethyl ammonium chloride (CDMACl) and KClO3. In the presence of additives CDMACl and KClO3 with and without SWCNTs-COOH, see figure 2a-d, it is observed that the current response of doped PANI films increases with addition of the additive with SWCNTs-COOH, especially when the cetyl benzyl dimethyl ammonium chloride is added. In this situation from figure 2, the ciclovoltammograms show greater and larger oxidation and reduction peaks and in general the anodic and cathodic currents are much higher than the case from figure 1 inset. Moreover, the current increases with continuous cycling in the potential domain as seen in figure 1-2. This case can be explained considering the fact that SWCNTs-COOH/dopant is negatively charged and they are able to function as anions and consequently, the conductivity of PANI/SWCNTs-COOH/additive composite film is higher.

Examining in comparison the cyclic voltammograms of PANI, PANI/SWCNTs-COOH and PANI/SWCNTs-COOH/additive composite film, (figures 1, 2 and tables 1-3), clearly were indicated differences. Also, the voltamogram curves have the same shape in all cases, but the current intensities are lower in situation of pure PANI than with respect to nanocomposite/dopant and they increase upon continuous cycling as it can be seen from voltammograms from figures 1-2 and tables 1-3. The PANI/SWCNTs-COOH composites presents higher currents (20.42 mA/cm2) than PANI films (12.48 mA/cm2), which interprets into greater capacitance. Hence, the PANI/SWCNTs-COOH presenting more a porous composition for ion mobility a greater and potential-separate electronic conductivity by the adsorbed SWCNTs film, can explicate the difference in current from PANI and PANI/FSWCNTs-COOH/dopant. Therefore, in fully reduced state the PANI chains get neutral and the negative charge of immobile CNTs and ions of dopant (cetyl benzyl dimethyl ammonium chloride and KClO3) are equalized of the cations with small dimension from the supporting electrolyte solution. The exhibited data show a quicker kinetics in the composite, that can be assigned to the higher electronic conductivity of the FSWCNTs network and dopant. Consequently the redox reactions that occur in nanocomposite film are more complex and more intensive than the ones in the pure PANI/ film.

The electrochemical behaviour of the PANI, PANI/SWCNTs-COOH, PANI/SWCNTs-COOH/dopant composite films deposited electrochemically from synthesis solution in the absence and presence of additives: cetyl benzyl dimethyl ammonium chloride and KClO3 has been characterized further using cyclic voltammetry. The electrochemical characteristics of achieved PANI/Pt film was studied in the cycling solutions of 0.25M H2SO4 (see figure 3 Inset) and it was presented in previous work.
Table 1
Electrochemical parameters from polymerization curves achieved at the formation of PANI/SWCNTs-COOH composite film

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Table 2
Electrochemical parameters from polymerization curves achieved at the formation of PANI/KClO3/SWCNTs-COOH composite film

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Table 3

Electrochemical parameters from polymerization curves achieved at the formation of PANI/ cetyl benzyl dimethyl ammonium chloride SWCNTs-COOH composite film

<table>
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<th>Cycles</th>
<th>Anodic peaks</th>
<th>Cathodic peaks</th>
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<td>ia1, mA/cm²</td>
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<tr>
<td>Cycle 1</td>
<td>Ea2, mV</td>
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<tr>
<td>Cycle10</td>
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</table>

| Cycle 1 | 136  | 0.157422 | 408  | 0.33086 | -7    | -0.83633 | 394  | -0.46445 |
| Cycle 2 | 138  | 1.16055  | 409  | 0.666798| -10   | -1.70586 | 393  | -0.92539 |
| Cycle 3 | 143  | 2.55039  | 426  | 1.22617 | -12   | -2.81993 | 390  | -1.57735 |
| Cycle 4 | 157  | 4.17969  | 430  | 2.01172 | -12   | -4.20274 | 390  | -2.46211 |
| Cycle 7 | 199  | 11.0547  | 462  | 5.95704 | -14   | -9.05469 | 371  | -6.23048 |
| Cycle 8 | 216  | 13.7461  | 474  | 7.65625 | -14   | -10.6602 | 363  | -7.66016 |
Figures 3-5 represent the cyclic voltammograms of PANI/SWCNTs-COOH, PANI/SWCNTs-COOH/additive (cetyl benzyl dimethyl ammonium chloride and KClO3) composite films accomplished in aqueous solution of 0.25M H2SO4 in wide potential domain to explore all eventual electrochemical properties of this composite film in electrolyte. The modified electrode type PANI/SWCNTs-COOH/dopant/Pt was achieved on the potential domain from -250 up to 900 mV with a sweep rate of 50mV/s and for a cycles number of 50, see figures 3-5. These films can be cycled repeatedly between the conducting (oxidized) and insulating (neutral) state without significant decomposition of the material, which is consistent with the results reported in the literature.9,10,16,17,23-26 The first redox peak is commonly ascribed to the electron transfer from/to the PANI film. In sequence to compensate the charge of the PANI film, anion doping/de-doping of the PANI film appears. The second redox peak assigned to a deprotonation and protonation process. In addition, the proton/cation shift the anion is also excluded from the PANI film through deprotonation. A small peak at around 400 mV is presumably as a result to a side reaction in the PANI film. At the negative and positive ends of the potential scan, the pure PANI film transformed into its non-conducting states. The same appeared to the PANI-CNTs-COOH/dopant composite film. The capacitance of PANI/CNTsF and PANI/CNTsFs/dopant is larger than that of the pure polymeric PANI films since the composition of CNTsF achieves the doping ions enters into/eject from PANI/CNTsF composite films more readily. Also, the PANI-CNTs-COOH and PANI-CNTs-COOH/dopant composite films showed larger currents than the pure PANI film, especially at the peak potentials (see in comparison tables 4-6). This is a demonstration of quicker kinetics in the composite, that can be ascribed to the higher electronic conductivity of the CNTs-COOH network and the dopants.
### Table 4

Electrochemical characteristics of PANI/SWCNTsF modified electrode established from cyclic voltammograms in 0.25 M H$_2$SO$_4$ aqueous solution (monomer free) at 25°C

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<th>Cycles</th>
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<th>Cathodic peaks</th>
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<tbody>
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<td>Ea1, mV</td>
<td>ia1, mA/cm$^2$</td>
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<tr>
<td>Cycle 1</td>
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<td>Cycle 2</td>
<td>275</td>
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### Table 5

Electrochemical characteristics of PANI/cetyl benzyl dimethyl ammonium chloride/SWCNTsF modified electrode established from cyclic voltammograms in 0.25 M H$_2$SO$_4$ aqueous solution (monomer free) at 25°C

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Table 6
Electrochemical characteristics of PANI/KClO3/SWCNTsF modified electrode established from cyclic voltammograms in 0.25 M H$_2$SO$_4$ aqueous solution (monomer free) at 25°C

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</table>
The electrochemical activity of PANI/SWCNTs-COOH/Pt, PANI/CDMACI/SWCNTs-COOH/Pt and PANI/KClO₃/SWCNTs-COOH/Pt modified electrode in cycling solution is much greater than PANI/Pt in the same cycling solution. In all the cases, in the same circumstances, the PANI/SWCNTs-COOH/Pt, PANI/CDMACI/SWCNTs-COOH/Pt and PANI/KClO₃/SWCNTs-COOH/Pt composite film showed anodic peaks much superior and much wider than PANI/Pt film and also, the currents, especially the peak currents much higher. Analyzing in comparison the electrochemical activity of this composite with dopant it can be observed as PANI/CDMACI/SWCNTs-COOH/Pt is much bigger like PANI/KClO₃/SWCNTs-COOH/Pt composite film in same condition. The electronic conductivity properties increases in the order: PANI/CDMACI/SWCNTs-COOH/Pt > PANI/SWCNTs-COOH/Pt > PANI/KClO₃/SWCNTs-COOH/Pt > PANI/Pt. Consequently, the redox processes that occur in nanocomposite film are more complex and more strong than the ones in the pure PANI film.

Also, the composite layers were analyzed by electrochemical impedance spectroscopy (EIS) at open circuit potential, in an aqueous solution of 0.25 M H₂SO₄ at 25°C. The obtaining Nyquist and Bode diagrams for PANI/Pt, PANI/CNTs-COOH/Pt and PANI/CNTs-COOH/additive/Pt modified electrodes are presented in figures 6-7. The impedance plot is formed of a semicircle at high and middle frequencies and a capacitive slope at low frequencies (see figures 6-7). The semicircle indicated at high frequencies is determined to the charge transfer resistance, which is created at the interface composition between the porous electrode surface and the electrolyte. At low frequencies, the impedance diagram gets an almost vertical line. The Nyquist plots for PANI/Pt, PANI/CNTs-COOH/Pt and PANI/CNTs-COOH/dopant/Pt composite films are presented by a vertical tendency at low frequencies, showing a capacitive behaviour conformable to the equivalent circuit theory. Bode diagrams reveal also the capacitive comportment in conformity with Nyquist plots (see in comparison Figures 6-7).
The capacitances \(C\) of the electrode materials were estimated, conformable to the equation:

\[ C = -\frac{1}{2\pi f Z_{im}}. \]

\(f\) = frequency; \(Z_{im}\) = imaginary impedance), from the slope of the linear correlation between the imaginary impedance and the reciprocal of the frequency at low frequencies.

We can see the 10 times higher capacitance value for PANI/CNTsF and PANI/CNTsF/dopant film in regarding with PANI pure polymeric films (see Table 7). Higher capacitance of the composite films derives clearly from the share of the embedded CNTsF/dopant that ensure interconnected ways for electrons by the CNTsF and ions in the pore network or the direct interaction between the delocalised electrons on polymer chains the CNTsF and the dopant. The real impedance at low frequencies, when the capacitive comportment controls, is an evidence of the involved resistance of the electrolyte and the film through both electronic and ionic shares. The values of the real impedance at 0.01 Hz are given also in Table 7. It can be observed that the PANI/CNTsF and dopants films have been meaningfully lower in resistance than PANI films. It has been presented that, in the main one the real impedance of a composite film (modified electrode) too decreases as the material’s porosity increases because to enhanced ionic accessibility. It can be said that PANI/CNTsF/dopant offered much greater overall conductivity in comparison with the PANI film. As presented that, in general, the real impedance of an electrode material also decreases as the material’s porosity increases because of enhanced ionic accessibility.19-25

![Fig. 6](image-url)
Fig. 7 – The Bode plots for modified electrodes (PANI/Pt, PANI/CNTs-COOH/Pt, PANI/KClO3/CNTs-COOH/Pt and PANI/CBDACl/CNTs-COOH/Pt) at open circuit potential in an aqueous solution of 0.25M H2SO4 and 25°C.
Table 7
Real impedance and capacitance values of pure PANI film and PANI/SWCNTs-COOH nanocomposite film with different dopants obtained by electropolymerization using the cyclic voltammetry (CV) at 0.01Hz

<table>
<thead>
<tr>
<th>Polymeric film</th>
<th>Slope values obtained From graph: $-Z_{\text{im}} = f(\frac{1}{2\pi f})$</th>
<th>$C_{\text{ESS}}, \text{F/cm}^2$</th>
<th>$Z_{r}, \Omega\text{cm}^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PANI</td>
<td>42.8</td>
<td>0.023</td>
<td>92.12</td>
</tr>
<tr>
<td>PANI/CNTs-COOH</td>
<td>3.68</td>
<td>0.271</td>
<td>58.53</td>
</tr>
<tr>
<td>PANI/KClO$_3$/CNTs-COOH</td>
<td>4.25</td>
<td>0.235</td>
<td>78.32</td>
</tr>
<tr>
<td>PANI/cetyl benzyl dimethyl ammonium chloride/CNTs-COOH</td>
<td>2.65</td>
<td>0.378</td>
<td>65.06</td>
</tr>
</tbody>
</table>

The electrochemical impedance spectroscopy measurements are in concordance with the SEM results exhibited in figure 8 that displayed a smaller porosity in the PANI film than in the situation of the composite film PANI/CNTs-COOH and PANI/CNTs-COOH/dopant.
In figure 8 are submitted the SEM images of the PANI films, of PANI/CNTs-COOH and of PANI/CNTs-COOH/dopant composite film. This porous morphology enable a superior electrolyte entrance with less resistance by assuring sufficient ways for the displacement of ions and solvent molecules into the composite films that determines to enhanced electrochemical properties. These microstructural shifts have great effect on the capacitive comportment of the composites, as indicated above.

Examining the figures 8 a-d, it can be said that, the PANI and CNTsF/dopant films indicate a morphological structure formation of nanofibers, however for the pure polymeric ones they are little thicker than those in the PANI/CNTsF/dopant composite film. This constitutional similarity can describe the comparatively small difference in electrochemical comportment among PANI, PANI/CNTsF and PANI/CNTsF/dopant as presented previously. Similarly, the morphological structure of the PANI was established to be distinct, the PANI/CNTsF/dopant composite film displaying a more porous morphology. These microstructural transformations have deep effect on the capacitive behavior of the composites, as presented above.

The SEM images showed that the nanocomposite films, PANI/CNTs-COOH and PANI/CNTs-COOH/dopant have been more porous than PANI films (see figure 8a-d). Microstructures of these composites suppose that PANI was wrapped around SWCNTs.

CONCLUSIONS

Were obtained nanocomposite films type PANI/SWCNTs-COOH with cetyl benzyl dimethyl ammonium chloride and KCIO₃ as dopants by cyclic voltammetry method from a synthesis solution.

The electrochemical activity of PANI/FSCNTs/dopant/Pt modified electrode in 0.25 M H₂SO₄ cycling solution is much more higher than of PANI/Pt modified electrode in the same cycling solution;

Electrochemically synthesized composite film of conducting polymer PANI and FSCNTs/dopant have in common a porous structure at micro- and nano-meter scales.

Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) demonstrated that these composite films had similar electrochemical response rates to pure polymeric films but a lower resistance and much improved mechanical integrity.

The electronic conductivity properties increases in the order:

PANI/CDMACl/SWCNTs-COOH/Pt > PANI/SWCNTs-COOH/Pt > PANI/KClO₃/SWCNTs-COOH/Pt > PANI/Pt.

Nearly rectangular shaped cyclic voltammograms are obtained for all composite films suggesting that the charge and the discharge reversibly occur at the electrode/electrolyte interface. The best electrochemical properties are presented by PANI/CNTs-COOH/CDMACl/Pt and PANI/CNTs-COOH/Pt.

The Nyquist plots for PANI and composite films PANI/SWCNTs-COOH and PANI/SWCNTs-COOH/dopant are featured by a vertical trend at low frequencies, indicating a capacitive behaviour in concordance to the equivalent circuit theory.

In this study, we have achieved a higher capacitance value for PANI/CNTsF and PANI/CNTsF/dopant film in regarding with PANI pure polymeric films.

The capacitance value increases in the order:

PANI/CDMACl/SWCNTs-COOH/Pt > PANI/SWCNTs-COOH/Pt > PANI/KClO₃/SWCNTs-COOH/Pt > PANI/Pt

The SEM micrograph of the composite films PANI/SWCNTs-COOH and PANI/SWCNTs-COOH/dopant shows a porous morphology that wrapped on the surface of FSCNTs.

The PANI/SWCNTs-COOH/dopant composite is a very important electrode material for employment in the supercapacitor domain.

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REFERENCES
