Electrochemical evaluation of polyaniline/multi-walled carbon nanotube composite synthesized by microwave plasma polymerization as a supercapacitor electrode

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Abstract. PANI/MWCNT nanocomposite supercapacitor electrodes were synthesized by in-situ microwave plasma polymerization of aniline in the presence of MWCNT-COOH. The SEM image of the composite illustrates the formation of the core-shell MWCNT-PANI ordered structure that has a strong effect on the electrical conductivity and porosity, in addition to the appearance of agglomerated polymerized islands. The electrochemical performance of PANI/MWCNT composite was evaluated with respects to the obtained specific capacitance, energy and power density, and cyclic stability, using cyclic voltammetry, galvanostatic charge/discharge at a constant current and electrochemical impedance spectroscopy. The highest obtained specific capacitance was 112 F/g at a charging current density of 1.6 A/g, provides the highest energy density of 34.8 Wh/Kg and a power density of 1670 W/Kg. While the highest achieved power density was 8381 W/Kg with an energy density of 12.8 Wh/Kg. The delivered energy density crossed the threshold energy density limit of the battery, which meets the scientific motivation to use supercapacitor as an independent energy source.

Keywords: Plasma polymerization, Carbon nanotubes, Polyaniline, Nanostructure composite, Core-shell structure, Supercapacitor.

1. Introduction

Supercapacitors (also known as electrochemical capacitors) are attracting significant attention due to their high capacitance and potential applications in electronic devices. They can be categorized into two classes according to their charge storage mechanism; electrochemical double-layer capacitors (EDLCs) and pseudocapacitors [1-6].

EDLC can be accomplished using materials that have a high accessible surface area as electrodes, like porous carbon materials (activated carbons, carbon nanotubes, carbon nanofibers and reduced graphene oxide etc.) [7-10], while the electrode materials in the case of pseudocapacitors are transition-metals oxides (RuO$_2$, SnO$_2$, NiO, MnO$_2$, etc.) or conductive polymers, such as polypyrrole (PPy) and polyaniline (PANI) [1-5, 11-17]. Amongst the electrically conducting polymers, PANI has gained further attention as a potential pseudocapacitive candidate material owing to its benefits over the others; for instance, low cost, uncomplicated synthesis, high environment constancy, and facile doping and de-doping which offer a reversible control of the electrical properties [18, 19]. On the other hand, it undergoes poor cycling stability due to repetitive swelling and shrinkage of its backbone structure during the charge-discharge process. As well as, low achievable doping besides mass transfer drawback within massive polymer layers [11-13]. In the direction of resolving these difficulties, PANI should be highly crosslinked [20],
nanostructured, or can be grown on several nanomaterials as composites [21], and the polymerization process can control all these problems. Thus, the choice of the polymerization scheme has always been regarded as a substantial filed of interest. Conductive polymers are usually formed employing electrochemical and chemical polymerization; however, in recent decades, plasma polymerization is recognized as a considerable single-step low-cost approach to producing films of conductive polymers [22-25]. The conductive polymers that are plasma polymerized possess chemical structures that are rather unlike the polymers produced by electrochemical and chemical polymerization and are reliant on the plasma polymerization parameters [23, 24]. The produced plasma polymerized films are considerably more uniform, smoother, greatly adherent, and pinhole-free. The polymer chains are randomly branched and shorter, with a high degree of crosslinking. However, a higher conductivity can be achieved with electrochemically and chemically synthesized polymers due to the in situ doping through these methods of polymerization, whereas in the plasma polymerization, the synthesized polymer is an insulator and needs to be doped to get a conductive polymer film [23-27]. Consequently, the in situ plasma polymerization of aniline monomer in the presence of CNTs is a standout technique amongst the most proficient approaches to combine PANI nanocomposite due to the proper interfacial interaction between the CNTs and the PANI matrix. The main idea in the use of CNTs in the field of the polymer-based composite is to transfer their electrical properties to the insulating polymer matrices to obtain conducting composites, such composites have shown a high potential as supercapacitor electrodes due to their conductivity, high surface area, and capability to store energy by means of two charge storage mechanisms [14-16, 28-30].

In the present work, a microwave plasma polymerization technique was used to synthesize the PANI/CNT composite that was tested as a supercapacitor electrode. The aniline monomer with dispersed multiwalled carbon nanotubes (MWCNTs) was directly injected into the plasma induced by the microwave discharge. The morphological and electrochemical characterizations using cyclic voltammetry (CV), galvanostatic charge-discharge (CD), and electrochemical impedance spectroscopy (EIS) revealed the detailed features of these composites and their performance as a supercapacitor electrode.

2. Experimental

2.1 Materials and characterization instruments:
The aniline of purity 99.99% was provided from Hopkin and Williams Ltd., England, and distilled before used. Nanostructured and Amorphous Materials Inc. USA, provided the functionalized MWCNTs-COOH, with a purity of 95%, 10-30 nm diameter, and 10-30 μm length. A Titanium of 0.2 mm thickness was used as a substrate for the deposition of the composite. The morphological investigation was carried out using a scanning electron microscope (SEM), Philips XL 30, and KYKY-EM3200. While the electrochemical performance of the composite electrodes was examined using IVIUMSTAT.XR (Electrochemical Interface & Impedance Analyzer). A conventional three electrodes cell with a piece of Ti sheet that coated by active materials as working electrode, Platinum wire, and an Ag/AgCl (Argental, 3M KCl) were used as counter and a reference electrode, respectively. The EIS test was conducted in a wide frequency range of 10 mHz -100 kHz with a perturbation amplitude of 5mV.

2.2. Synthesis of PANI/MWCNT composite electrode
A microwave plasma CVD apparatus that was built in our laboratory was used in the plasma polymerization process and was described in detail in earlier publications [31, 32]. The functionalized MWCNTs, of different loading percentages, were dispersed ultrasonically for 30 min in the aniline monomer to form a colloidal solution. Then the colloidal solution was injected into the plasma vessel as pulses by a car fuel injector. The deposited film thickness depends on the injected colloidal solution
am
amount in the plasma vessel as pulses of controlled period, and the MWCNTs-COOH loading percentage
in the monomer. However, the period control of the pulse and their repetition rate are essential to maintain
the vessel pressure within 0.1 - 1.0 mbar, which is the plasma working pressure range. The solution
minute droplets of the spraying pulse will directly evaporate when they entered the evacuated plasma
reactor and turned into high concentration radicals nearby the substrate as a result of the surrounding
plasma activity in the vessel. Two simultaneous processes will take place within the formation of the
PANI/MWCNT-COOH composite; the plasma surface functionalization of the MWCNTs, and the aniline
plasma polymerization. Whereas the walls of the MWCNTs-COOH adsorb the aniline due to their high
surface area and chemical activity. Therefore, the polymerization process begins on the MWCNTs walls
in their pathway to the substrate through the plasma, and the produced composite film will enclose
MWCNTs that were implanted and chemically bonded with the PANI
3. Results and discussion
The characteristics of PANI, MWCNTs, and their nanocomposite films were investigated using many
techniques to evaluate its electrochemical performance.

3.1. Scanning Electron Microscopy Analysis
The SEM images of pure PANI that was plasma polymerized revealed a spherical granular morphology of
massive spheres, up to many micrometers in dimension, uniformly distributed on the Titanium substrate.
Each large sphere composed of aggregations of small nanospheres, which relatively offer a high surface
area to the structure, as it can be shown in figure (1- a, and b). While figure (1-c) illustrates the SEM
image of the functionalized MWCNTs film, it can be seen that the MWCNTs are entangled and
interconnected, creating 3D network, with an arrangement of macroporous and mesoporous structures,
facilitating excellent electrical conductivity. Whereas, the SEM images of PANI/MWCNT nanocomposite
of 1.5wt. % MWCNTs loading are shown in figure (1- d, and e), which represent the top and the cross-
sectional view, respectively. The SEM top-view image illustrates a high-density MWCNTs which are well
dispersed, implanted, and completely enclosed with PANI, creating a continuous matrix. Moreover, a
core-shell MWCNT-PANI structure was formed, which enhanced the composite porosity and could offer
a high surface area for excellent electrode/electrolyte interfacial contact. This kind of open structure can
provide better accessibility to the electrolyte [21, 30]. Also, it can be seen the appearance of big
agglomerated polymerized islands that is unfavorable growth tends to block the pores structure of the
electrode and reduce the surface area. The SEM cross-sectional view image of the composite indicates the
formation of a thick composite layer of thickness about 35 µm, which may have a negative effect on
increasing the electrode material resistance.

3.2. Electrochemical Investigations
The electrochemical behavior of pure PANI, MWCNTS, and PANI/MWCNT composite films was
examined by cyclic voltammetry (CV), galvanostatic charge-discharge (CD) and electrochemical
impedance spectroscopy (EIS) measurements, to evaluate their performance as a supercapacitor electrode.
The experiments were done in a conventional three-electrode glass cell of a platinum counter electrode,
Ag/AgCl reference electrode, and a Titanium with the deposited materials as a working electrode, in 1M
H2SO4 aqueous electrolyte. Figure (2-a) shows the current response profile of the CV voltammograms of
pure PANI, functionalized MWCNTs-COOH and PANI/MWCNT-COOH composite electrodes at a scan
rate of 50 mV/s and a potential range of -0.5 to 1 V. The CV voltammograms of the MWCNTs show a nearly rectangular-like symmetrical shape which is an electric double-layer capacitive behavior [1, 7]. The same behavior is recognized with PANI CV voltammograms as a result of its insulating state (leucoemeraldine form) due to its preparation method by the plasma polymerization [31, 46], and its EDLC behavior coming from its nanostructure surface morphology. However, the CV voltammograms of PANI/MWCNT-COOH composites of 0.2 and 0.5 wt.% MWCNTs loading show the same previous trend with a bit increase in the peak current due to the enhancement of the nanopores structure of the composite, but they are still suffering from the poor electronic conductivity. Whereas, the CV voltammograms of the 1.5 wt.% MWCNTs loading composite shows a good rectangular shape with a jump in the peak current representing an increase in the capacitance. Furthermore, two pairs of redox peaks were appeared, caused by the insertion/removal of counter ions that lead to the reversible redox transition. That is a pseudocapacitance behavior due to the synergistic effect between PANI and the CNTs [13-16]. It appears that the doping of PANI with 1.5 wt. % of the functionalized MWCNTs were adequate to transfer PANI to its conductive electronic state.

Figure 1. SEM images of (a, b) Pure PANI, (c) MWCNTs and (d, e) PANI/MWCNT composite films deposited under similar circumstances.
(polaronic emeraldine form), which increase the electrical conductivity of the nanocomposite [16, 31], and simplifies the electron transport through the CV scan process. In addition to the significant enhancement of the nanopores structure of the composite, which offers a large surface area that permits better accessibility to the transport of electrolyte ions and providing lower internal resistance. It is well known that the dynamic interaction among the π-bonds in the aromatic ring of PANI and the graphitic structure of the CNTs should powerfully enable the charge-transfer reaction between the two components [34-37]. The CV voltammograms of PANI/MWCNT-COOH composite of 1.5 wt. % MWCNTs at different scan rates extending from 10 to 300 mV/s in the given potential range are shown in figure (2-b). Through the increase of the scan rate, the redox current increased, which revealed a good rate ability. The symmetric and nearly rectangular shape of the curves and their fast current response at the voltage reversal points even at high scan rates specify the rapid diffusion of the electrolyte in the film [5, 9].

Figure 2. (a) Cyclic voltammograms of pure PANI, MWCNTs, and PANI/MWCNT composites at a scan rate of 50 mV/s in 1M H₂SO₄. (b) Cyclic voltammograms of 1.5 wt. % MWCNTs composite at different scan rates in 1 M H₂SO₄.

The rate capability and the electrode capacitance are best determined from the galvanostatic charge/discharge cycling curves at a constant current. Figure (3-a) shows the charge/discharge behavior of PANI, MWCNT-COOH, and PANI/MWCNT-COOH electrodes in the potential range of -0.5 to 1.0 V at a current density of 1.6 A/g in 1M H₂SO₄ aqueous electrolyte. The charge/ discharge curves through this potential range have nearly triangular shapes with almost mirror images that indicating an excellent capacitive behavior of the PANI/MWCNT-COOH nanocomposite electrodes [17]. The initial part of the discharge curves exhibit an IR voltage drop owing to the internal resistance of the electrodes [17, 38], and the rest of the curve is linear for the non-faradic materials like the nanostructure PANI in its insulating state. While the pseudocapacitive and hybrid system exhibits a deviation in linearity created by varying the capacitance with the voltage as it can be seen clearly in the nanocomposite electrode of 1.5 wt.% MWCNT loading [17]. The specific capacitance (Cs) of the electrodes in the cell was calculated from the discharge portion of the curve using equation (1) [16, 17, 38, 39]:

\[
Cs = \frac{I}{\Delta V/\Delta t} m
\]

where I is the applied constant current, ΔV is the change in potential, Δt is the discharge time, ΔV/Δt is the slope of the discharge curve after the IR voltage drop, and m is the mass of the active material on the electrode. The calculated Cs of pure PANI was 16 F/g, and for MWCNTs was 65 F/g, while Cs of
PANI/MWCNT-COOH nanocomposite films were 26, 36, and 112 F/g for MWCNTs loadings of 0.2, 0.5, and 1.5 wt.%, respectively. The low capacitance of pure PANI may be attributed to two reasons, the first is due to the insulating conductive state of the produced PANI by the plasma polymerization method, and this is clear in the absence of any redox peaks in its CV voltammograms. The second reason is due to the structural nature of the deposited PANI that is of the form of big aggregations of macro sizes, in spite of the nano granular morphology of its surface, causing a great lack in the PANI porosity, which is a decisive factor affecting the capacitance greatly. Figure (3-b) presents the charge/discharge curves of the nanocomposite film of 1.5 wt. % MWCNTs loading at various current densities. From this figure, it can be realized that the curves have an almost triangular shape with the discharge curves approximately symmetric with their corresponding charge counterparts. This trend suggests that the electrode has good charge propagation across the composite that means good charge/discharge performance and electrochemical reversibility [16,17]. Moreover, the slight asymmetry, which is clear in the charge/discharge curve at a low current density of 1.6 A/g is due to the strong influence of the pseudocapacitance since a redox reaction usually spends more time than pure EDL formation [17]. The IR drops are seen at the high charge current densities, decreased with lowering the current density, as marked in figure (3-b). The specific capacitances can be determined from the discharge curves using equation 1, where Cs is 112, 78, 68, 62, and 59 F/g at a constant charging current density of 1.6, 3.3, 6.6, 10, and

![Graph](image-url)
13.3 A/g, respectively. Figure (3-c) illustrates the relation between Cs and the charging current density. At high charge current densities, the specific capacitance decreases because only the outer pores of the active materials at the electrode/electrolyte interface are accessible to the electrolyte ions since they will not have enough time to reach the deeper ones to enable the doping/dedoping process [40]. Cyclic stability is a crucial requirement for supercapacitor applications.

The stability test of 5000 charge/discharge cycle was done for pure PANI and PANI/MWCNT electrodes at a constant current density of 13.3 A/g in a potential window ranging from -0.5 to 1.0 V. Figure (3-d) illustrates the stability of the two electrodes in the relation of losing their capacitance as a stability percentage. The electrode stability can be calculated from equation (2):

\[
\text{Stability} = \frac{C_n}{C_1} \times 100
\]

where \(C_n\) is the capacitance of the electrode in each cycle, and \(C_1\) is the capacitance of the first cycle. From figure (3-d), it can be seen that the PANI electrode loses its capacitance fast and gets 20% of the first cycle capacitance after 5000 cycles. This poor cycling stability is due to repetitive swelling and shrinkage of the polymer backbone structure during the charge-discharge process. While PANI/MWCNT of 1.5 wt. % MWCNTs nanocomposite electrode maintains its stability and saves more than 86% of its capacitance of the first cycle after 5000 cycles, which is a good and reasonable retention in the stability percentage compared with that of pure PANI electrode that suggests long term high stability for the charge/discharge applications.

The electrochemical impedance spectrum (EIS) is one of the main methods to inspect the fundamental behavior of the electrode materials for supercapacitors. Figure (5-a) shows a complex-plane plot of the impedance (Nyquist plot) of PANI and PANI/MWCNT-COOH of 1.5 wt.% MWCNTs loading electrodes in 1 M \(\text{H}_2\text{SO}_4\) that were performed at an open circuit potential of 0.3V through a frequency range of 10 mHz -100 kHz. In the Nyquist complex-plane, the imaginary vertical component signifies the capacitive properties, while the real component signifies the ohmic features. Typically, the impedance spectrum of the supercapacitor consists of a semicircle arc at the high-frequency region and a straight line parallel to the imaginary axis at the low-frequency region. The semicircle represents the charge transfer limiting process resulting from the charge transfer resistance \(R_{ct}\) caused by the Faradic reactions at the interface between the electrode and the electrolyte solution in parallel with the double-layer capacitance \(C_{dl}\) [39, 40]. The \(R_{ct}\) can be measured from the semicircle diameter [39], where it is (152 Ω) for PANI, which is a high value that consistent with its insulating state. Whereas, the small semicircle diameter of the composite and its low \(R_{ct}\) (12.8 Ω) value, indicating that incorporation of MWCNTs is highly improving the charge transfer performance of PANI/MWCNT electrode, due to the significant enhancement of the electronic conductivity and porosity structure of the composite electrode.

The equivalent series resistance (ESR), which is the sum of the electrolyte resistance, the contact resistance of the active material/current collector and the resistance of the active electrode material, can be found from the intercept of the semicircle with the real axis of the Nyquist plot [39]. The ESR defines the Cs charged/discharged rate as an essential factor in the evaluation of the supercapacitor power density. From figure (5-a), the measured ESR value of the PANI electrode is (8.2 Ω), whereas it is (6.2 Ω) for the composite electrode of 1.5 wt.% MWCNTs loading. Therefore the use of the MWCNTs have relatively improved the power performance of the electrode due to the reduction in its internal electrical resistance, but the value of the ESR is still higher than the requirement to get a high power density, and it needs to be reduced. Furthermore, the impedance curve intersects the real axis at an angle of 45°, which is compatible with the porous structure of the nanocomposite electrode when saturated with the electrolyte [41].

At the low frequency region the composite electrode exhibits a nearly linear branch, which frequently departs from that predicted for ideal capacitor with a slope angle near to 90° due to the presence of “constant phase element” [42], representing a good capacitive behavior due to the reduced diffusion
resistance of the electrolyte ions in the nanostructure electrode. The transition point between the high and low-frequency regions being mentioned as the knee that represents the maximum frequency where the capacitive behavior is dominant and a sign of a supercapacitor power ability [43]. The knee frequency of the composite electrode is about (41 Hz), higher than that of pure PANI electrode, which is (8 Hz), indicating better power ability.

The energy density \( (E_s) \) and the power density \( (P_s) \) are given in equation (3) and (4), respectively:

\[
E_s = \frac{1}{2} C_s V^2
\]

\[
P_s = \frac{E_s}{t}
\]

They were calculated using the galvanostatic charge/discharge curves at a constant current density, where \( C_s \) is the specific capacitance, \( V \) is the charging voltage (potential operating window), and \( t \) is the time to charge or discharge [6, 41, 42, 44]. Figure (4) is a Ragone plot of PANI/MWCNT of 1.5 wt.% MWCNTs composite electrode. For the lower charging current density of 1.6 A/g, the energy density of the composite electrode of 1.5 wt. % MWCNTs is 34.8 Wh/Kg, and the power density is 1670 W/kg. While, for the higher charging current density of 13.3 A/g, the electrode exhibited a good supercapacitance performance, as it can deliver an energy density of 12.8 Wh/Kg and a power density of 8381 W/kg.

**Figure 4.** (a) AC impedance spectra of PANI and PANI/MWCNT of 1.5 wt. % MWCNTs composite electrodes that were performed at an open circuit potential of 0.3V through a frequency range of 10 mHz - 100 kHz. (b) Ragone plot of PANI/MWCNT of 1.5 wt. % MWCNTs composite electrode.

**4. Conclusion**

The possibility of using a microwave plasma in the polymerization of polymer composite materials as a powerful one-step method in the synthesis of the supercapacitor electrodes was demonstrated successfully in this work. Although the obtained results of the capacitance and the power density were nonoptimal, they can be optimized by better control of the plasma parameters and the deposition scheme that strongly affect the composite material thickness and structure. The SEM images didn't show a homogeneous coating of the CNTs with PANI, indicating that the polymer tends to grow both on the CNTs and on itself, creating micro-agglomerated polymerized islands. This growth may affect negatively on the three-dimensional nanopores structure of the CNTs that may be one of the reasons for the relatively low
electrode capacitance values achieved by PANI/MWCNT composite. The other reason is may be due to the high composite thickness, which limits the accessibility of the electrolyte ions into the pores structure inside the electrode. So that, to increase the efficiency of the supercapacitor, the thickness of the electrode material should be reduced, and PANI coated layer on the nanotubes should be as thin as possible to earn the benefits of both the double-layer capacitance and pseudocapacitance performance of the composite constituents. In spite of the previous drawbacks, the achieved energy density crossed the threshold energy density limit of the battery [7,45], which is a favourable aim and meet the scientific ambition to use the supercapacitor as an independent source of energy by further enhancing of the energy density.

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