Effects of frequency on supercapacitor properties of multi walled carbon nanotubes-polypyrrole film prepared by alternating current-electrophoretic deposition method

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Keywords: electrophoretic deposition, frequency, multi walled carbon nanotubes, polypyrrole, supercapacitor

Abstract
An electroactive supercapacitor electrodes have been prepared through deposition of multi walled carbon nanotubes-polypyrrole (MWCNTs-PPy) via alternating current electrophoretic deposition method (AC-EPD). Using safranin (SAF) as co-dispersant, a stable and well-dispersed MWCNTs were obtained and the deposits of MWCNTs-PPy were successfully formed using AC peak to peak voltage of 8 V but at difference frequencies of 0.01 Hz, 4 Hz and 250 Hz. Varying the frequencies of the applied voltage has been found influencing the morphology and electrochemical properties of the deposited films. A more porous and highest deposited mass of 0.021 g was obtained at frequency of 4 Hz, while at 250 Hz the deposited mass reduces to 0.017 g. The lowest deposited mass of 0.015 g was obtained at the lowest frequency (0.01 Hz). In addition, the morphology structure of the composite film at 4 Hz shows that the PPy were well-distributed throughout MWCNTs surface. The XRD result shows the presence of amorphous PPy and graphite-like MWCNTs for all deposited samples. It has been shown that the specific capacitance values for the composites also strongly depends on the frequency of applied voltage. In the case of frequency of 4 Hz, higher values can be found at 76.08 F g⁻¹ which was more than two folds increment from the lowest frequency (0.01 Hz), however at the highest frequency (250 Hz) a specific capacitance values of 65.03 F g⁻¹ have been measured. The AC-EPD provides avenue for depositing nanocomposites film at relatively low applied voltage however, there have no linear correlations been observed on the morphology and electrochemical properties of the deposited films as the frequencies of applied voltage increases.

1. Introduction
Composites contain materials in two or more phases that mixed together to form a single material. The combination of two or more materials indirectly improves the mechanical properties of individual base materials. The materials used to form the composite material are usually in reasonable size and consistently dispersed among each other. Some of composites that have been discovered its potential specifically as energy...
storage devices are MWCNTs-PANI [1], SiC/SiC [2], biopolymer composites [3], metal-polyaniline [4] and MWCNTs-PPy [5].

Although there have been several techniques for depositing nanocomposites thin film on conductive substrates such as spray coating, deep coating, pulse electrodeposition, chemical vapor deposition and many others to name but however, electrochemical deposition (EPD) still gaining popularity due to its versatility and produces thin films that exhibit good microstructure homogeneity. EPD’s has been broadly used method for coatings preparation that applicable to any materials that can form colloidal suspensions using appropriate solvents [6]. In this technique, the charged particles in suspensions move and accumulate towards the electrodes of the opposite polarity under the influence of electric fields [7]. Conventional EPD method uses continuous direct current (DC) as source voltage to deposit film on conductive substrates. Recent studies show innovations in EPD method using modulated current such as pulsed-EPD to prepare collagen membranes [8], NGr-Co3O4 [9] and AC-EPD to prepare TiO2 [6], hydroxyapatite on titanium [10], BaTiO3 [11] and bovine serum albumin coatings [12]. The pulsed DC-EPD has been demonstrated to control bubbles incorporation throughout the deposition process [13]. On the other hand, the deposition yield in AC-EPD has been reported to directly proportional to the applied electric voltage and deposition time while the deposited particle size is inversely proportional to the frequency applied [2]. Both pulsed DC-EPD and AC-EPD methods influence the morphology and electrochemical properties of deposited films. Therefore, further investigations on AC-EPD are essential in search for high performance nanocomposite materials specifically for energy storage device applications.

This work focuses on the evaluation of the effects on varying the frequency in the deposition of nanocomposite MWCNTS-PPy films using AC-EPD process. The applied peak to peak voltage was set at 8 V while three frequencies have been selected at 0.01 Hz, 4 Hz and 250 Hz. Higher frequency regime has not been evaluated since it’s shorter wavelength resemblance to DC behaviour. To establish stable and yet well-dispersed colloids, SAF has been used as co-dispersant of MWCNTs. SAF is water soluble dye which frequently used in staining of cellular substances. This cationic organic dye has been reported to improve the binding of PPy and colloids, SAF has been used as co-dispersant of MWCNTs. SAF is water soluble dye which frequently used in colloids production, magniﬁcations of MWCNTs-PPy films. Therefore, further investigations on AC-EPD are essential in search for high performance nanocomposite materials specifically for energy storage device applications.

2. Methodology

For preparing the nanocomposite materials, the MWCNTs with outer diameter of 30–50 nm, length of 5–20 μm and purity greater than 95 wt% was purchased from Universiti Sains Malaysia. Other chemicals were pyrrole with 99.5 wt% (MERCK), ammonium persulphate (APS) with purity of 98 wt% (SIGMA ALDRICH) and SAF with purity of 90 wt% (MERCK). All chemicals were of analytical reagent grades and have been used without purification.

Initially, MWCNTs colloids were prepared by adding 0.15 g of as-received MWCNTs in 200 ml of deionized (DI) water and stirred for 1 h. SAF was then added into the colloids and again stirred for 1 h followed by sonication for 2 h to stabilize the MWCNTs colloids. The colloids were further stirred for 15 min in an ice bath to lower the temperature down to 4 °C before the addition of pyrrole. Upon addition of pyrrole, the colloids were stirred again for 15 min. Subsequently, APS was slowly added, drop by drop into the colloids for 30 min followed by stirring for 3 h. The function of APS is to initiate the in situ polymerization of pyrrole. Finally, the homogenous colloids were sonicated for 2 h. Figure 1 summarizes the preparation of MWCNTs-PPy colloids.

The EPD set up as shown in figure 2 was used to deposit MWCNTs-PPy films on nickel electrodes separated at 10 mm each. The films were then deposited using applied peak to peak voltage of 8 V at three different frequencies of 0.01 Hz, 4 Hz and 250 Hz using asymmetrical rectangular waves with 80% duty cycle.

The surface morphological, microstructural and functional groups of MWCNTs-PPy film were assessed using field emission scanning electron microscope (FESEM), x-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR), respectively. The working voltages for FESEM analysis are 10 kV and 15 kV. Meanwhile, the electrochemical properties of film as supercapacitor were evaluated using cyclic voltammetry (CV) and galvanostatic charge-discharge (CD). The measurements were carried out using three-electrodes cell which is Ag/AgCl/KCl as reference electrode, platinum sheet as counter electrode and deposited film as working electrode. The potential window used was 0.45 V at a scan rate of 10 mV s−1. The electrolyte solution used was 6 M KOH solution.

3. Results and discussion

Figures 3(a)–(c) shows FESEM images of MWCNTs-PPy films produced, magnified at 50 k, deposited at three different frequencies. Frequency do has some effects on the films coating as higher frequency will minimized the

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reaction of water and can prevent bubbles formation. This phenomenon occur because the higher the frequency, the higher the number of the complete cycle wave. In other word, the hydrolysis reaction will not occur due to insufficient amount of time during the polymerization process. However, a high frequency is not a guarantee to have a good result as the film deposition posses unique range of frequency depends on the material used. The selection of the frequency need to consider several aspects related to the deposition yield and the coatings quality.

As can be observed in the figure 3(a), at lower frequency, MWCNTs and PPy are not distributed uniformly. The PPy structure (granular particles) in the red circle appeared at the centre of the FESEM image rather than...
coat onto MWCNTs surface (long tubes). It could be say that the energy provided at 0.01 Hz is insufficient for PPy to coat onto the MWCNTs surface. Meanwhile, in figures 3(b) and (c), it can be seen that both films have porosity between the entangled nanotubes. This porous structure increase the surface area of the MWCNTs-PPy that allow an easy access for ions to the active material. Both films also have good morphology structure compare with film at 0.01 Hz as the PPy is well dispersed with the MWCNTs. The frequency used is compatible for the PPy to coat well onto the MWCNTs surface. However, there are small aggregates of PPy attached at the wall of MWCNTs shown at the red arrow in both films. This aglomeration will decrease the specific surface area of PPy.

Figure 4 shows the morphology of all films, at lower magnification of 50. The crack surface is shown by the red arrow in figure 4(a). Meanwhile, figure 4(b) shows an uneven surface area spotted in the red circle. This possibly due to the structure of the nanotubes entangled unevenly at certain area of the film. The purpose of observing the films at lower magnification is to study the roughness of the films. By comparing this three FESEM images of films, film at 0.01 Hz has the roughest surface while the film at 250 Hz has the smoothest surface.

Figure 5 shows the XRD result of MWCNTs-PPy film deposited at (a) 0.01 Hz, (b) 4 Hz and (c) 250 Hz, respectively. The broad and weak peak at 26.1° represents the MWCNTs-PPy composite, indicating that the PPy is amorphous and graphite-like characteristic of MWCNTs, respectively [15]. The overlapped XRD result of the MWCNTs with PPy describe the self-growing of MWCNTs-PPy by polymerization synthesis. Strong peaks at 2θ = 44.8°, 2θ = 51.8°, and 2θ = 76.7° corresponds to the reflection of the nickel atoms, respectively.

FTIR studies were performed in order to confirm the presence of PPy and SAF on MWCNTs surface. The molecular structure of PPy and SAF are shown in figure 6.

The FTIR spectra of MWCNTs-PPY film are taken in the range of 650 – 4000 cm⁻¹ which is shown in figure 7.

The presence of PPy was proved from FTIR spectra which shows the PPy characteristic. The peak at 788 cm⁻¹ and 928 cm⁻¹ were attributed to C-H stretching. The peak located at 1014 cm⁻¹ was assigned to σ-C-H in plane deformation vibration. The broad peak at 1362 was assigned to N-C stretching [16]. The peak at 1800 cm⁻¹ was assigned to C=C in PPy ring. The peak at 860 cm⁻¹ and 2650 cm⁻¹ were attributed to C-H bond which fall under functional group of aromatics and alkanes respectively [17].

The peak of the dispersant used were also presence in the FTIR spectra of MWCNTs-PPy film which is confirmed by the peak of primary amine at 3742 cm⁻¹ and 3828 cm⁻¹ which is presence in SAF. The addition of SAF into the suspension enable the MWCNTs to disperse well in the water. The π-π interactions allowed SAF adsorption on MWCNTs which cause the dispersion of MWCNTs [14]. The adsorption increase with increasing number of the aromatic rings in dispersant structure [18].
The MWCNTs-PPy films were tested by CV and CD analysis to determine the electrochemical supercapacitor properties. As shown in figure 8, all the CV curves were deviate from the ideal shape (rectangular shape) due to the PPy redox. At anodic peak, the PPy is oxidized while at cathodic peak the PPy is reduced.

The redox reaction of polypyrrole is shown in figure 9. It is reported that the anion play an important role on the properties of the polymer [19]. During the oxidation-reduction process, an electron transition occurs within the polymer and this transition offer an alternative chemical route for the preparation of some conductive polymer complexes.

Based on figure 8, the film deposited at 4 Hz has the largest integrated area under the curve compared to other tested frequency. It is eported that the larger the integrated area under the curve, the higher the capacitance, means the film deposited at 4 Hz have the highest capacitance. The film at 4 Hz has a deposited mass
of 0.021 g higher than 0.01 Hz and 250 Hz that have deposited mass of 0.015 g and 0.017 g respectively. The decrease in deposited mass between films at 4 Hz and 250 Hz shows the limitation of the frequency.

The electrochemical properties were calculated by using equation stated in the other journal [20]. The film at 4 Hz also has the highest specific capacitance and energy density of 76.08 F g⁻¹ and 7703.17 W h kg⁻¹ respectively. Based on the specific capacitance equation [20], the lower the mass deposited on the nickel film, the higher the specific capacitance. However, the result obtained in this study shows that film at 4 Hz has highest specific capacitance with the highest deposited mass compared to other film. This result is probably due to good porosity at 4 Hz which allow easy ion exchange between active material and electrolyte. Meanwhile, the film at 0.01 Hz has lower electrochemical properties is due to agglomeration of PPy as shown in figure 3(a).

Based on figure 10, the film deposited at 0.01 Hz show fastest charging and discharging process therefore the film posses highest power density. It is an expected result as the power density is influence by the discharging time. The shorter the discharging time, the higher the power density.
Figure 11 displays the energy efficiency of MWCNTs-PPy films deposited at three different frequencies along 70 CD cycles. For all films, the energy efficiency is fluctuate due to the different energy consume at each cycle. The film deposited at 4 Hz show increasing energy efficiency for the first 20 cycles, start to drop between 20 to 30 cycles, begin to stable between 30 to 60 cycles and start to increase back after 60 cycles.

Table 1. Electrochemical properties of MWCNTs-PPy film deposited at 0.01 Hz, 4 Hz and 250 Hz.

| Frequency (Hz) | 0.01  | 4     | 250   |
|---------------|-------|-------|-------|
| Deposited mass (g) | 0.015 | 0.021 | 0.017 |
| Capacitance (F) | 0.46  | 1.6   | 1.1   |
| Specific capacitance (F g⁻¹) | 30.52 | 76.08 | 65.03 |
| Energy density (Wh kg⁻¹) | 3090.24 | 7703.17 | 6583.82 |
| Power density (W kg⁻¹) | 5.56 × 10⁶ | 4.33 × 10⁶ | 1.58 × 10⁶ |
| Average energy efficiency (%) | 31.20 | 45.13 | 49.63 |

Figure 11 displays the energy efficiency of MWCNTs-PPy films deposited at three different frequencies along 70 CD cycles. For all films, the energy efficiency is fluctuate due to the different energy consume at each cycle. The film deposited at 4 Hz show increasing energy efficiency for the first 20 cycles, start to drop between 20 to 30 cycles, begin to stable between 30 to 60 cycles and start to increase back after 60 cycles.

Table 1 summarized all the electrochemical properties that has been calculated which include capacitance, specific capacitance, energy density, power density and energy efficiency. These values were obtained for half-cell configuration; hence it cannot be compared to Ragone plot, which stated values from full cell supercapacitor setup. From table 1, obviously shows that different frequencies affect the deposited mass and electrochemical properties of the films.
4. Conclusion

This study proved that frequency need to be consider in preparing MWCNTs-PPy film via AC-EPD method in order to improve the microstructural and electrochemical properties as supercapacitor. FESEM analysis display a uniform and well distributed of PPy onto the MWCNTs surface at 4 Hz. The presence of PPy and SAF on the MWCNTs surface was also proven by using FTIR analysis. The amorphous phase of PPy and graphite-like MWCNTs were confirmed by XRD measurement. At CV analysis, 4 Hz shown to be the best frequency for film deposition as the film has the highest value on deposited mass, capacitance, specific capacitance and energy density compared to the other films. While at CD analysis, the film also has a moderate value of power density and energy efficiency. From all the analysis, it can be concluded that the optimum frequency for this study is 4 Hz.

Acknowledgments

The authors would like to thank the Ministry of Education, Malaysia that supports this work through Fundamental Research Grant Scheme (FRGS/1/2016/STG07/UiTM/03/5).

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