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Optimization of Specific Capacitance for Hybrid Supercapacitor Material Based on Nickel-Manganese Oxides/multiwalled Carbon Nanotubes/ Poly (3, 4-Ethylenedioxythiophene) Using Response Surface Methodology

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Abstract: Nickel-manganese oxide/Poly (3, 4-ethylenedioxythiophene) (NMO/MWCNTs/PEDOT) nanocomposites have been prepared from emulsification of as-prepared NMO/MWCNT and aqueous acetonitrile solutions of EDOT by oxidation using Ferric chloride. The uniform coating of PEODOT on NMO/MWCNTs nanocomposite was confirmed by Energy dispersive x-ray (EDX) and scanning electron microscope (SEM) images. The effects of emulsification amplitude and emulsification time on the SC value of NMO/MWCNTs/ PEDOT nanocomposite were examined. The process optimization using response surface methodology (RSM) was performed and the interactions between the process parameters were also demonstrated. The optimum conditions of the emulsion polymerization were found to be 47.25% emulsification amplitude and 12.17 min emulsification time to achieve 836.27 F/g of specific capacitance (SC) value.

Key words: Supercapacitor · PEDOT · NMO/MWCNTs · Emulsion polymerization · Optimization

INTRODUCTION

Recently, the demand for supercapacitor has increased due to needs of electronic devices that requires significant burst of electrical energy. Long cycle life, high efficiency, high power density and environmental friendly characters, all of these specifications have made the supercapacitor being special attention of modern civilization [1]. Hybrid materials are of the great interest of supercapacitor electrode materials that can be prepared from composition of carbon materials with transition metal oxide or/and conductive polymers [2-5].

In our previous study [6] nanocomposites of MWCNTs with nickel oxide and manganese oxide have been found as promising electrode materials for hybrid supercapacitor. However, in present work the conductive polymer coated on prepared nickel manganese oxide/MWCNT (NMO/MWCNTs) in order to enhance the electrochemical properties and specific capacitance (SC) value of NMO/MWCNTs.

The practical application of conductive polymer is often depending on their stability in ambient surrounding. The problem of using conductive polymers in supercapacitors is their degradation during electrochemical cycling, but the problem can be dissolved with the usage of MWCNTs which provides the entangled mesopores network of nanotubes in composites that can adapt with the volume change leading to more stable capacitance during the cycling process. Poly (3, 4-ethylenedioxythiophene) or PEDOT which belong to the family of conductive polymers is characterized by its high electrical conductivity in p-doped state, good thermal and chemical stability and also its fast electrochemical switching [7]. The conductivity of PEDOT ranges from 300 to 550 S/cm [8]. PEDOT based composites have wide potential window [9], environment-friendly feature [10] and better cycleability than other types of conductive polymers [7].

Emulsion polymerization is a common procedure used for uniform synthesizing of conductive polymers [11-14]

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especially in chemical oxidation technique. To our knowledge, emulsion polymerization of PEDOT over MWCNTs has attracted less attention. Hence, this procedure is suggested to coat PEDOT on as-prepared NMO/MWCNTs for the present study. The effects of two parameters: (i) emulsification amplitude and (ii) emulsification time, on the SC value of NMO/MWCNTs/ PEDOT nanocomposite will be investigated. This study also focused on reliability of the design of experiment (DOE) method for the optimization of the effective parameters in polymerization process of PEDOT. Response Surface Methodology (RSM) was applied to simultaneously relate these two parameters with the aim of maximizing the response i.e. SC value. The interactions between these parameters were statistically demonstrated and elucidated.

MATERIALS AND MATHODS

Experimental: The NMO/MWCNTs nanocomposite was synthesized by filling the cavities of the MWCNTs (supplied by Chinese Academic of Science, China) with the mixed solution of 0.3M of manganese nitrate and nickel nitrate (supplied by ACROS, 98%) with mass ratio of 1:1 using wet chemical method. The complete description of the filling process explained in our previous work [13]. EDOT (supplied by Sigma-Aldrich) and ferric chloride hexahydrate ($FeCl_3.6H_2O$) from Bendosen have been served as monomer and oxidant reagent, respectively. The solvent for making the solution was acetonitrile which had been provided by Sigma-Aldrich).

Synthesis of NMO/ MWCNTs/ PEDOT Nanocomposites: The NMO/MWCNTs nanocomposite prepared in our previous study [6] was undergone the coating with PEDOT to enhance its electrochemical properties. PEDOT synthesized from the in-situ chemical oxidation polymerization of the EDOT monomer with both ferric chloride ($FeCl_3$) as the oxidants and acetonitrile as the solvent. For example, the EDOT monomer with 0.1 M concentration was mixed with 0.2g of NMO/ MWCNTs nanocomposite together with 20 ml of acetonitrile. This solution was undergone emulsification process according to the conditions established by DOE as summarized in the Table 1. The product from the emulsification process is transferred to Pyrex-3 necked flask and undergoes stirring and refluxing at 95°C for 4hrs. The oxidant ($FeCl_3$) is added into the flask drop wise at fixed concentration of 0.5M within 30min. The refluxing process was carried out in 4 hrs. The sample then filtered and washed thoroughly with acetonitrile and this step followed by drying process at 60°C in the oven. The final product is called NMO/MWCNTs/PEDOT.

Table 1: Experimental design by DOE for the two independent variables

Run No.	Type	Amplitude (A) (%)	Emulsification time (B) (min)
1	Fact	0	10
2	Fact	100	10
3	Fact	0	150
4	Fact	100	150
5	Axial	25	80
6	Axial	75	80
7	Axial	50	45
8	Axial	50	115
9	Center	50	80
10	Center	50	80
11	Center	50	80
12	Center	50	80
13	Center	50	80

Electrochemical Tests: The electrochemical performance was investigated using cyclic voltammetry (CV) and galvanostatic charge–discharge (CD) techniques. All electrochemical tests were performed on the Versatile Multichannel Potentiostat 3 (VMP3, Biologic). Two-electrode system consisted of two almost identical NMO/MWCNTs/PEDOT nanocomposite electrodes was fabricated for the electrochemical testing. Potassium hydroxide (KOH, 6M) was used as electrolyte. The scanning rates of CV tests and current density for CD test were set at 5mV/s and 10mA/cm^2, respectively.

The specific capacitance (C_m) for the two-electrode system is calculated from the discharge curves using Equation (1):

$$C_m = \frac{2i \times \Delta t}{m \times \Delta V} \quad (1)$$

Where i is the current density, Δt is the time interval for the change in voltage ΔV and m is the average mass of materials on both electrodes.

RESULTS AND DISCUSSION

Morphology and Structure of MWCNTs and NMO/MWCNTs/PEDOT: Fig. 1 gives the SEM images and EDX analysis of the MWCNTs and the prepared NMO/MWCNTs/PEDOT nanocomposite. The morphological images of the nanocomposites obtained by chemical oxidation polymerization for the MWCNTs and NMO/MWCNTs/PEDOT are presented

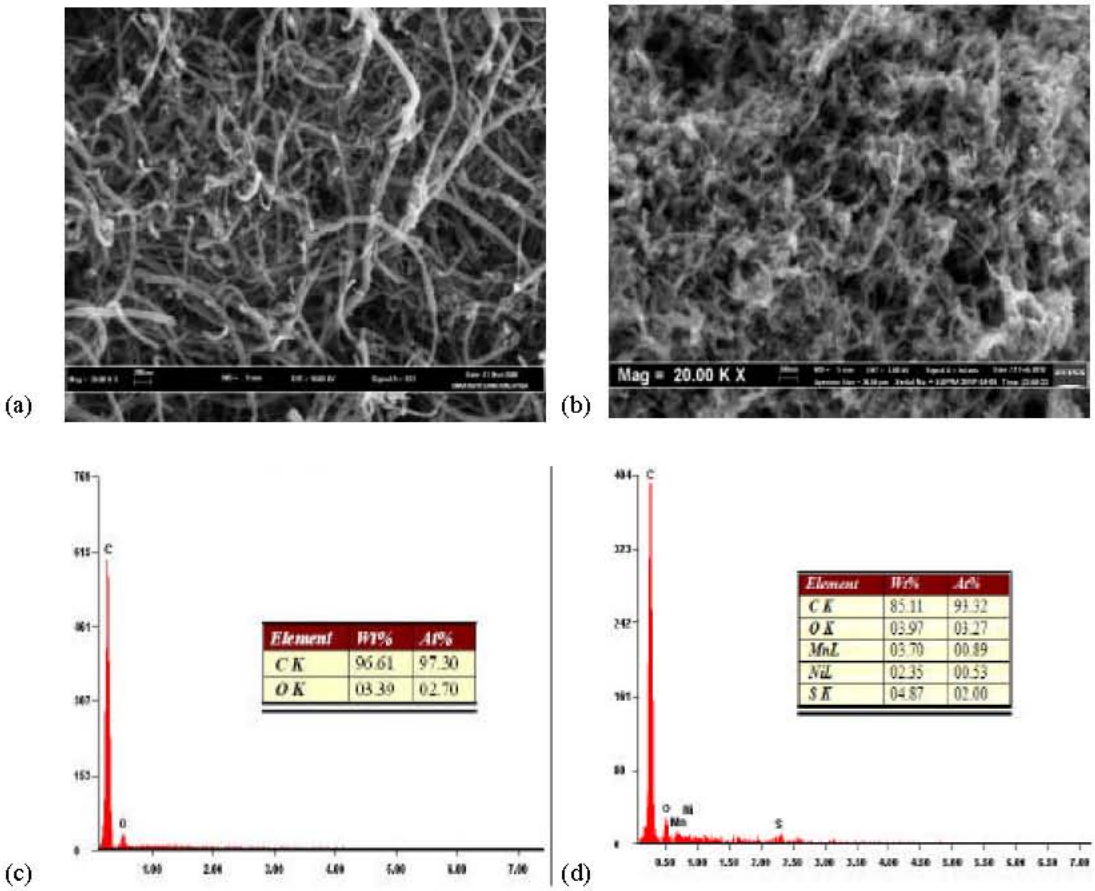

Fig. 1: SEM images of (a) MWCNTs, (b) NMO/MWCNTs/PEDOT and EDX spectra of (c) MWCNTs, (d) NMO/MWCNTs/PEDOT

in Figs. 1(a and b), respectively. The nanotubes became thicker as the PEDOT coated on the outer surface of the tubes. Most of the MWCNTs were coated with a homogeneous layer of polymers and the nanocomposites formed a coralloid network.

The result of EDX analysis for pure MWCNTs in Fig. 1(c) shows that the structure is solely carbon and oxygen and no catalyst elements were detected. Fig. 1(d) confirmed that nanocomposite is consisted of the elements; C, Mn, Ni, O and S indicated that the EDOT was successfully polymerized [15] over NMO/MWCNTs.

Electrochemical Characterization of NMO/ MWCNTs/ PEDOT Nanocomposite: The electrochemical properties of the NMO/MWCNTs/PEDOT nanocomposites prepared from chemical oxidation polymerization have been studied by CV and CD techniques. CV curve of the best sample, as shown in Fig. 2(a) is quasi-rectangular in shape, which is in accordance with the behavior of an ideal capacitor [16]. This behavior of rectangular CV shape represents the rapid response of current to change of potential, which is essential to ensure optimum energy storage during fast charge and discharge processes. Fig. 2(b) shows the CD graph of NMO/MWCNTs/PEDOT nanocomposite in which the graph was linear and symmetrical. These characteristics imply that all electrode materials have excellent electrochemical reversibility and capacitive properties [17]. Sample No. 7 with longest discharge time of almost 60s has shown the best SC value of 630.86 F/g.

Optimization of Design Parameters via Response Surface Methodology (RSM): RSM is a tool, which is capable of analyzing the data of one or more factors at the time and reveals the relation and the interaction between those factors. The RSM is function by identifying the important factors, which can affect or alter the performance of the product yields. The method aims are to study such factors collectively under different set of condition that can affect the response [18].

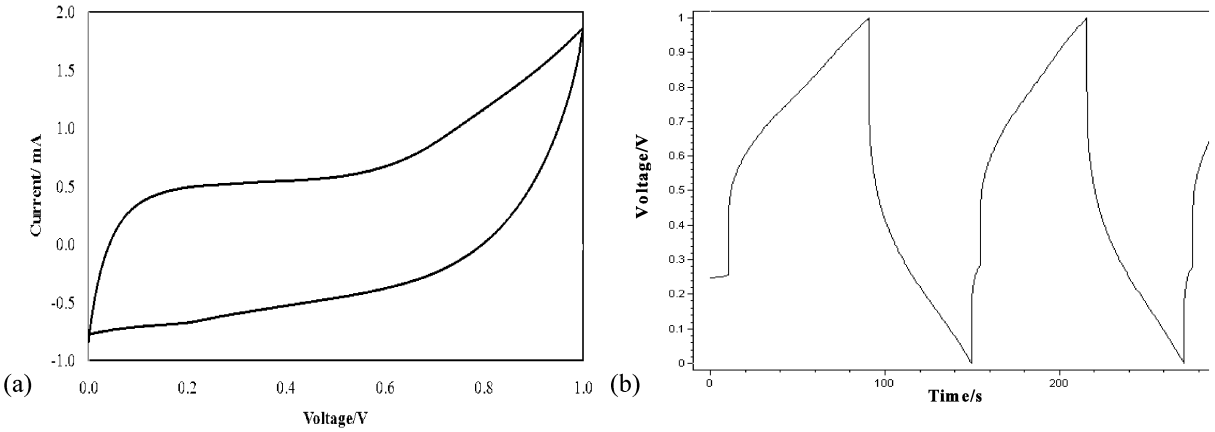

Fig. 2: (a) Cyclic voltammograms and (b) Galvanostatic charge–discharge curves of NMO/MWCNTs/PEDOT at 5mV/s and 10mA/cm^2

Table 2: Design experimental boundaries employed in emulsification process

Factor	Name	Unit	Low actual	High actual	Low coded	High coded
A	Amplitude	%	0	100	-1.0	1.0
B	Emulsification time	min	10	150	-1.0	1.0

Table 3: Response of SC value of NMO/MWCNTS/PEDOT nanocomposites at different emulsification conditions

Run No.	Actual SC value (F/g)	Predicted SC value (F/g)
1	297.14	298.73
2	480.00	486.89
3	160.00	149.21
4	80.00	74.51
5	350.42	376.65
6	400.00	405.01
7	640.00	630.86
8	450.00	490.38
9	502.85	507.64
10	550.00	507.64
11	520.00	507.64
12	480.00	507.64
13	540.00	507.64

In this study, the other factors such as polymerization temperature, concentration of $FeCl_3$ and concentration of EDOT are fixed. The factors selected for study were the percentage of amplitude at constant 20 kHz of frequency and time, both parameters involved in emulsification process.

Development of Regression Model Equation: There are two design parameters used in this study to discover the response of the SC, which are shown in Table 2.

Referring to these experimental boundaries, 13 experiments were created by using the DOE program with full factorial design and responses. Coding A is referred to amplitude change at constant frequency of 20 kHz and coding B referred to period used for the emulsification process. The response studied as the SC value of each samples and the results in terms of actual and predicted SC value are shown in Table 3.

A polynomial regression model was developed using the Central Composite Design (CCD) to analyze the factors interaction that affecting the regression model significantly. According to the sequential model sum of squares, the model was developed by selecting the highest order polynomial where the additional terms are significant and the model is not aliased. A quadratic polynomial equation was suggested to predict the response as a function of independent variables and their interactions. The final empirical model in term of actual factors is shown in Equation (2):

$$SC = 374.28251 + 20.75867A - 7.98810B - 0.18689A^2 + 0.043251B^2 - 0.018776AB \quad (2)$$

Each factor was evaluated by using the response value which is the SC. The R-squared values obtained from the analysis done by DOE. The value of R-squared is 0.9792, which is closer to unity. The significance of R-squared value is it shows better correlations between the experiment and predicted value and besides that it prove that the equations can be used to predict SCs. Fig. 3 depicts that actual data are closed to the predicted data by the DOE.

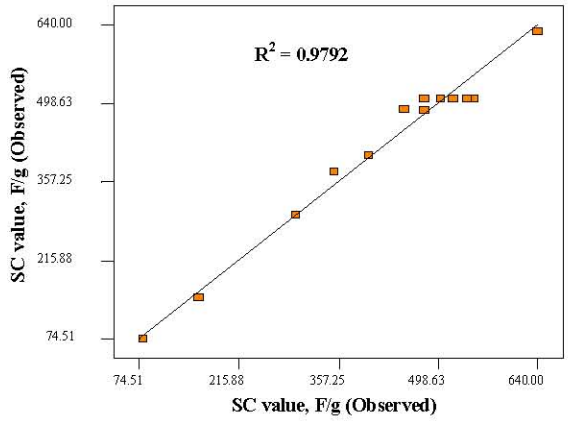

Fig. 3: The relationship between the predicted and actual data for SC value of NMO/MWCNTs/EDOT nanocomposites.

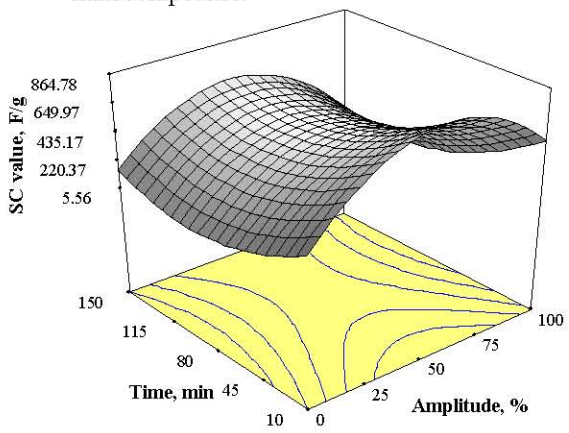

Fig. 4: 3D contour plot of the effects of Amplitude and Time towards SC value of NMO/MWCNT/PEDOT nanocomposites.

Based on the 3D contour plot hown in Fig. 4, the relationship between both manipulated factors of amplitude and emulsification time towards the change in SCs value can be investigated. From Fig. 4, the SC values are maximized if we run the emulsification process at 50% of amplitude at fixed constant frequency of 20 kHz at lower period. From the figure, it can also be detected that if the experiment is carried out under lower period, the value of SC is much higher compared to those with longer period condition. For instance, by having the experiment run at 50% of amplitude and fixing the period at 10 min, the SC value given can reach to a value of 864.77 F/g. In the other hand, by implying the amplitude at 50% and running the emulsification process for about 150 min, the value of SC given is 649.97 F/g. In order to maximize the SC value, emulsification process at lower period and fixed 50% of amplitude at constant 20 kHz frequency is more favored.

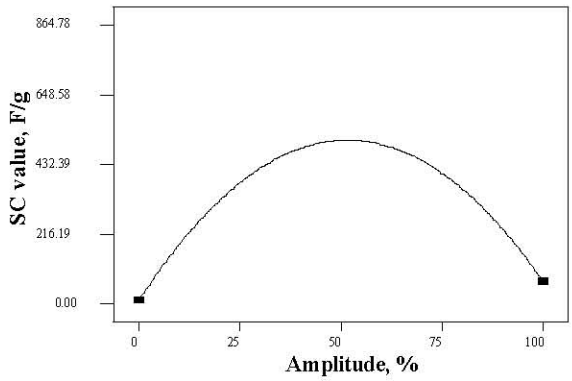

Fig. 5: Main effect plot of SC value response versus amplitude.

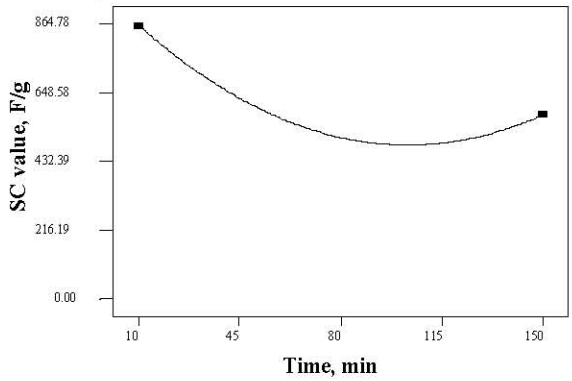

Fig. 6: Main effect plot of SC value response versus emulsification time.

The relationship between SC values and the amplitude is shown in Fig. 5. Most of high SC values are obtained while fixing the amplitude at 50% point. This factor is one of the factors which affecting the SC values significantly. Using 100% amplitude gives better result in comparison to the 0% amplitude. This may occur due to less emulsification effect towards the dispersion of the polymer on the embedded MWCNTs at lower amplitude applied.

Fig. 6 shows the relationship between SC values and emulsification time. From this figure, it is clearly shown that higher SC values are obtained when the emulsification time is shortened. These phenomena occurred possibly because of the early stage of emulsification process, the best structure and network of nanocomposites is obtained. If the emulsification process is further continued, the structure maybe destroyed due to high emulsification effect. The key to increase the electrochemical performance of nanocomposites is the highly uniform structure of the nanocomposites, resulting in large surface area which easily contacted by the abundant electrolyte ions through

Table 4: Optimum conditions for maximum SC value from NMO/MWCNTs/PEDOT nanocomposite

No.	Amplitude (%)	Emulsification time (min)	SC(F/g)	Desirability
1	47.25	12.17	836.27	1.000
2	56.41	17.58	804.87	1.000
3	42.64	21.21	752.67	1.000
4	54.99	38.38	668.16	1.000
5	61.61	36.82	665.71	1.000
6	41.07	30.62	683.93	1.000
7	41.38	11.67	816.89	1.000
8	39.39	18.47	755.54	1.000
9	48.02	150.00	579.83	0.893

the three-dimensional conducting matrix [19]. Hence the operational parameters need to be optimized to achieve the highest electrochemical performance and the maximum SC value.

Process Optimization: In the production of supercapacitor that having high SCs values, its yield can be increased by optimizing the factors studied previously, which are the time and the amplitude percentage. The optimization process was carried out by Design of Expert 6.0 software. In order to optimize the process response (SCs), the function of desirability was applied. For this purpose, numerical optimization has been used as it presents the comprehensive and up to-date optimization. Table 4 indicates the results predicted by Equation (2) developed earlier. In this study, solution number 2 ((A) 47.25% amplitude and (B) 12.17min emulsification time) showed the highest prediction of response (836.27 F/g).

CONCLUSION

In summary, the experimental work has been done to study the effect of the emulsification technique towards the polymerization process. Emulsion polymerization technique leads to the uniform distribution of PEDOT over the surface of NMO/MWCNTs. The EDX spectra and SEM image demonstrated the successful preparation and uniform coating of EDOT over NMO/MWCNTs nanocomposite. Quasi-rectangular shape of CV curve and symmetrical CD graph confirmed that NMO/MWCNTs/PEDOT contains promising electrode materials for supercapacitors. The relation between the two effective parameters of amplitude and emulsification time on the SC value of supercapacitor was studied and optimized by DOE. The highest value of SC achieved in this study was 630.86 F/g. The high accuracy of the model indicates that a quadratic model could be used to optimize the SC value. Using this model, a maximum capacitance of 836.27 F/g was obtained under the condition of 47.25% amplitude at constant 20 kHz frequency and 12.17 min period of emulsification process.

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