

## **Electrochemical Reduction and Deposition of Reduced Graphene Oxide/Manganese Oxide Composite for Supercapacitor Applications via Pulse-Chronoamperometry**

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**Abstract:** The reduced graphene oxide/manganese oxide composite was deposited on the nickel current collector using the Pulse-Chronoamperometry method in a mixture of graphene oxide dispersion and manganese acetate as the precursor. The graphene oxide (GO) was electrochemically reduced to reduced graphene oxide (rGO) and deposited with manganese oxide ( $MnO_x$ ) at the same time. The effects of manganese acetate ( $Mn(Ac)_2$ ) concentration, deposition temperature, voltage and time on the specific capacitance of rGO/ $MnO_x$  electrode were investigated. The electrochemical properties were characterized using galvanostatic charge-discharge and cyclic voltammetry. The effects of electrochemical reduction and deposition parameters on the specific capacitance of rGO/ $MnO_x$  electrode were studied using Central Composite Design methodology and a 2 factors interaction model equation was evaluated. The rGO/ $MnO_x$  electrode synthesized using 0.2 M of  $Mn(Ac)_2$ , at 70 °C and -1.0 V versus Saturated Calomel Electrode (SCE) with a total deposition time of 800s exhibited a specific capacitance of 665 F/g was obtained at the current density of 5 A/g. The high specific capacitance of rGO/ $MnO_x$  electrode showed its potential application for the fabrication of supercapacitors. This study provides an environmental friendly, time effective and costs efficiency way to reduce graphene oxide and to deposit the rGO/ $MnO_x$  composite for electrochemical energy storage application.

**Keywords:** Reduced graphene oxide; Manganese oxide; Electrochemical reduction; Supercapacitor; Pulse chronoamperometry

### **1. Introduction**

The graphene or reduced graphene oxide (rGO) and metal oxide composite has shown high potential application for energy storage devices such as lithium ion batteries and electrochemical capacitors due to their synergistic effects. Graphene or rGO provides a good conductive porous matrix for metal oxide to enhance its electrical conductivity and reduce the charge transfer resistance, while the metal oxide suppresses the restacking of graphene layers and provides a large capacity for energy storage [1]. Various rGO/metal oxide composites have been reported in the application of electrochemical capacitor or supercapacitor such as rGO/SnO<sub>2</sub> [2], rGO/Co<sub>3</sub>O<sub>4</sub> [3], rGO/MnO<sub>2</sub> [4], rGO/Fe<sub>3</sub>O<sub>4</sub> [5], rGO/ZnO [6] and rGO/NiO [7] for the past few years. These composites were prepared using sol-gel, hydrothermal, solvothermal and

electrochemical reduction and deposition methods [8].

Yao and co-workers [4] prepared the rGO/MnO<sub>2</sub> composite using the hydrothermal method with the reflux process. Potassium permanganate, KMnO<sub>4</sub> was used as the precursor and mixed with oxalic acid in the GO dispersion. The resulting mixture was refluxed at 187 °C for 4 hours to obtain MnO<sub>2</sub>-GO composite. The composite was further reduced to graphene nanosheet by mixing with sodium borohydride powder which is a strong reductant, refluxed at 207°C for another 4 hours and finally dried for 12 hours in a vacuum oven at 187°C. The specific capacitance of 467 F/g was measured at the current density of 1 A/g. Ezeigwe et al. [9] reported the solvothermal method to produce graphene/MnO<sub>2</sub> composite with 380 F/g at a scan rate of 5 mV/s. The composite was prepared using manganese sulphate and

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potassium manganate in the graphene dispersion and was autoclaved at 90°C for 15 hours. These methods require a large amount of energy during the heating process and a very long time to synthesize the composite.

The pulse electrodeposition of rGO/MnO<sub>2</sub> composite under supergravity field has been reported by Liu and co-workers [10]. A high specific capacitance of 595.7 F/g at a current density of 0.5 A/g was achieved for the composite prepared using a two-step fabrication method. The microwave assisted exfoliated and reduced GO was dispersed with 4 mM MnSO<sub>4</sub> and pulse deposited with a current density of 0.8 mA/cm<sup>2</sup> with the frequency of 1000 Hz for 60 minutes under intensified supergravity condition. Although rGO/MnO<sub>2</sub> composite prepared by this method exhibited high specific capacitance, the deposition time was long and involved processes of multiple steps.

Recently, the one-step electrochemical reduction and deposition of rGO/metal oxide reported by Liu et al. [11] has attracted extensive attention due to its low temperature, less time consumption, simple with highly controllable processing steps. The electrochemical reduction and deposition can be controlled and carried out with potentiostatic, cyclic voltammetry, potentiodynamic or pulse chronopotentiometry to reduce the graphene oxide to rGO and deposit the metal oxide onto the current collector simultaneously [7].

In this study, rGO/MnO<sub>x</sub> composite was prepared via the pulse chronoamperometry and its specific capacitance was measured as a function of concentration, voltage, temperature and deposition time. The effect of the synthesis parameters on the specific capacitance of rGO/MnO<sub>x</sub> composite was studied using the central composite method. The electrochemical reduction and deposition mechanisms were investigated using the pulse chronoamperometry curves. The rGO/MnO<sub>x</sub> composite prepared with pulse chronoamperometry showed higher specific capacitance compared with those of pure MnO<sub>x</sub> and pure rGO. This method used less energy, less time and no other toxic chemicals were involved. It could be considered as a greener approach for producing the rGO/MnO<sub>x</sub> composite for supercapacitor applications.

## 2. Materials and Methods

### Preparation of graphene oxide (GO).

The GO was prepared using the modified Hummer's method [12]. 6.0 g of graphite powder was mixed with 6.0 g of sodium nitrate, NaNO<sub>3</sub> in 270 mL of concentrated sulfuric acid, H<sub>2</sub>SO<sub>4</sub>, in an ice bath to keep the temperature lower than 5°C. The mixture was stirred for 5 hours using a magnetic stirrer. After that, 36.0 g of potassium permanganate, KMnO<sub>4</sub> was added slowly into the mixture within 90 minutes by keep stirring it at 300 rpm, while the temperature was controlled below 15°C. The mixture was left to be stirred overnight at room temperature in a fume hood until it became yellowish brown color. 1.2 L of deionized water was added to the mixture and stirred for another 10 minutes.

The yellow dispersion containing GO was vacuum filtered by using Buchner Funnel with Whatman filter paper No. 1. The filtered graphene oxide was washed with hydrochloric acid to remove the metal ions and rinsed with deionized water to remove the acid residue. The filtered GO was further exfoliated by dispersing in deionized water and sonicated with ultrasonic cleaner for an hour.

The dispersion was later transferred into the centrifuge bottles and centrifuged at 3000 rpm for 30 minutes with centrifuge machine (Labafuge 400) to separate GO from the solution. The supernatant was decanted and the remaining GO slurry was collected and dried in an oven at 60°C until constant weight. The dried GO was further grinded into powdery form and kept in a sealed container.

**Electrochemical reduction and deposition of rGO/MnO<sub>x</sub> composite.** 0.5 g of GO powder was well dispersed in 500 mL of deionized water by sonicating it for an hour. The GO dispersion was centrifuged at 500 rpm for 20 minutes to remove the bigger size of GO. The supernatant was separated and kept for further use. 0.2 M of Manganese Acetate (Mn(Ac)<sub>2</sub>) solution was prepared by dissolving 12.25 g of Manganese Acetate tetrahydrate in 250 mL of volumetric flask. The precursor solution mixture was prepared by mixing 20 mL of GO dispersion and 20 mL of 0.2 M Mn(Ac)<sub>2</sub> (volume ratio of 1:1) in the coating cell's beaker.

The rGO/MnO<sub>x</sub> composite was electrochemically reduced and deposited on the nickel current collector. Nickel plate with a thickness of 0.15 mm was cut into a smaller size of 1.5 cm x 2.5 cm. Each nickel plates was cleaned, air dried and kept in a sealed container before the deposition. The electrochemical reduction and deposition was carried out using a potentiostat (Ivium CompactStat.e) with the Pulse Chronoamperometry method. Nickel plates were used as both working and counter electrodes, whereas the Saturated Calomel Electrode (SCE) acted as the reference electrode. The voltage was set to -1.0 V for 50 s and followed by 1.0 V for another 50 s and repeated for 5 cycles, with the total reduction and deposition time of 500 s at temperature of 40°C. After the deposition, the working electrode was rinsed with deionized water and air dried. The weight of the nickel plate before and after the deposition was measured and recorded.

The four factors of electrochemical reduction and deposition of rGO/MnO<sub>x</sub> composite were investigated by using Central Composite Design. 30 runs of experiment were generated by using Design Expert V10 with the following working ranges as shown in Table 1. Each factor was set to 5 levels with 16 factorial points, 8 axial points and 6 center points. The experiments were repeated by conducting the whole 30 runs of experiment generated.

**Table 1** Four factors' working ranges for Central Composite Design.

Code	Factors	Low	High	-alpha	+alpha
A	Voltage (V)	1.0	1.5	0.75	1.75
B	Deposition Time (s)	500	800	350	950
C	Temperature (°C)	40	70	25	85
D	Concentration (M)	0.2	0.4	0.1	0.5

**Electrochemical characterisation of rGO/MnO<sub>x</sub> electrodes.** The electrochemical properties of rGO/MnO<sub>x</sub> electrodes were characterized using Galvanostatic charge-discharge (GCD) and Cyclic Voltammetry (CV) with three electrodes system with rGO/MnO<sub>x</sub> electrode as working electrode, platinum as counter electrode while SCE was

used as reference electrode. The 1.0 M sodium sulphate, Na<sub>2</sub>SO<sub>4</sub> was used as the electrolyte.

For GCD, the current density of 5 A/g was used to charge the rGO/MnO<sub>x</sub> electrode from open circuit voltage up to 1.0 V and discharge it at the same current density to 0 V for 5 cycles. The specific capacitance (*C<sub>sp</sub>*) was calculated using Eq. 1 from the 5th cycle.

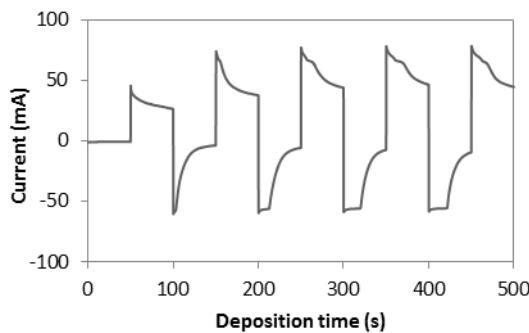
$$C_{sp} = (I \times \Delta t) / (m \times \Delta V) \quad (1)$$

where *I* is the charging/discharging current (A),  $\Delta t$  is the charging/discharging time (s), *m* is the mass of the active material (g) and  $\Delta V$  is the changes of voltage (V). For CV, the current was measured in the potential range of 0 to 1.0 V vs. SCE at the scan rates of 50 mV.

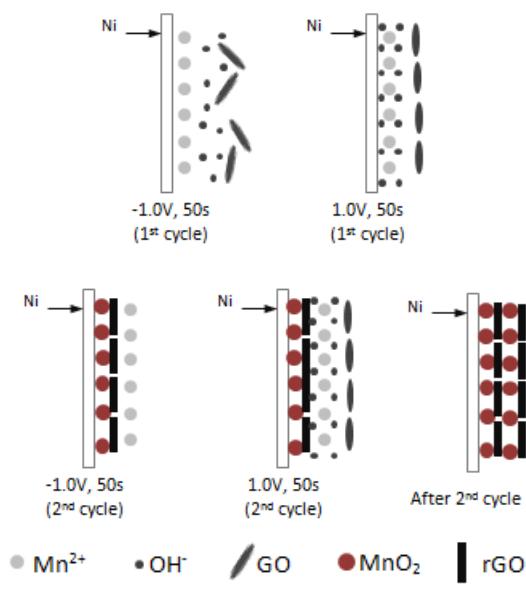
### 3. Results and Discussions

Fig. 1 shows the pulse chronoamperometry curve of electrochemical reduction and deposition of rGO/MnO<sub>x</sub> composite prepared with -1.0 V for 50 s and followed with 1.0 V for another 50 s per cycle. It was conducted using 0.2 M Mn(Ac)<sub>2</sub> in the GO dispersion as the precursor at temperature of 40°C. In the initial 50 s, the current measured was small and maintained at a constant value of 0.65 mA due to the high polarization resistivity of the GO and Mn(Ac)<sub>2</sub> solution. The manganese ions, Mn<sup>2+</sup> were moved towards the surface of the working electrode due to the electrostatic attraction force. After 50 s, a spike current of ~45mA was measured when the voltage of 1.0 V was supplied to the working electrode; the electrical double layer was charged and the deposition of MnO<sub>2</sub> occurred according to the Eq. 2. At the same time, the negatively charged of GO was attracted towards the surface of the working electrode. As the thickness of deposited MnO<sub>2</sub> increases at the working electrode, the current has dropped from 45 mA to 26 mA due to the resistivity of the deposited MnO<sub>2</sub>, the diffusion of free ions in the electrolyte and the concentration gradient between the working electrode and counter electrode.





**Fig. 1** The pulse-ch chronoamperometry curve for electrochemical reduction and deposition of rGO/MnO<sub>2</sub> composite using voltage of -1.0 V for 50 s and 1.0 V for 50 s per cycle with 0.2 M of Mn(Ac)<sub>2</sub> at the temperature of 40°C.

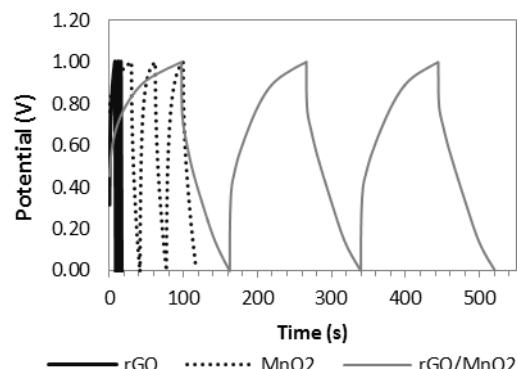


**Fig. 2** Schematic diagram of the proposed mechanism for the electrochemical reduction and deposition of rGO/MnO<sub>2</sub> composite via pulse chronoamperometry with 1.0 V for 50 s and followed by -1.0 V for another 50 s.

At 100s, the voltage -1.0 V was supplied, a peak of -60 mA was observed, a large current has been consumed to reduce the GO to rGO on the surface of the working electrode. As the GO on the working electrode surface was consumed, the resistivity increases and the current decreased dramatically to -3 mA before the 1.0 V was applied. The deposition of MnO<sub>2</sub> and electrostatic migration of GO

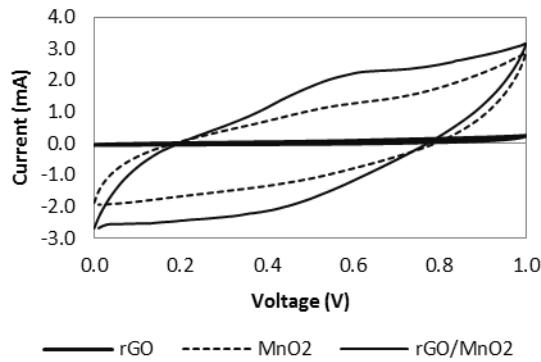
toward the working electrode repeated again in the next cycles.

Fig. 2 shows the proposed mechanisms for electrochemical reduction and deposition of rGO/MnO<sub>2</sub> composite which were corresponding to the pulse-ch chronoamperometry curve at different stages and cycles as shown in Fig. 1. The electrochemical reduction and deposition was repeated until layers of rGO and MnO<sub>2</sub> were obtained on the nickel current collector. Starting from the 3rd cycles of pulse chronoamperometry, the interval for current to be held at a current of 60 mA was increased from 20 s to 50 s which showed that the concentration of GO was decreased and a longer time is required to reach the equilibrium concentration on the diffusion layer.



**Fig. 3** The galvanostatic charge-discharge curve for rGO/MnO<sub>2</sub> compared with pure MnO<sub>2</sub> and rGO prepared with -1.0 V and 1.0 V for 60 s respectively using 0.2 M Mn(AC)<sub>2</sub> at 60°C.

Fig. 3 shows the comparison of charge-discharge curves from which the specific capacitance of rGO/MnO<sub>2</sub> (383 F/g), pure MnO<sub>2</sub> (103 F/g) and rGO (6 F/g) were calculated. The synergistic effects of rGO/MnO<sub>2</sub> resulted in substantial improvement in specific capacitance which could be due to reduced agglomeration of metal oxide, increased total effective surface area, as well as preventing the restacking of rGO layers that acted as conductive networks for the metal oxide.



**Fig. 4** Cyclic voltammetry curve for rGO/MnO<sub>2</sub> compared with pure MnO<sub>2</sub> and rGO prepared with -1.0 V and 1.0 V for 60 s respectively using 0.2 M of Mn(Ac)<sub>2</sub> at 60°C.

Fig. 4 shows the cyclic voltammetry of rGO/MnO<sub>2</sub> composite as compared with pure MnO<sub>2</sub> and rGO. Due to its low resistivity of rGO, the CV curve of rGO showed very small area. By comparing the CV curves of rGO/MnO<sub>2</sub> and MnO<sub>2</sub>, the rGO appeared to play an important role in increasing the electrical conductivity of MnO<sub>2</sub> and hence increasing the specific capacitance of MnO<sub>2</sub>.

The effects of voltage, deposition time, temperature and concentration of Mn(AC)<sub>2</sub> on the specific capacitance were further investigated with 30 runs of experiment generated from the Central Composite Design as presented in Table 2. Based on the first 16 factorial designs, increasing applied voltage significantly increased the specific capacitance at lower deposition time, temperature and also concentration, but decreased specific capacitance at higher deposition time and temperature while maintaining the same concentration of 0.2 M Mn(Ac)<sub>2</sub>. As a whole, increased applied voltage could have led to reduction in the specific capacitance of rGO/MnO<sub>x</sub> composite when the experiments were conducted at higher concentration of 0.4 M of Mn(AC)<sub>2</sub>, especially at higher temperature of 70°C. The highest specific capacitance of 665 F/g was obtained for rGO/MnO<sub>x</sub> composite prepared using 1.0 V for 800 s of deposition time at 70°C with 0.2 M of Mn(AC)<sub>2</sub> in ~1 mg/mL of GO dispersion.

**Table 2** The specific capacitance of rGO/MnO<sub>x</sub> as a function of voltage, deposition time, temperature and concentration of Mn(Ac)<sub>2</sub>.

Run	A:Voltage (V)	B:Deposition time (s)	C:Temperature (°C)	D:Concentration (M)	Specific Capacitance (C <sub>sp</sub> )
1	1	500	40	0.2	232
2	1.5	500	40	0.2	476
3	1	800	40	0.2	203
4	1.5	800	40	0.2	188
5	1	500	70	0.2	308
6	1.5	500	70	0.2	349
7	1	800	70	0.2	665
8	1.5	800	70	0.2	330
9	1	500	40	0.4	244
10	1.5	500	40	0.4	244
11	1	800	40	0.4	150
12	1.5	800	40	0.4	239
13	1	500	70	0.4	302
14	1.5	500	70	0.4	69
15	1	800	70	0.4	128
16	1.5	800	70	0.4	62
17	0.75	650	55	0.3	610
18	1.75	650	55	0.3	228
19	1.25	350	55	0.3	495
20	1.25	950	55	0.3	172
21	1.25	650	25	0.3	222
22	1.25	650	85	0.3	128
23	1.25	650	55	0.1	525
24	1.25	650	55	0.5	198
25	1.25	650	55	0.3	286
26	1.25	650	55	0.3	286
27	1.25	650	55	0.3	453
28	1.25	650	55	0.3	237
29	1.25	650	55	0.3	192
30	1.25	650	55	0.3	365

The experimental data were further analyzed using ANOVA (Table 3). The final equation for the specific capacitance of rGO/MnO<sub>x</sub> composite is expressed in Eq. 3,

$$\text{Specific Capacitance (C}_{\text{sp}}\text{)} = +286.20 - 43.29\text{A} - 37.70\text{B} + 2.04\text{C} - 81.95\text{D} - 23.68\text{AB} - 56.93\text{AC} - 9.06\text{AD} + 35.81\text{BC} - 18.81\text{BD} - 54.31\text{CD} \quad (3)$$

where, A is the applied voltage, B is the deposition time, C is the temperature and D is the Mn(AC)<sub>2</sub> concentration.

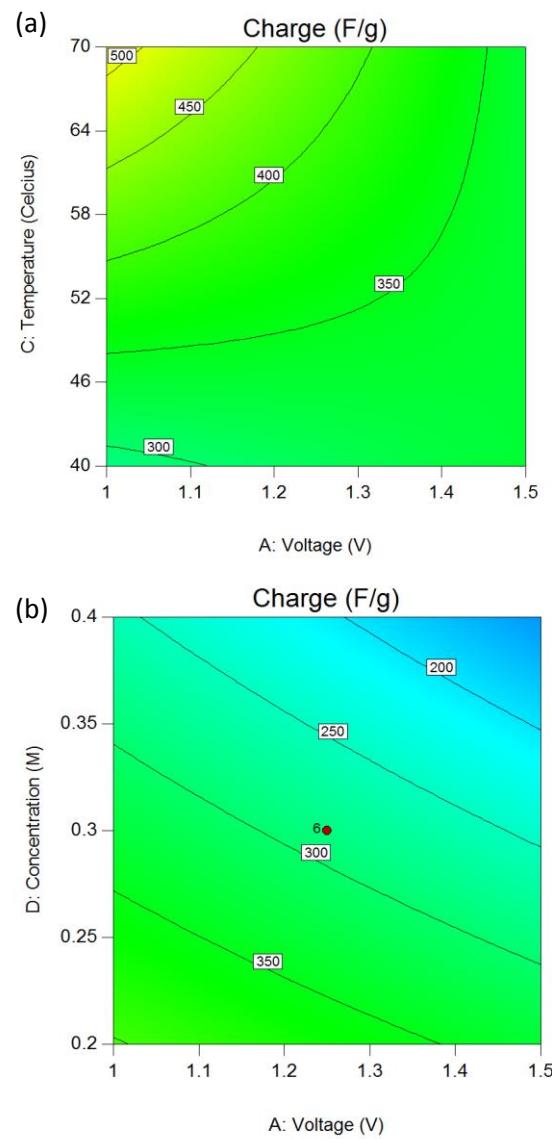
In the ANOVA test, the Prob > F for the specific capacitance is 0.0382 which is less than 0.05, hence, the 2-Factors Integration model is deemed significant. There is a 3.82% chance that the F-value for the specific capacitance could occur due to noise.

**Table 3.** Analysis of ANOVA for response surface 2FI model.

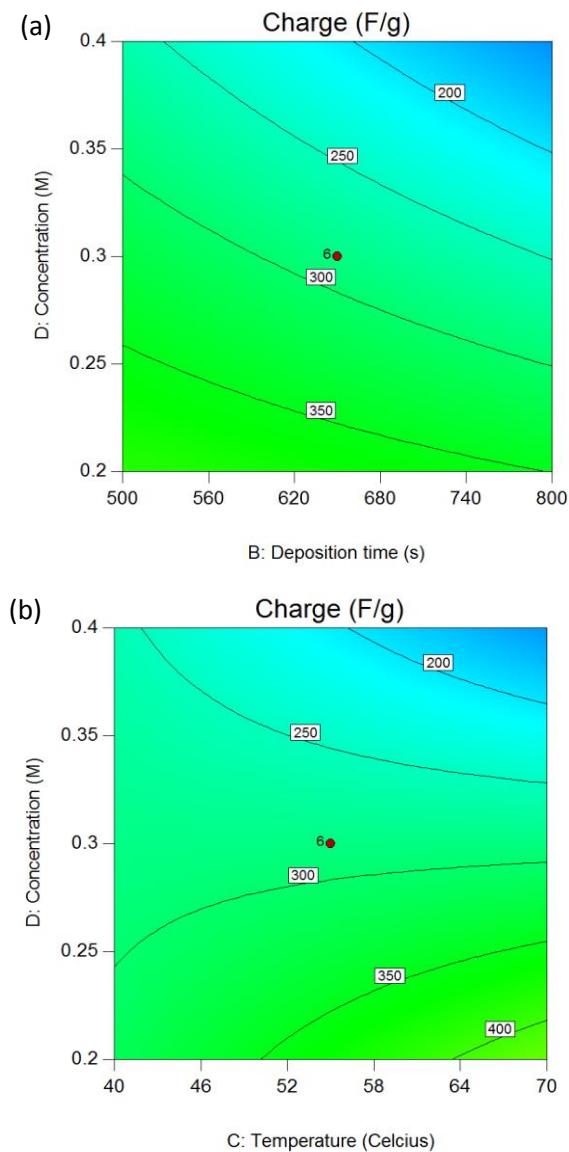
Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F
Model	$3.760 \times 10^{+005}$	10	3759.6	2.55	0.038
A-Voltage	44980.04	1	44980	3.05	0.097
B-Deposition time	34126.04	1	34126	2.31	0.145
C-Temperature	100.04	1	100	$6.77 \times 10^{-003}$	0.935
D-Concentration	$1.612 \times 10^{+005}$	1	$1.612 \times 10^{+005}$	10.9	0.004
AB	8977.56	1	8978	0.61	0.445
AC	51870.06	1	51870	3.51	0.076
AD	1314.06	1	1314	0.09	0.769
BC	20520.56	1	20520	1.39	0.253
BD	5662.56	1	5662	0.38	0.543
CD	47197.56	1	47198	3.20	0.090
Residual	$2.806 \times 10^{+005}$	19	14769		
Lack of Fit	$2.370 \times 10^{+005}$	14	16929	1.94	0.239
Pure Error	43598.83	5	8720		
Cor Total	$6.566 \times 10^{+005}$	29			

Fig. 5 and 6 show the effects of electrochemical reduction and deposition of rGO/MnO<sub>x</sub> composite on its specific capacitance under various controlled conditions. By referring to the generated Eq. 3, Fig. 5 and 6, higher deposition temperature and time with lower applied voltage and concentration of Mn(AC)<sub>2</sub> could significantly contribute to a high specific capacitance. A specific capacitance of ~500 F/g could be

achieved when the applied voltage of 1.0 V was used for the reduction and deposition at the temperature of 70°C using 0.2 M of Mn(AC)<sub>2</sub> for 650 s (Fig. 5(a)). Although the factor of temperature was analysed to be not significantly affecting the reduction and deposition process in the ANOVA test, the contour plots in Fig. 6 show the opposite trend where there is a reduction in specific capacitance with the decreasing of temperature especially when low concentration of Mn(AC)<sub>2</sub> was used (Fig. 6(b)).



**Fig. 5** The effects of electrochemical reduction and deposition parameters on the specific capacitance of rGO/MnO<sub>x</sub> composite (a) using 0.2 M of Mn(AC)<sub>2</sub> with deposition time of 650 s, (b) at temperature of 55°C with deposition time of 650 s



**Fig. 6** The effects of electrochemical reduction and deposition parameters on the specific capacitance of rGO/MnO<sub>x</sub> composite (a) using applied voltage of 1.25 V at temperature of 55°C and (b) using applied voltage of 1.25 V with deposition time of 650 s.

The model results suggested that using a lower concentration of Mn(AC)<sub>2</sub> for the electrochemical reduction the deposition processes literally provides a free space for the mass transfer of GO towards the surface of the electrode and get reduced to become rGO and to be embedded within the MnO<sub>x</sub> matrix and hence improved the charge transfer process. Higher concentration of Mn(AC)<sub>2</sub> precursor, would restrict the movement of GO towards the electrode, and increased the compactness of the MnO<sub>x</sub> layer formed on the surface,

which led to a lower specific capacitance due to higher charge transfer resistance. This explained the concentration factor was found to significantly affect the specific capacitance in the ANOVA test with its Prob > F for the specific capacitance is 0.0037, which is less than 0.05. Using higher temperature and lower concentration of precursor during the electrochemical reduction and deposition process would facilitate the mass transfer of GO and Mn<sup>2+</sup> precursor towards the surface of the electrode by reducing the concentration gradient. Meanwhile, the lower voltage of 1.0 V reduced the formation of hydrogen gas bubbles on the surface of the electrode, as the voltage of 1.25V and above could cause the hydrolysis of water.

#### 4. Conclusions

The rGO/MnO<sub>x</sub> composite electrode prepared using the pulse-chronoamperometry is a single step preparation method that is ergonomic and environmental friendly. MnO<sub>x</sub> and the GO was reduced and deposited on the Ni current collector at the same time to form a composite which could be a potential electrode material for supercapacitor. The specific capacitance of rGO/MnO<sub>x</sub> could be tailored by controlling the preparation parameters of applied voltage, deposition time, temperature and the Mn(AC)<sub>2</sub> concentration according to the 2FI model generated from Central Composite Design.

Generally, rGO/MnO<sub>x</sub> composite of high specific capacitance can be prepared by using 0.2 M Mn(AC)<sub>2</sub> mixed with GO dispersion as the precursor, and electrochemically reduced and deposited onto a current collector using 1.0 V at a temperature of 70 °C for 500 s. Increasing concentration of Mn(AC)<sub>2</sub> and applied voltage would tend to reduce the specific capacitance of rGO/MnO<sub>x</sub> composite due to lower mobility of GO towards the surface of the electrode and the formation of hydrogen bubbles from the hydrolysis of water. However, the composition ratio of deposited rGO/MnO<sub>x</sub> composite prepared using different Mn(AC)<sub>2</sub> concentrations need to be accurately determined in order to support assumptions on the mass transfer of GO towards the surface electrode.

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