

Short Communication

## Structural and Morphological Properties of MnO<sub>2</sub>/MWCNT Composite Grown Using the Hydrothermal Method for Supercapacitor Application

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Received: 8 May 2019 / Accepted: 14 August 2019 / Published: 30 August 2019

Manganese dioxide and multi-walled carbon nanotubes (MWCNT) have received considerable recent interest for their potential application in supercapacitors, MnO<sub>2</sub> as a pseudocapacitor material and MWCNT as an electrochemical double layer capacitance (EDLC) material. The combination of MnO<sub>2</sub> and MWCNT is expected to make promising supercapacitor electrodes. In this study, MnO<sub>2</sub> was mixed with MWCNT during the hydrothermal process. The difficulty in obtaining MnO<sub>2</sub>/MWCNT composite homogeneity in the hydrothermal process provides a challenge to scaling up production. KMnO<sub>4</sub> and MWCNT were mixed with 20 mL distilled water and stirred using a magnetic stirrer for 2 minutes, then placed into an autoclave. Heating of autoclave was carried out at 160°C for 3 hours in an oven and followed by cooling at room temperature naturally. Manganese dioxide/MWCNT composites were made in 1:1 and 3:1 ratios. The diffraction peaks of composites indicated that incorporation of MWCNT into MnO<sub>2</sub> has provided a crystalline orientation derived from MnO<sub>2</sub> and MWCNT. Scanning electron microscopy and TEM imaging demonstrated that MnO<sub>2</sub>/MWCNT 3:1 composite attained better homogeneity than MnO<sub>2</sub>/MWCNT 1:1 as indicated by the attachment of MnO<sub>2</sub> to the entire nanotubes surface of MWCNT. Increasing of conductivity values have been supported by MWCNT marked decreasing in the R<sub>ct</sub> value in electrochemical impedance spectroscopy measurements. Based on cyclic voltammogram measurements, the MnO<sub>2</sub>/MWCNT electrode 3:1 produced specific capacitance (C<sub>s</sub>) of 252 F/g with stability up to 1000 cycles.

**Keywords:** MWCNT, MnO<sub>2</sub>, hydrothermal method, structural, morphology, supercapacitor

### 1. INTRODUCTION

To date, many materials have been studied as supercapacitor electrodes such as manganese dioxide (MnO<sub>2</sub>), nickel oxide/hydroxide, cobalt oxide/hydroxide and conducting polymer. In recent

years, manganese oxide has garnered increasing attention for its potential use in energy storage media, catalysis, ion transport, molecular adsorption and biosensors due to its unique physical and chemical properties [1-11]. As an energy storage material, manganese oxide is especially important because of its high capacitance capability, abundance in nature, very low inherent toxicity, potential produced (approaching one volt) is large enough to trigger high energy storage, environmentally friendliness and low cost.

Manganese dioxide has a layered or tunnel-shaped crystal structure that can facilitate the diffusion of ions into bulk material. It has very low electrical conductivity ( $10^{-4}$ - $10^{-6}$  S.cm<sup>-1</sup>) by itself however, which can be increased by combining it with multiwalled carbon nanotubes (MWCNT) that have high electrical conductivity and mechanical strength [12]. In general, supercapacitors can provide higher power than most batteries because a large amount of charge can be stored in a double layer. But for power density relatively low, because of series resistance of two electrodes. Increasing power and power density requires material with high capacitance and low resistance. Manganese dioxide combined with MWCNT should optimize the performance of supercapacitors as MWCNT will provide percolation of the active particles more efficiently compared to traditional carbon materials and form the open mesopore network that drives the ion diffusion to the composites' active surface [13].

Manganese dioxide has been synthesized in a number of ways, including by thermal decomposition [13], the sol-gel process [14], refluxing [15], sonochemical reduction [16] and hydrothermal [17]. The hydrothermal method is the preferred method because it can produce multiple shapes with a simple process [18]. Other advantages include energy savings (carried out at low temperatures), cost-effectiveness, simplicity, high purity (conducted within tightly-closed containers), high reaction rates and low temperatures when using the right solvent [19]. In previous studies, the synthesis between MnO<sub>2</sub> and MWCNT was carried out separately so that the incorporation of MnO<sub>2</sub> and MWCNT materials became less than perfect. This causes low homogeneity and restricts transfer of redox reaction charges. In addition, the composition between MnO<sub>2</sub> and MWCNT under *in-situ* hydrothermal process also affects homogeneity of composite. High homogeneity of MnO<sub>2</sub>/MWCNT composites will decrease composite agglomeration. Charge transfer is mediated by the high conductivity of MWCNT, so that the homogeneity of composites achieved with the hydrothermal method is advantageous to scaling up. This necessitates appropriate composition adjustment between MnO<sub>2</sub> and MWCNT under *in-situ* hydrothermal conditions.

In this study, MnO<sub>2</sub>/MWCNT was synthesized using the hydrothermal method. Multi-walled carbon nanotubes were mixed with MnO<sub>2</sub> in certain ratios and subjected to an *in-situ* hydrothermal process so that the composite of materials maximized homogeneity. The incorporation of MWCNT and MnO<sub>2</sub> can make promising supercapacitor electrodes.

## 2. EXPERIMENTAL

### 2.1. Preparation of MnO<sub>2</sub>/MWCNT composites.

Synthesis of MnO<sub>2</sub> was carried out in a 20 ml Teflon-lined stainless-steel autoclave [18]. MnO<sub>2</sub> nanorods were synthesized using 2.5 mmol KMnO<sub>4</sub> dissolved in distilled water at room temperature. Hydrochloric acid was added and the solution was stirred for ten minutes using a magnetic stirrer then placed into an autoclave (20 ml). Separately, MWCNT were synthesised using the spray pyrolysis

method. Three g of ferrocene and 50 ml benzene were combined and stirred using a magnetic sterilizer for 30 minutes, and the solution injected into a tube heated at 900°C and flooded with argon gas for 30 minutes. After cooling to room temperature [20], the product was refluxed using 65% HNO<sub>3</sub>, cured with distilled water to neutral pH and dried to produce MWCNT [21].

Multi-walled carbon nanotubes and KMnO<sub>4</sub> were combined using the hydrothermal process. After mixing with 20 mL distilled water and stirred using a magnetic stirrer for 2 minutes, the MWCNT and KMnO<sub>4</sub> solution was placed into an autoclave. The autoclave was heated in oven mode at 160 °C for 3 hours then cooled to room temperature. Four samples were used in this study MWCNT powder, MnO<sub>2</sub> powder, MnO<sub>2</sub>/MWCNT 1:1 and MnO<sub>2</sub>/MWCNT 3:1.

## 2.2. Structure characterization

The intensity and angle of x-ray scattering of the material was obtained using X-ray diffraction spectroscopy (XRD, Philip Analytical X-Ray) with CuK $\alpha$  radiation ( $\lambda=1.5418$  Å) at 40 kV and 20 mA adjusted to the MnO<sub>2</sub>/MWCNT crystal structure database. Morphology of samples was characterized using a scanning electron microscope (SEM, JEOL-6510LA) and transmission electron microscope (TEM). The FTIR spectra were obtained using a Nicolet Avatar 360 FTIR spectrometer.

## 2.3. Electrochemical measurement

To fabricate supercapacitor electrodes, 0.2 g of ethylcellulose was dissolved in 4 mL ethanol and the solution stirred for 10 minutes, followed by mixing 1.6 g terpeneol into the binder. The MnO<sub>2</sub>/MWCNT was dispersed in the binder by stirring for 10 minutes. Then MnO<sub>2</sub>/MWCNT paste was deposited onto the SS foil substrate by using the doctor blade method and drying at 150 °C for 2 hours. Electrochemical impedance spectroscopy (EIS) and cyclic voltametry (CV) measurements performed using LCR meter HIOKI 3532-50 chemical impedance meter and WBCS3000S Wonatech, respectively. The measurements were carried out in a standard double cell containing 1 M KCl aqueous solution.

## 3. RESULTS AND DISCUSSION

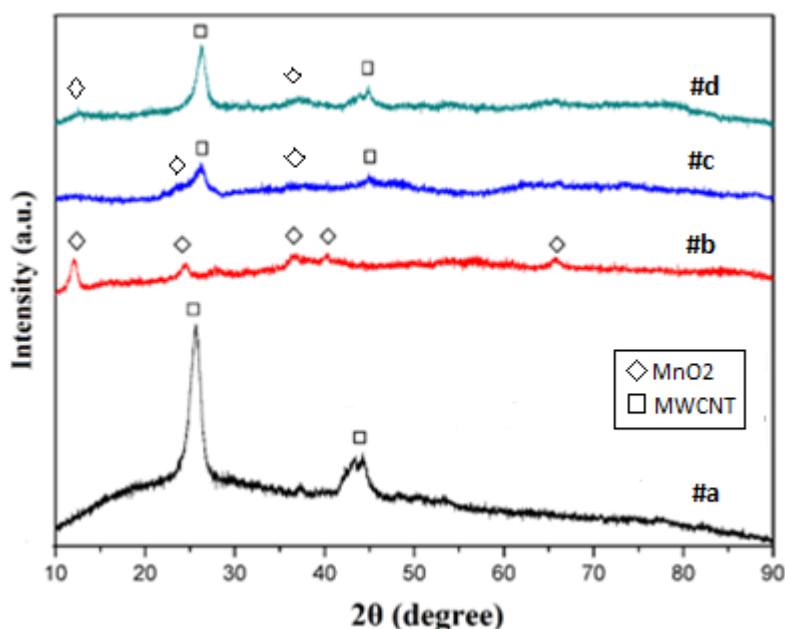
As the hydrothermal process synthesis of MnO<sub>2</sub>/MWCNT was carried out within a closed container, the ideal gas laws were applicable. In the ideal gas law, there are three related quantities: pressure, temperature and volume. In the hydrothermal method, the volume of gas in a closed space is fixed [22]. The formation of MnO<sub>2</sub> from the hydrothermal process using KMnO<sub>4</sub> and HCl in the form of a KMnO<sub>4</sub> reduction reaction can be written [23]:



The reaction also reflects the nucleation or growth process of MnO<sub>2</sub>. After heating to a sufficiently high temperature (>140°C), KMnO<sub>4</sub> atoms become active, forming the MnO<sub>2</sub> nucleus by decomposition in HCl and water [24]. After that, the growth process of MnO<sub>2</sub> is strongly influenced by the environment, affecting the shape and aggregation of particles. The number of MnO<sub>2</sub> nuclei at the initial nucleation stage and the crystal growth process is influenced by KMnO<sub>4</sub> concentration [25]. Thus, the MnO<sub>2</sub> nanostructure is very much determined by the concentration of KMnO<sub>4</sub> during synthesis. In

the hydrothermal process, MWCNT does not react with  $\text{KMnO}_4$  and  $\text{HCl}$ . The hydrothermal method can help increase crystallinity in materials through the influence of temperature and reaction time [26]. X-ray diffraction spectroscopy characterization was used to determine the crystallinity level of MWCNT and  $\text{MnO}_2$ . Characterization of XRD-synthesized compounds was performed using instruments with an angle range of  $2\theta = 10\text{-}90^\circ$  and wavelength of  $1.5418\text{\AA}$ . The test was carried out on a synthesis sample based on the difference in the MWCNT and  $\text{MnO}_2$  mass ratios in the hydrothermal process. The XRD test results were analyzed by Match! Program using Crystallography Open Database (COD) and based on references in previous studies.

Figure 1a shows that the formed MWCNT has a graphene type carbon structure, based on standard powder diffraction data and previous studies conducted by Hashemzadeh, et.al. (2009) [14]. Presence of graphene shown at peak  $2\theta$  of  $26.3^\circ$  and  $43.9^\circ$  is at the angle of  $2\theta$  formed C (002). The synthesized XRD pattern of  $\text{MnO}_2$  can be seen in Figure 1b. The diffraction pattern shows a peak at  $2\theta$  of  $12.9^\circ$ ,  $24.2^\circ$ ,  $37.8^\circ$ ,  $60.5^\circ$  and  $66.2^\circ$  with the Miller index of (110), (131), (200), (411) and (231) with the index representing a reflection of the plane of the phase  $\alpha\text{-MnO}_2$ . The peak of  $40.9^\circ$  with Miller index of (400) representing the phase  $\beta\text{-MnO}_2$  in accordance with COD databases No.96-151-4235, 96-151-4117, 96-810-3499 and 96-151-4108 [16]. The diffraction peaks of  $\text{MnO}_2/\text{MWCNT}$  3:1 composite compared with those of  $\text{MnO}_2/\text{MWCNT}$  1:1 composite showed that the crystallinity of MWCNT increased with increasing MWCNT mass.

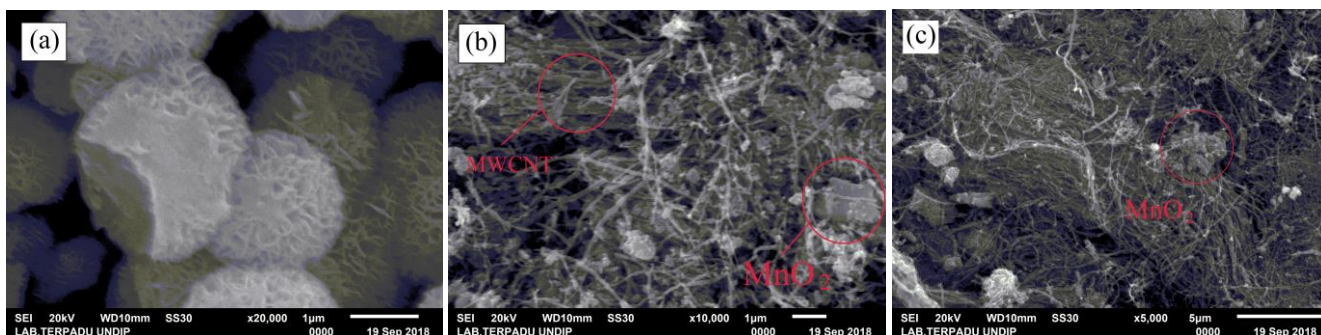


**Figure 1.** XRD image of a) MWCNT; b)  $\text{MnO}_2$ ; c)  $\text{MnO}_2/\text{MWCNT}$  3:1 and d)  $\text{MnO}_2/\text{MWCNT}$  1:1

The morphology of MWCNT,  $\text{MnO}_2$ , and  $\text{MnO}_2/\text{MWCNT}$  with mass ratio 1:1 and 3:1 was determined using the SEM image as shown in Figure 2. Figure 2(a) shows the morphology of  $\text{MnO}_2$  nanorods which coagulate to form nanoflowers (such as flowers). Figures 2(b) and 2(c) show the morphology of  $\text{MnO}_2/\text{MWCNT}$  nanorods with a combination of  $\text{MnO}_2$ .

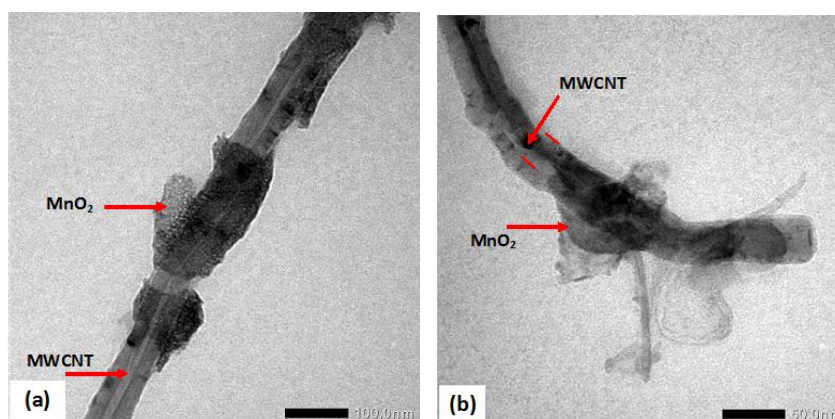
The result of  $\text{MnO}_2/\text{MWCNT}$  synthesis by the hydrothermal method shows the results of even mixing. During the  $\text{KMnO}_4$  reduction process, crystals grown from  $\text{MnO}_2$  condense into two-dimensional (2D)  $\text{MnO}_2$  sheets. Then, at high temperatures and pressures under hydrothermal

conditions, MnO<sub>2</sub> forms small nanorods. Morphology of one-dimensional MnO<sub>2</sub> such as nanotubes, nanowires and nanorods has more advantages compared to other structures, such as short ion diffusion paths and continuous electron transport pathways. Nanorod morphology provides a high surface area to volume ratio which increases material sensitivity, ion diffusion ability and specific capacitance values. Smaller nanorods grow to be bigger and more stable [23]. Stability in the morphology of nanorods also results in oriented attachments to MnO<sub>2</sub> material which can produce morphology of nanorods with aggregation.



**Figure 2.** SEM images of (a) MnO<sub>2</sub>, (b) MnO<sub>2</sub>/MWCNT 1:1, (c) MnO<sub>2</sub>/MWCNT 3:1.

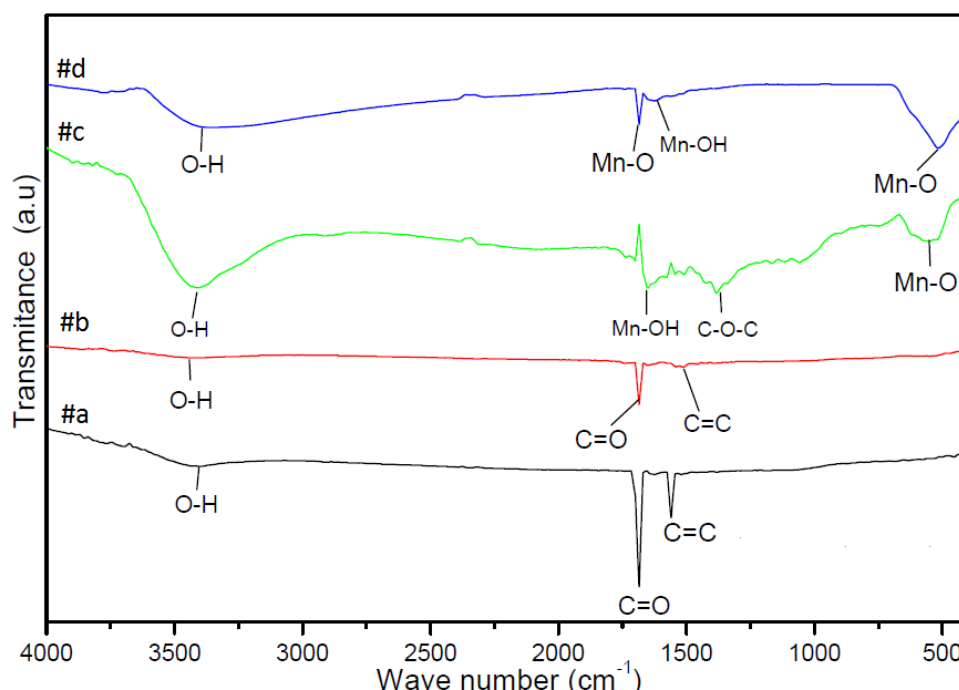
Manganese dioxide morphology was further characterized by transmission electron microscopy (TEM). The results of this analysis showed morphological and distribution images in the sample. The TEM results shown in Figure 3 indicate that MnO<sub>2</sub> material sticks to the wall of MWCNT due to the hydrothermal method. The MWCNT tube size was approximately 40 nm. In the MnO<sub>2</sub>/MWCNT 1:1 sample the surface of the nanotubes were not evenly coated by MnO<sub>2</sub>, whereas in the MnO<sub>2</sub>/MWCNT 3:1 sample MnO<sub>2</sub> could coat all surfaces of the nanotubes. The homogeneity of MnO<sub>2</sub> coating on the MWCNT surface will greatly affect the capacitor performance of the composite. The addition of a larger MnO<sub>2</sub> composition allows the MnO<sub>2</sub> coating process on the surface of the nanotube to be more thorough during the hydrothermal process.



**Figure 3.** TEM image of (a) MnO<sub>2</sub>/MWCNT 1:1 and (b) MnO<sub>2</sub>/MWCNT 3:1

The FTIR spectra of MWCNT, MnO<sub>2</sub>/MWCNT 3:1, MnO<sub>2</sub>/MWCNT 1:1 and MnO<sub>2</sub> are shown in Figure 4. FTIR spectra were recorded in the range of 4000-500 cm<sup>-1</sup> in transmittance mode. The peak

near  $3400\text{ cm}^{-1}$  is attributed to the vibration of the free or bonded OH/COOH groups. This peak could be allocated to the -OH group of the carboxylic groups attached with  $\text{MnO}_2/\text{MWCNT}$ . The peak around  $1430\text{ cm}^{-1}$  was attributed to C-O vibrations from epoxy groups. The peak at  $1429\text{ cm}^{-1}$  was due to the Mn-OH deformation vibration. The peaks located at  $1513\text{ cm}^{-1}$  and  $1322\text{ cm}^{-1}$  were attributed to the C=C and C=C stretching. The peak located at  $1200\text{ cm}^{-1}$ , originated from the stretching vibration of C-O-C bond. The peak at  $553\text{ cm}^{-1}$  was attributed to the Mn-O stretching vibration, indicating the presence of the  $\text{MnO}_2$  crystal, evidence of successful  $\text{MnO}_2$  deposition. The FTIR results indicated the creation of the composites of MWCNT and  $\text{MnO}_2$ . The major groups such as -OH, -COOH, -C=C, -C-O, Mn-OH and Mn-O appeared on the surface of  $\text{MnO}_2/\text{MWCNT}$  composite. These results are consistent with that in other works [27-30].

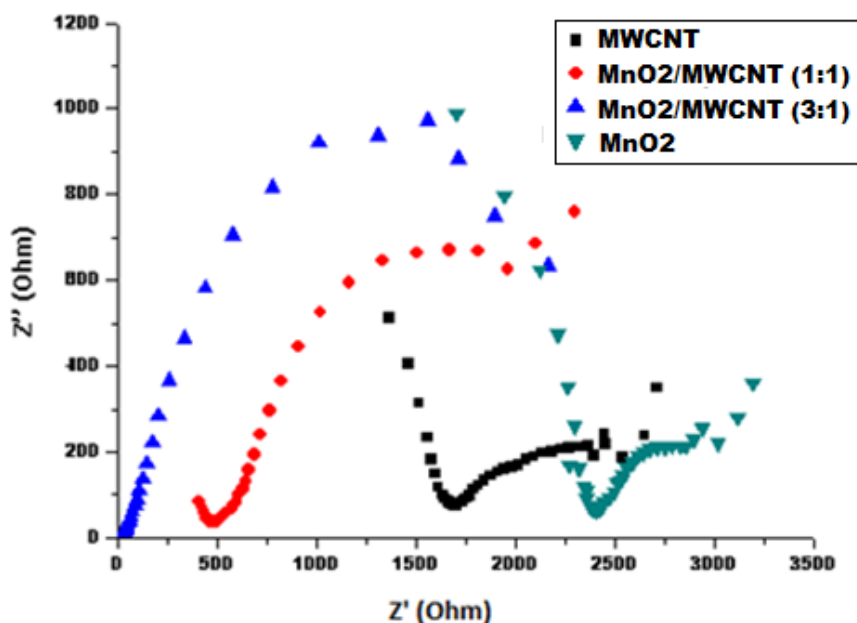


**Figure 4.** FTIR spectra of a) MWCNT; b)  $\text{MnO}_2/\text{MWCNT}$  1:1; c)  $\text{MnO}_2/\text{MWCNT}$  3:1 and d)  $\text{MnO}_2$

Electrochemical impedance spectroscopy measurements were carried out in the frequency range from 100 kHz to 10 mHz in order to evaluate the frequency response of  $\text{MnO}_2$ , MWCNT and  $\text{MnO}_2/\text{MWCNT}$  electrodes. These measurements were useful in evaluating the resistive factor of the electrode and characterization of EIS was conducted to understand the interaction between electrolyte and electrode. Figure 5 represents the Nyquist plot of supercapacitor of  $\text{MnO}_2/\text{MWCNT}$  electrodes to obtain the circuit resistance ( $R_{ct}$ ) of the electrode by measuring the semicircular diameter on the real axis. This resistance corresponds to the resistance at the electrolyte/electrode interface [31]. The magnitude of  $R_{ct}$  obtained from the semicircle loop of the Nyquist plot were found to be  $28\ \Omega$ ,  $412\ \Omega$ ,  $1512\ \Omega$  and  $2418\ \Omega$  for  $\text{MnO}_2/\text{MWCNT}$  3:1,  $\text{MnO}_2/\text{MWCNT}$  1:1, MWCNT and  $\text{MnO}_2$ , respectively. Manganese dioxide/MWCNT samples had smaller  $R_{ct}$  values than others indicating that the load transfer process was well-mediated in the presence of MWCNT which increases the material conductivity value. The  $R_{ct}$  value for  $\text{MnO}_2/\text{MWCNT}$  3:1 was greatly improved after the incorporation of MWCNT to



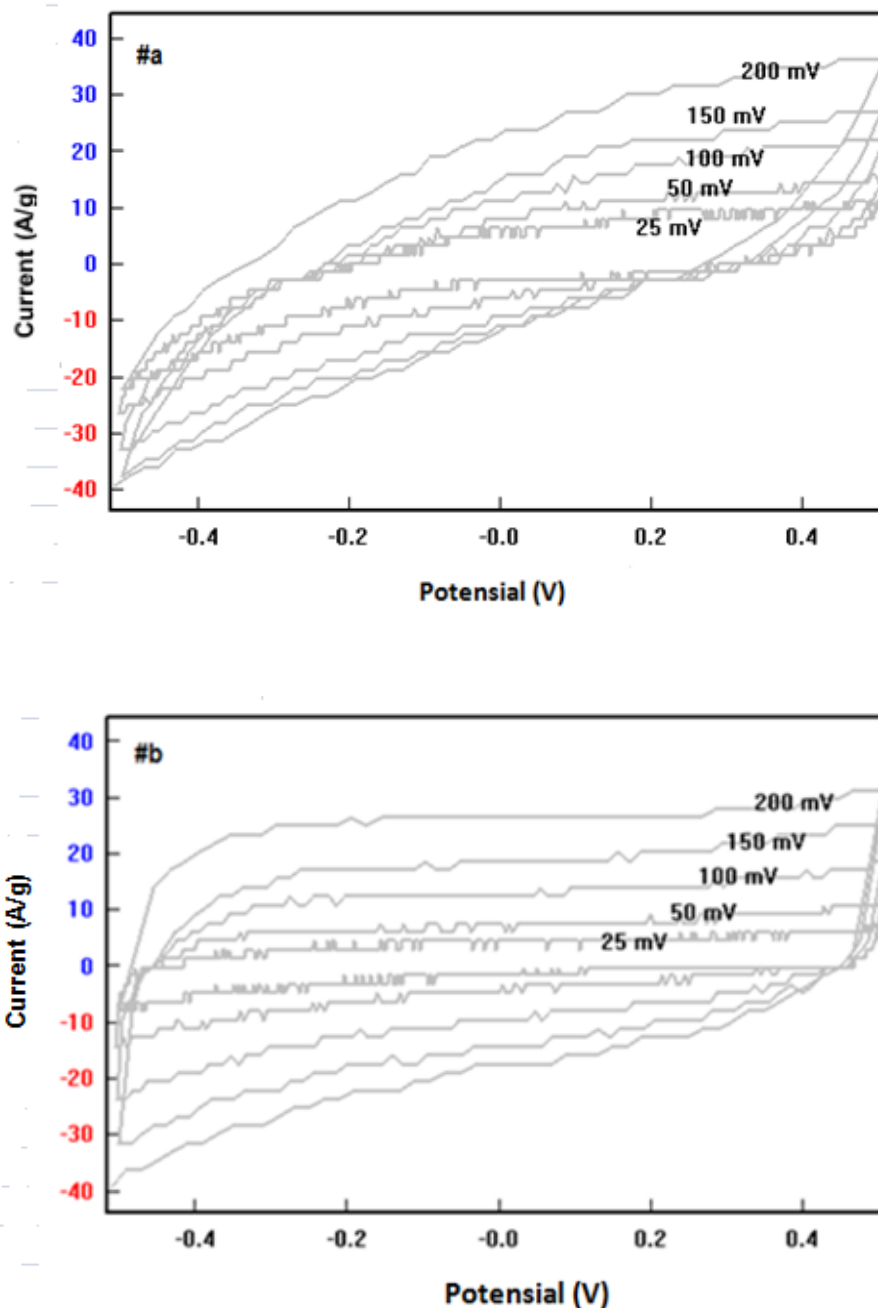
MnO<sub>2</sub>. However, the MWCNT electrode still had relatively high  $R_{ct}$  due to the presence of an ion diffusion mechanism which should be mediated by oxide material (in this case MnO<sub>2</sub>).



**Figure 5.** Nyquist plots of the EIS of MWCNT, MnO<sub>2</sub>/MWCNT 1:1, MnO<sub>2</sub>/MWCNT 3:1 and MnO<sub>2</sub>.

Cyclic voltammetry testing was carried out using a WBCS3000 tool, Automatic Battery Cycler Ver.3.2. The purpose of cyclic voltammetry testing was to determine the capacitive properties of MnO<sub>2</sub>/MWCNT 1:1 and MnO<sub>2</sub>/MWCNT 3:1 electrodes in 1 M KCl aqueous solution. Data obtained from testing cyclic voltammetry in the form of a potential curve to the current. The measurement of the specific capacitance values was with variations in scan rates of 200, 150, 100, 50 and 25 mV/s. The curve pattern formed a hysteresis curve with quasi square or rectangular shapes. The hysteresis pattern showed that the supercapacitor electrodes used have capacitive properties, i.e., when the voltage reaches 0.4 volts and is reduced to -0.4 volts, the current value produced does not have the same current value as before.

Figure 6 shows cyclic voltammograms of (a) MnO<sub>2</sub>/MWCNT 1:1 and (b) MnO<sub>2</sub>/MWCNT 3:1 electrode material at scan rates from 25 mV/s to 200 mV/s. The ion diffusion process at a low scan rate is lengthy. Ions and electrons coming from the current collector will diffuse evenly to the electrode surface to the pore meso depending on the homogeneity of MnO<sub>2</sub>/MWCNT. Increasing the homogeneity of MnO<sub>2</sub>/MWCNT through the hydrothermal process will support this diffusion process. An increase in the width of the charge current and discharge curve will occur, indicated by a large capacitance value. On the other hand, at a high rate of induction, the ion diffuses rapidly but only just reaches the surface of the electrode, resulting in a small charge and discharge current curve which indicates a low capacitance value.



**Figure 6.** Cyclic voltammograms of (a) MnO<sub>2</sub>/MWCNT 1:1 and (b) MnO<sub>2</sub>/MWCNT 3:1 electrode material at scan rates from 25 mV/s to 200 mV/s.

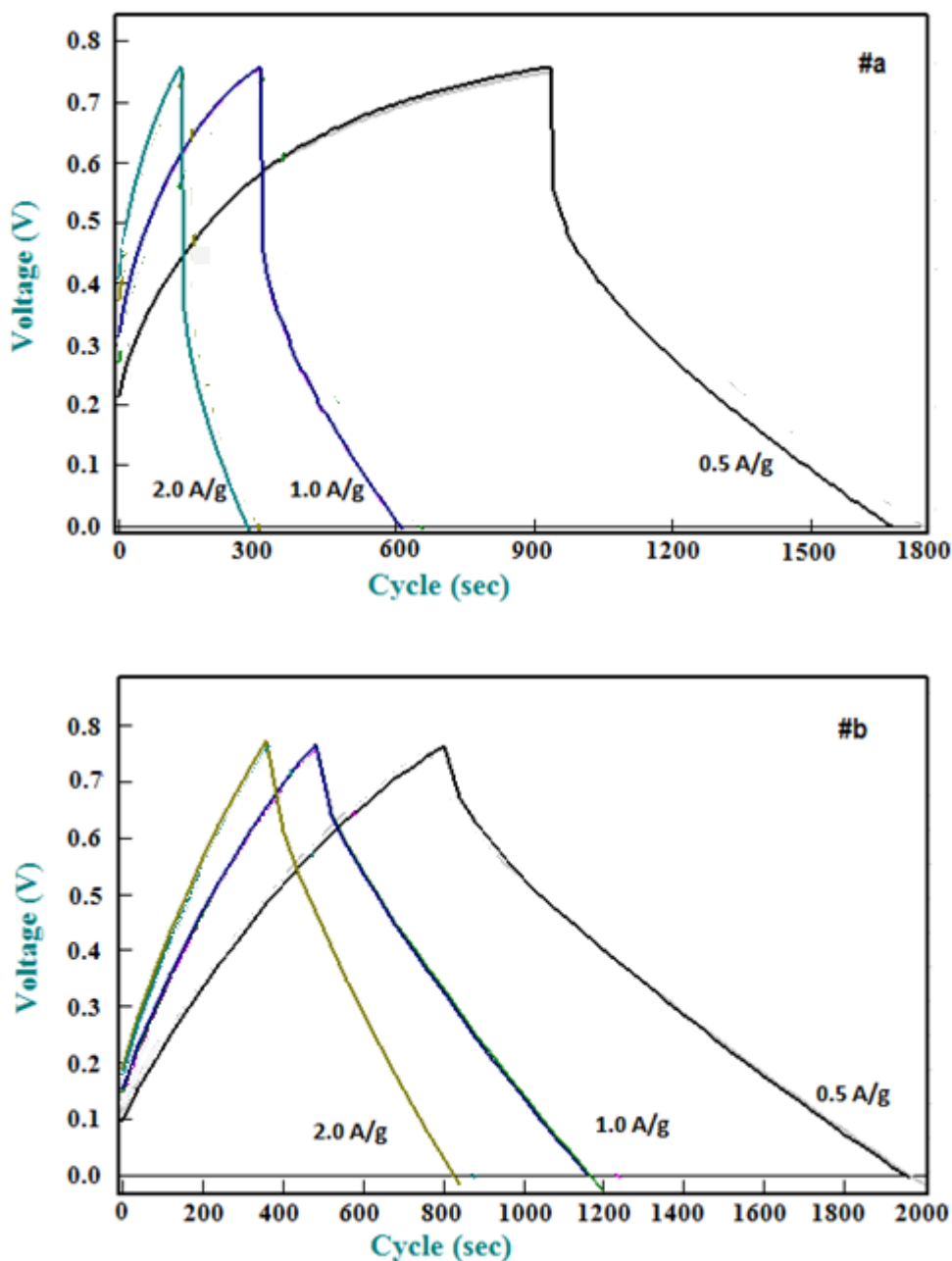
The galvanostatic charging/discharging curves of the composites electrodes at a current density of 0.5, 1.0 and 2.0 A/g are shown in figure 7. The sample MnO<sub>2</sub>/MWCNT 3:1 in figure 7b shows the charging/discharging curves have more symmetrical properties than sample MnO<sub>2</sub>/MWCNT 1:1 in figure 7a. This shows that the sample MnO<sub>2</sub>/MWCNT 3:1 has good electrochemical capacitive characteristics and superior reversible Faradaic reactions, implying excellent reversibility and high coulombic efficiency. The specific capacitance can be calculated from the discharging curve based on the equation [32,33,34]:



$$C_s = \frac{I \cdot \Delta t}{m \cdot \Delta V}$$

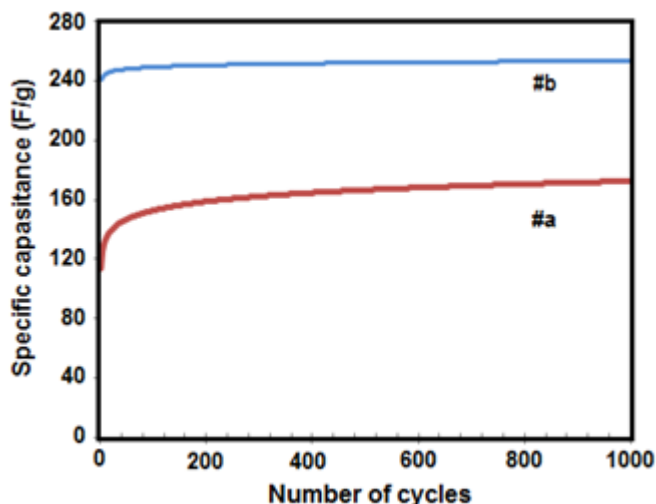
Here I (A) is the applied current, Δt (s) is the discharge time, m (g) is the mass of active material, ΔV (V) is the discharging potential window.

In the curve produced a specific capacitance value calculated at 0.5 A/g for the sample MnO<sub>2</sub>/MWCNT 3:1 of 252 F/g and this value was greater than the sample MnO<sub>2</sub>/MWCNT 1:1 of 170 F/g. This shows that the homogeneity of the sample MnO<sub>2</sub>/MWCNT 3:1 was better than that of MnO<sub>2</sub>/MWCNT 1:1 because MnO<sub>2</sub> can fully coat the surface of the nanotube of MWCNT as shown in TEM images.



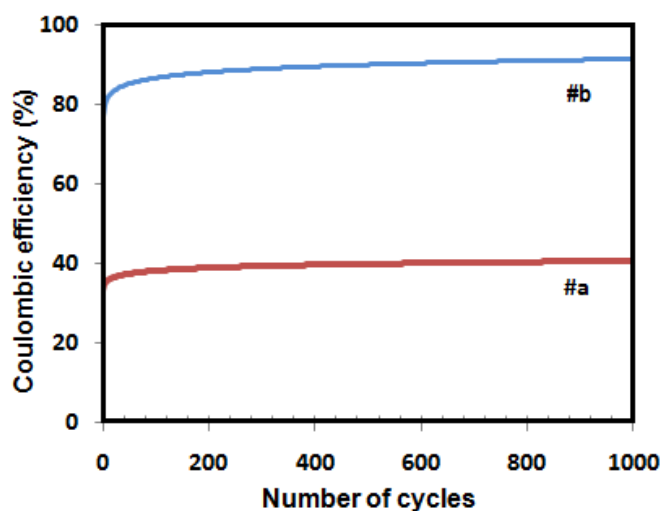
**Figure 7.** The galvanostatic charging/discharging curves at current density of 0.5, 1.0 and 2.0 A/g of (a) MnO<sub>2</sub>/MWCNT 1:1 and (b) MnO<sub>2</sub>/MWCNT 3:1 electrodes.

Figure 8 shows the variation of specific capacitance ( $C_s$ ) with cycle numbers of charge–discharge at a constant current density of 0.5 A/g based on the calculation of above equation. The change of  $C_s$  with the increase in deposition time was consistent with CV analysis. The  $MnO_2/MWCNT$  3:1 electrode achieved the highest  $C_s$  of 252 F/g. After 1000 cycles of testing, its  $C_s$  remained at 245 F/g, about 97% of the initial value, though electrolyte is used. It indicates that the  $MnO_2/MWCNT$  3:1 electrode process good reversibility in the repetitive charge/discharge cycling and showed their potential in the application of supercapacitors. Conversely, there was instability in the  $MnO_2/MWCNT$  electrode 1:1 with a  $C_s$  starting at 120 F/g that increased to around 160 F/g at 200 cycles and then reaching 170 F/g at the end of the 1000 cycles.



**Figure 8.** The specific capacitance ( $C_s$ ) of (a)  $MnO_2/MWCNT$  1:1 and (b)  $MnO_2/MWCNT$  3:1 electrodes is as a function of number of cycles at a constant current density of 0.5 A/g.

Figure 9 shows Coulombic efficiency remained at an average 95% after the 920 cycles indicating the remarkable long-term stability of the  $MnO_2/MWCNT$  3:1 electrode. It also indicates the excellent charge-discharge reversibility of the electrode and potential for supercapacitor application.



**Figure 9.** Variation of the Coulombic efficiency of (a)  $MnO_2/MWCNT$  1:1 and (b)  $MnO_2/MWCNT$  3:1 electrodes as a function of number of cycles at a constant current density of 0.5 A/g.

Table 1 shows the specific capacitance values of the MnO<sub>2</sub>/MWCNT electrodes obtained from other methods. It can be seen that the results of the research that we did produce relatively high C<sub>s</sub> values

**Table 1.** MnO<sub>2</sub>/MWCNT specific capacitance (C<sub>s</sub>) of several methods.

Samples	Method	Electrolite	Specific Capacitance (C <sub>s</sub> ) F/g	Ref.
MnO <sub>2</sub> /MWCNT 3:1	hydrothermal	KCl	252	This study
CNT@NCT@MnO <sub>2</sub> 3D	chemical method	Na <sub>2</sub> SO <sub>4</sub>	210	[1]
CNT-MnO <sub>2</sub> nanoflaky	chemical method	Na <sub>2</sub> SO <sub>4</sub>	145.6	[10]
MWCNT/MnO <sub>2</sub>	sonochemical	Na <sub>2</sub> SO <sub>4</sub>	394	[16]
3D MnO <sub>2</sub> -CNT	in-situ hydrothermal	Na <sub>2</sub> SO <sub>4</sub>	214	[26]
MnO <sub>2</sub> /rGO-CNT	modified hummers	KCl	295.83	[28]
MnO <sub>2</sub> @NCNTs@MnO <sub>2</sub>	solvothermal	Na <sub>2</sub> SO <sub>4</sub>	253.1	[30]

#### 4. CONCLUSION

In conclusion, this results show that successful synthesis of MnO<sub>2</sub>/MWCNT can explain incorporation of MWCNT into MnO<sub>2</sub> using the hydrothermal method. The diffraction peaks of MnO<sub>2</sub>/MWCNT 1:1 and MnO<sub>2</sub>/MWCNT 3:1 showed that the crystallinity of MWCNT increased with increasing MWCNT mass. Both TEM images of MnO<sub>2</sub>/MWCNT 1:1 and 3:1 composites showed that MnO<sub>2</sub> material was attached to MWCNT walls by the hydrothermal process, and MnO<sub>2</sub>/MWCNT 3:1 allowed for MnO<sub>2</sub> to cover all surfaces of MWCNT. This demonstrated better homogeneity so that the specific capacitance (C<sub>s</sub>) of 252 F/g was produced with stability up to 1000 cycles.

#### ACKNOWLEDGMENTS

The authors gratefully acknowledge Ministry of Research, Technology and Higher Education of the Republic of Indonesia (University Collaboration Research 2018) for financial support.

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