

## HIGH PERFORMANCE FLOWER SHAPE MANGANESE OXIDE FOR ASYMMETRIC SUPERCAPACITOR DEVICE

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### ABSTRACT

*A flower shaped manganese oxide have been synthesized using simple and low temperature procedure. Subsequently, an asymmetric supercapacitor is fabricated using manganese oxide and activated carbon as positive and negative electrode in aqueous electrolyte. The supercapacitor was measured at open windows 2.0 V showing energy density of 25.79 Wh/kg at power density of 100 W/kg. The supercapacitor stability was tested at 3 A/g and showing specific capacitance retention of 95% after 850 cycles.*

**KEYWORDS:** *Energy storage; supercapacitor; manganese oxide; asymmetric capacitor.*

### 1.0 INTRODUCTION

Supercapacitor is an energy storage devices that provide advantages compared to conventional capacitor including high specific capacitance ( $C_S$ ) and energy density ( $E_D$ ) (Conway, 1999). The energy stored in supercapacitor are governed by two mechanisms, (i) electrical double layer capacitor (EDLC)–ions adsorption on the electrode-electrolyte interface and fast and (ii) pseudocapacitance (PC)–a fast and reversible redox reaction mechanism (Simon & Gogotsi, 2008). Asymmetric supercapacitor (ASC) is usually fabricated by combining PC material (eg: metal oxides) as positive electrode and EDLC material (eg: activated carbon, AC) as negative electrode, separated by permeable separator in electrolyte environment. This combination is essential to obtained maximum working potential (1.8–2.4 V).

The current research focused on metal oxides and composites development to enhance  $E_D$  and power density ( $P_D$ ) as this type of material is having higher theoretical capacitance values exceeding 1000 F/g (Liang et al., 2012; Toupin et al., 2002; Vidyadharan et al., 2014; Zhang et al., 2012).

The supercapacitors fabricated using the hydrated ruthenium oxide ( $\text{RuO}_2 \cdot n\text{H}_2\text{O}$ ) electrodes are currently the record holder in terms of specific capacitance ( $C_S \sim 720$  F/g in case of hydrothermal synthesis). This contributes by several factors including high conductivity and crystallite water molecules enhance the electrons and ions hopping.

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However, RuO<sub>2</sub> are relatively rare abundance makes them expensive thereby offering barriers for mass production (Yan et al., 2014; Zheng et al., 1995). Several metal oxide has been studied to overcome this drawback, among them is manganese oxide (MnO<sub>2</sub>). Birnessite-type MnO<sub>2</sub> ( $\delta$ -MnO<sub>2</sub>) gained much attention as an electrode for supercapacitors because of its thin sheet-like layered structure stabilized by an alkali ion (eg: K<sup>+</sup> or Na<sup>+</sup>) and crystallized water is similar to that of the RuO<sub>2</sub>.*n*H<sub>2</sub>O (Dmowski et al., 2002; Kim & Kim, 2006).

In this article,  $\delta$ -MnO<sub>2</sub> is prepared through a simple and low temperature synthesis condition. The ASC was prepared in coin cell type assembly using aqueous potassium sulfate (K<sub>2</sub>SO<sub>4</sub>) electrolyte. This is in order to enhance the potential window of ASC and enhance  $E_D$ . The MnO<sub>2</sub>//AC ASC shows a promising potential window of 2.0 V and demonstrated  $E_D$  of 25.79 Wh/kg at  $P_D$  100 W/kg.

## 2.0 EXPERIMENTAL

### 2.1 Material Synthesis

The synthesis of MnO<sub>2</sub> was carried out using hydrothermal method. In a typical experiment 4.5 mmol of potassium permanganate (KMnO<sub>4</sub>, BDH Chemicals) solution was mixed with 1.5 mmol ammonium persulfate ((NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, Aldrich) in a Teflon lined stainless steel reactor. After being stirred for 20 min, the reactor was kept in an oven at 90 °C for 24 h. After cooling down to room temperature, the brownish precipitate product was filtered; wash thoroughly with DI water until the pH~7, dry at 50°C for 24 h.

### 2.2 Material Characterizations

The MnO<sub>2</sub> were characterized by X-ray diffraction (XRD), field emission scanning electron microscope (FESEM), and transmission electron microscopy (TEM). The XRD patterns were acquired on Miniflex II (Rigaku, Japan) X-ray diffractometer employing CuK <sub>$\alpha$</sub>  radiation ( $\lambda = 1.5406 \text{ \AA}$ ) and Ni- filter. Surface morphology of the samples were investigated using a JSM-7800F (JEOL, Japan) FESEM. The crystal structural details were obtained using Tecnai 20 (FEI, USA) operating at 200 kV accelerated voltage.

### 2.3 Electrode Fabrication and Supercapacitor Assembly

The positive electrode were prepared by mixing active material, MnO<sub>2</sub> (70 wt.%) with carbon (Super P, 15 wt.%) and polyvinylidene fluoride (PVDF) binder (15 wt%) using N-methyl pyrrolidone (NMP) as a solvent. The above mixture was stirred for 24 h and the slurry obtained thereby was coated onto a pre-cleaned nickel foam (pores per inch; 110 ppi) substrate. The coated electrode was annealed at 60°C oven 24 h and finally pressed at 5 MPa using hydraulic press.

The negative electrode were prepared following the similar procedure with positive electrode by replacing commercial activated carbon ( $S_{BET}$ : 1820 m<sup>2</sup>/g, Zhejiang Forest

Energy Technology Co. Ltd, China) as the active material. Supercapacitor was assembled in coin cell type case (CR2032) using fibrous glassy carbon as separator and using 0.5M K<sub>2</sub>SO<sub>4</sub> electrolyte.

## 2.4 Electrochemical Analyses

The electrochemical analysis of cyclic voltammetry (CV), Galvanostatic charge-discharge (CDC) and electrochemical impedance spectroscopy (EIS) were acquired using potentiostat (Autolab PGSTAT 30, Eco Chemie B.V., The Netherlands) employing NOVA 1.9 software. A platinum rod and Ag/AgCl electrode were used as counter and reference electrode for three-electrode configuration analysis. The supercapacitor cycle stability were measured using battery tester (Neware, China). The specific capacitance ( $C_s$ , F/g), energy density ( $E_D$ , Wh/kg), power density ( $P_D$ , W/kg), internal resistance ( $I_R$ ,  $\Omega$ ) and coulombic efficiency ( $\eta$ , %) were calculated according to the following Equation (1)–(6):

$$C_s (CV) = \frac{1}{mv(\Delta V)} \int_{V_a}^{V_b} i(V)dV \quad (1)$$

$$C_s (CV) = 4 \frac{it}{m\Delta V} \quad (2)$$

$$E_D = \frac{1}{2} C_s (\Delta V)^2 \quad (3)$$

$$P_D = \frac{E_D}{t_d} \quad (4)$$

$$I_R = \frac{V_{IR}}{2i} \quad (5)$$

$$\eta = \frac{t_d}{t_c} \times 100 \quad (6)$$

where  $m$  (g) is active mass,  $v$  (mV/s) is scan rate,  $\Delta V$  (V) is the applied potential window (i.e.  $V_a$  to  $V_b$ ),  $i$  (A) is current,  $t_d$  (s) and  $t_c$  (s) are the discharging time and charging time and  $V_{IR}$  (V) is the internal resistance potential drop.

## 3.0 RESULTS AND DISCUSSION

### 3.1 Physicochemical Properties of MnO<sub>2</sub>

The XRD pattern of hydrothermal reaction product of MnO<sub>2</sub> is shown in Figure 1a. The XRD pattern is indexed to the monoclinic potassium birnessite (JCPDF No 43-1456) structure with  $C2/m$  space group (No. 12) (Ghodbane et al., 2009). The (001) and the (002) planes are typical of the layered structure of  $\delta$ -MnO<sub>2</sub> whereas the broadened (100) plane indicates crystallized water and formation of water-MnO<sub>2</sub> interlayer (Truong et al., 2012). The basal plane spacing calculated from the (001) plane is ~0.73 nm,

which is the characteristic of the birnessite  $\text{MnO}_2$  due to water molecule and intercalated potassium ion.

The FESEM images of  $\text{MnO}_2$  at low magnification (Figure 1b) shows uniform flower-like morphology of  $\text{MnO}_2$ . Using Image-J software measurement, the average diameter of the flowers was  $\sim 1.23 \mu\text{m}$ . A higher magnification FESEM image in Figure 1c clearly shows that the curly and folded thin nanosheets of thickness  $\sim 20 \text{ nm}$  are branched out from one central zone.

The bright field TEM image of the  $\text{MnO}_2$  is shown in Figure 1d. The image indicates that the particles have a coronal spherical morphology, which in turn composed of multilayer hierarchical nanosheets. These curly nanosheets in the sphere are grown from a core during hydrothermal reaction. A high resolution TEM (HRTEM) image of a nanosheet is in Figure 1e. The measured spacing along the (001) plane is  $\sim 0.65 \text{ nm}$  in HRTEM, which is lower than that observed in the XRD pattern ( $\sim 0.73 \text{ nm}$ ). This lowering is due to the evaporation of interlayer water molecules under the high energy electron beam irradiation (Liu et al., 2011).

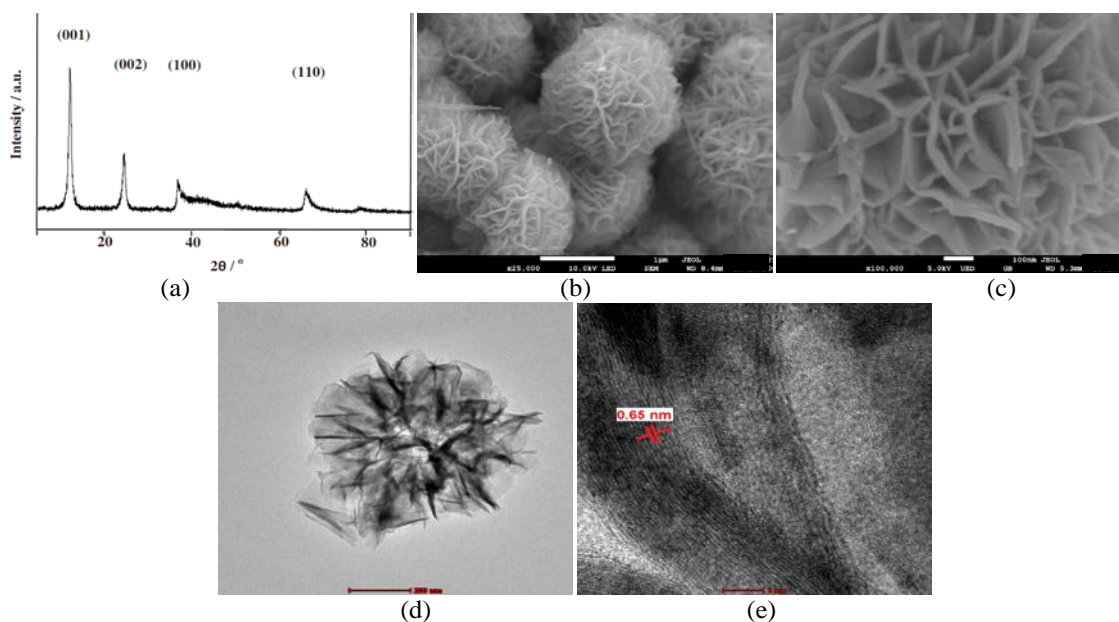


Figure 1. (a) XRD pattern of  $\text{MnO}_2$ ; FESEM micrograph of flower shaped  $\text{MnO}_2$  at (b) low and (c) high magnification; (d) TEM and (e) HRTEM image of  $\text{MnO}_2$

### 3.2 Determination of $\text{MnO}_2//\text{AC}$ Mass Ratio

To balance the charge ( $q$ ) and maximize  $C_s$ , the mass ratio of positive and negative electrode need to be measured. The individual CV scan of  $\text{MnO}_2$  and AC is shown in Figure 2a. The  $\text{MnO}_2$  electrode potential window is in range 0.0 to 0.9 V whereas for AC is in range -1.1 to 0.0 V, in order to archive supercapacitor working potential of 2.0 V. The CV was measured at scan rate 10 mV/s. The mass ratio of  $\text{MnO}_2$  to AC electrode is 0.89, calculated according to Equation (7).

$$\frac{m_+}{m_-} = \frac{C_{S-} \times \Delta V_-}{C_{S+} \times \Delta V_+} \quad (7)$$

### 3.3 Supercapacitor Performance Analysis

The MnO<sub>2</sub>//AC asymmetric supercapacitor CV curve at scan rate 10 mV/s is shown in Figure 2b. It shows that near rectangular CV shape in 2.0 V potential range. The calculated C<sub>S</sub> at this scan rate is 54 F/g. To understand the maximum open potential of MnO<sub>2</sub>//AC capability, the CDC at 1 A/g was measure in potential range 1.2 to 2.4 V. The CDC curve for CDC at different potential is shown in Figure 2c. The curve shows symmetric triangle of charge and discharge; indicate that the optimum reversibility during charging and discharging. The relation of η, C<sub>S</sub> and I<sub>R</sub> is shown in Figure 2d. The η is showing decrease trend respect to increased open potential where the efficiency drops from 99.3% at 1.2 V to 89.5% at 2.4 V. The C<sub>S</sub> and I<sub>R</sub>, however, increase respect to increasing open potential. The C<sub>S</sub> is increased from 93 to 137 F/g and the I<sub>R</sub> increased from 4.98 to 6.90 Ω. The optimize supercapacitor should having higher η and C<sub>S</sub> but minimum I<sub>R</sub>. Thus, open potential of 2.0 V is the most promising for MnO<sub>2</sub>//AC system.

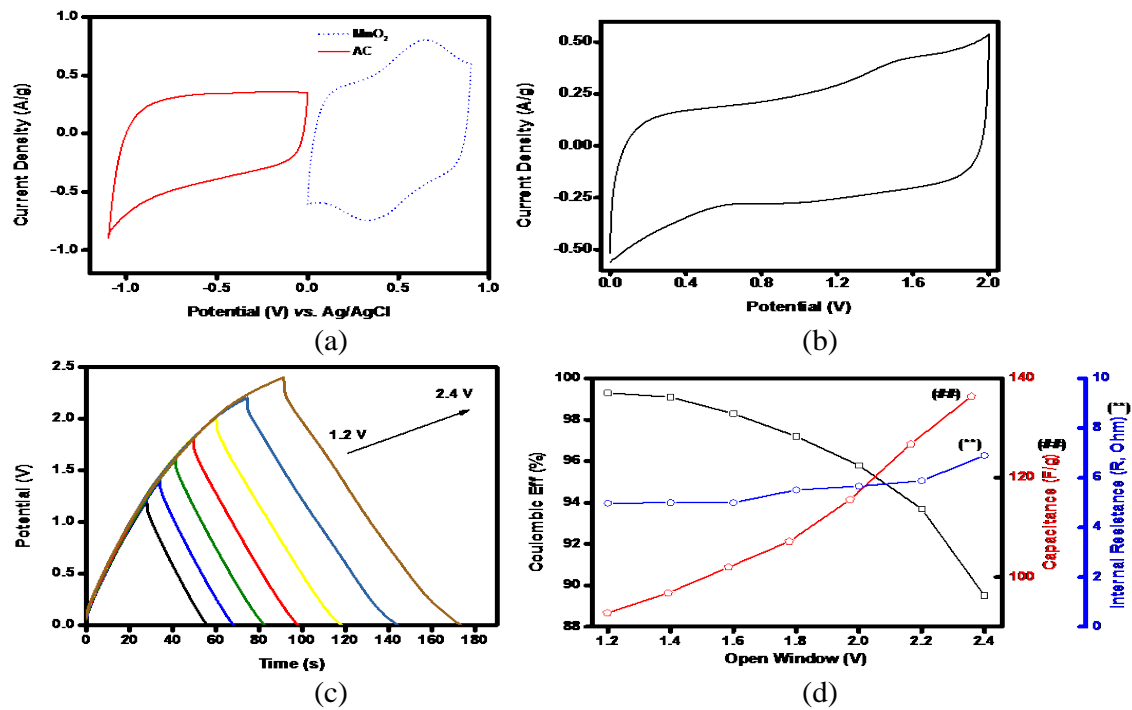


Figure 2. (a) CV curve for MnO<sub>2</sub> and AC electrode; (b) CV curve for MnO<sub>2</sub>//AC supercapacitor at 10 mV/s; (c) CDC curve at current density of 1 A/g for potential range 1.2 – 2.4 V; (d) Variation of η, C<sub>S</sub> and I<sub>R</sub> for different potential

Then, the performance of MnO<sub>2</sub>//AC was tested at different current densities ranging from 3 to 0.1 A/g and the CDC curve is shown in Figure 3a. Near triangle shape for each CDC test indicate that high reversibility of the supercapacitor for each current

density. Clearly, as the current density decreases, the discharge time was also increased. This phenomenon related to the higher fraction of active surfaces that contribute to the intercalation – deintercalation of electrolyte ions at lower current density. The ions have slower time to intercate and accumulate on the active site, hence increased the  $C_S$ .

The relation of  $\eta$ ,  $C_S$  and  $I_R$  for CDC analysis at different current density was shown in Figure 3b. Similar to analysis in Figure 2d, the  $\eta$  is showing decrease trend respect to decrease current densities where the efficiency is 95.2% at 3 A/g, increased to 97.4% (1 A/g) and decrease to 86.1% at 0.1 A/g. The  $C_S$  is dramatically increased from 96 F/g at 3 A/g to 186 F/g at 0.1 A/g. The same trend observed to the  $I_R$  where constant increase from 3.33 to 5.95  $\Omega$ . In this current density range, the  $E_D$  are 13.33, 16.39, 18.28, 19.83 and 25.79 Wh/kg at  $P_D$  of 3000, 1000, 500, 300 and 100 W/kg for current density of 3, 1, 0.5, 0.3 and 0.1 A/g, respectively. The Ragone Plot of  $E_D$  versus  $P_D$  is shown in Figure 3c. The  $MnO_2//AC$  supercapacitor was tested for cell stability test for 850 cycles and the evidence was shown in Figure 3d. the device show promising electrochemical stability with the  $C_S$  retention  $\sim 95\%$  after the end of cycle. The  $\eta$  is unchanged at the end of the stability cycle and shows  $\sim 94\%$  throughout the test.

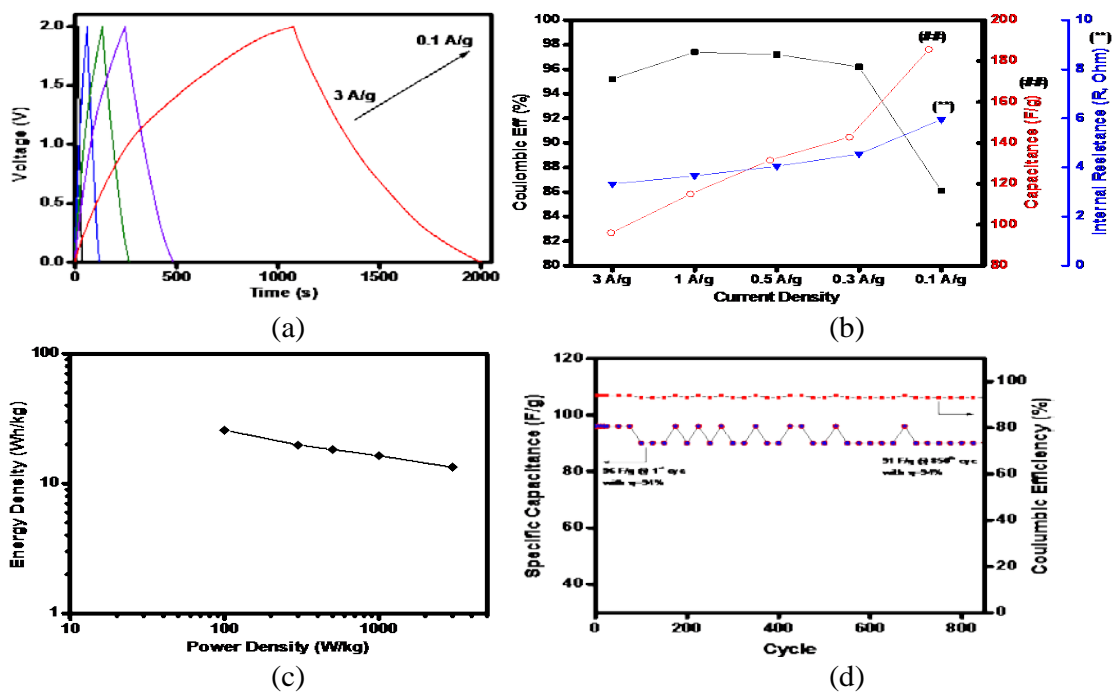


Figure 3. (a) CDC curve at current densities range from 3 – 0.1 A/g; (b) Variation of  $\eta$ ,  $C_S$  and  $I_R$  for different current densities; (c) Ragone plot of  $MnO_2//AC$  supercapacitor; (d) Cycle stability test of  $MnO_2//AC$  supercapacitor

Table 1 summarizes recent published  $MnO_2$  and AC based ASC. The ASC fabricated in this study shows comparable performance and in most cases it is superior than previous reported work. Finally, the Nyquist plot from EIS measurement of the  $MnO_2//AC$  supercapacitor device is shown in Figure 4. The EIS recorded in the frequency range 10

kHz – 10 mHz at a bias voltage of 0.1 V. The EIS spectrum of supercapacitors is routinely deconvoluted into three sections corresponding to three processes offering (i) series resistance ( $R_S$ ); (ii) Warburg ion diffusion; and (iii) capacitive behavior.

Table 1. Comparison of MnO<sub>2</sub> based ASC device

Electrode		Electrolyte	$C_S$ (F/g) @ rate	$P_D$ (kW/kg)	$E_D$ (Wh/kg)	Ref.
Positive	Negative					
MnO <sub>2</sub>	AC	0.1M K <sub>2</sub> SO <sub>4</sub>	31 (0.55 A/g)	0.605	17.3	(Cottineau et al., 2005)
(Y- $\alpha$ -) MnO <sub>2</sub>	AC	1M LiOH	62.4 (100 mA/g)		19.5	(Yuan et al., 2006)
$\alpha$ -MnO <sub>2</sub>	AC	0.1M K <sub>2</sub> SO <sub>4</sub>	21 (2.5 mA/cm <sup>2</sup> )	-	11.7	(Brousse et al., 2007)
MnO <sub>2</sub> nanorod	AC	0.5M K <sub>2</sub> SO <sub>4</sub>	53.7 (2C)	2	17	(Qu et al., 2009)
$\alpha$ -MnO <sub>2</sub>	AC	0.5M Na <sub>2</sub> SO <sub>4</sub>	23.1 (12.74 mA/cm <sup>2</sup> )	14.7 ( $P_{max}$ )	10.4	(Wang et al., 2011)
MnO <sub>2</sub> NF	Graphene	0.5M Na <sub>2</sub> SO <sub>4</sub>	41.7 (1 A/g)	1 (1 A/g)	23.2 (1 A/g)	(Gao et al., 2012)
$\delta$ -MnO <sub>2</sub>	AC	1M Na <sub>2</sub> SO <sub>4</sub>	-	0.4 4.0	20.9 8.0	(Zhu et al., 2013)
MnO <sub>2</sub>	AC	2M MgCl <sub>2</sub>	45 (10 mV/s)	1.0	20	(Tomko et al., 2011)
$\alpha$ -MnO <sub>2</sub> / CNT	AC	2M KNO <sub>3</sub>	35 (2 mV/s)	123 ( $P_{max}$ )	21	(Khomenko et al., 2006)
$\delta$ -MnO <sub>2</sub>	AC	0.5 M K <sub>2</sub> SO <sub>4</sub>	32.9 (1A/g) 54 (10mV/s)	0.3 24( $P_{max}$ )	19.8 25.79	This work

The  $R_S$ , determined from the high frequency off-set in the real part of complex impedance of the EIS spectrum are contributed by three main factors viz. (i) electrolyte resistance, (ii) electrode resistance and (iii) electrode–electrolyte resistance. The  $R_S$  value for the device is 0.76  $\Omega$ . The diameter of semicircle at the high frequency range is due to kinetic resistance to the transfer, known as charge transfer resistance ( $R_{ct}$ ). The  $R_{ct}$  value is 0.79  $\Omega$ , result from kinetic transfer of combination of MnO<sub>2</sub> and AC electrode. At the The equivalent distributed resistance ( $R_d$ ) was obtained from the linear projection of the vertical region of Nyquist plot to the  $x$ - intercept on the real impedance and subtracting the  $R_S$  from the intersection (Kötz & Carlen, 2000). The  $R_d$  arises from the ions diffusion resistance into the porous (micropores and mesopores) network of MnO<sub>2</sub>//AC supercapacitor device. The calculated  $R_d$  value for the device is 0.72  $\Omega$ .

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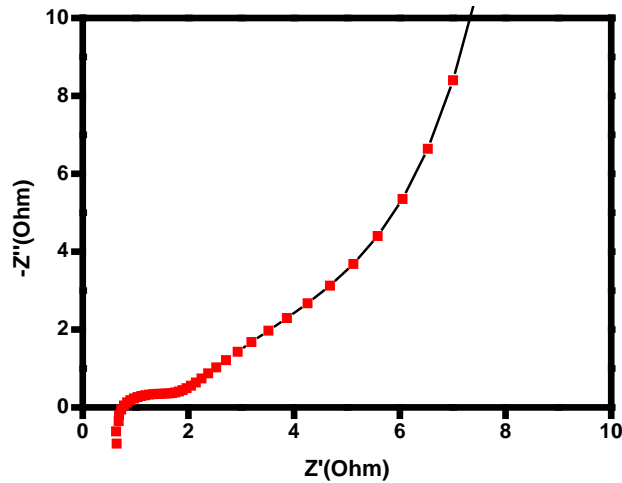


Figure 4. Nyquist plot of  $MnO_2//AC$  supercapacitor device.

#### 4.0 CONCLUSION

The synthesis flower shaped  $MnO_2$  and fabricated  $MnO_2//AC$  ASC device in aqueous electrolyte were presented. The outcome of the device shows the maximum  $E_D$  of  $25.79 \text{ Wh/kg}$  at  $P_D$   $100 \text{ W/kg}$ . The stability of the device has been study and shows  $\sim 95\%$   $C_S$  retention, a promising candidate to build energy storage device using the proposed system.

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