High performance flower shape MnO_2 for asymmetric supercapacitor device in aqueous electrolyte

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***Abstract*—A flower shaped MnO_2 have been synthesized using simple and low temperature procedure. Subsequently, an asymmetric supercapacitor is fabricated using MnO_2 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—supercapacitor; manganese oxide; asymmetric

I. 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) [1]. The energy stored in supercapacitor are through ions adsorption on the electrode – electrolyte interface (electrical double layer capacitor, EDLC) and fast and reversible redox reaction (pseudocapacitance, PC) mechanism [2]. Asymmetric supercapacitor (ASC) usually fabricated by combining PC material as positive electrode and high surface area activated carbon (AC) as negative electrode; separated by permeable separator in electrolyte environment. This combination is essential to obtained maximum open potential (1.8 – 2.4 V) as metal oxide alone offer limited open potential (0.8 – 1.2 V) due to water decomposition process. In case of AC, eventhough the open potential may archieved 2.0 V, this type of symmetric configuration resulted in lower C_S.

The researchers focused on metal oxides and composite development to enhance E_D and power density (P_D) as this type of material is having higher theoretical values that exceed 1000 F/g [3]–[8]. Among them, manganese oxide (MnO_2) is considered as a superior candidate in replacing ruthenium oxide hydrate ($RuO_2.xH_2O$) as working electrode material due to several factors, including low in cost, availability, non-toxic and environmentally friendly [9].

In this article, MnO_2 is prepared through a simple and low temperature condition. The ASC was prepared in coin cell type assembly using aqueous potassium sulfate (K_2SO_4) electrolyte. This is in order to enhance the open potential of the ASC and on the same time enhance the E_D as E_D is directly proportional to square of open potential. The MnO_2//AC ASC shows a promising open potential of 2.0 V and demonstrated E_D of 25.79 h/kg at P_D 100 W/kg.

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II. EXPERIMENTAL

A. Material Synthesis

The synthesis of MnO_2 was carried out using hydrothermal method. In a typical experiment 4.5 mmol of potassium permanganate [$KMnO_4$, BDH Chemicals] solution was mixed with 1.5 mmol ammonium persulfate (APS) [$(NH_4)_2S_2O_8$, Aldrich] in a Teflon lined stainless steel reactor. After being stirred for 20 min, the reactor was kept in an oven at 90 ^oC 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 ^oC for 24 h.

B. Material Characterizations

The MnO_2 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_α radiation (λ = 1.5406 Å) 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.

C. Electrode Fabrication and Supercapacitor Assembly

The positive electrode were prepared by mixing active material, MnO_2 (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^2/g, Zhejiang Forest Energy Technology Co. Ltd, China) as the active material. Supercapacitor was assemble in coin cell type case (CR2032) using fibrous glassy carbon as separator and using 0.5 M K_2SO_4 electrolyte.

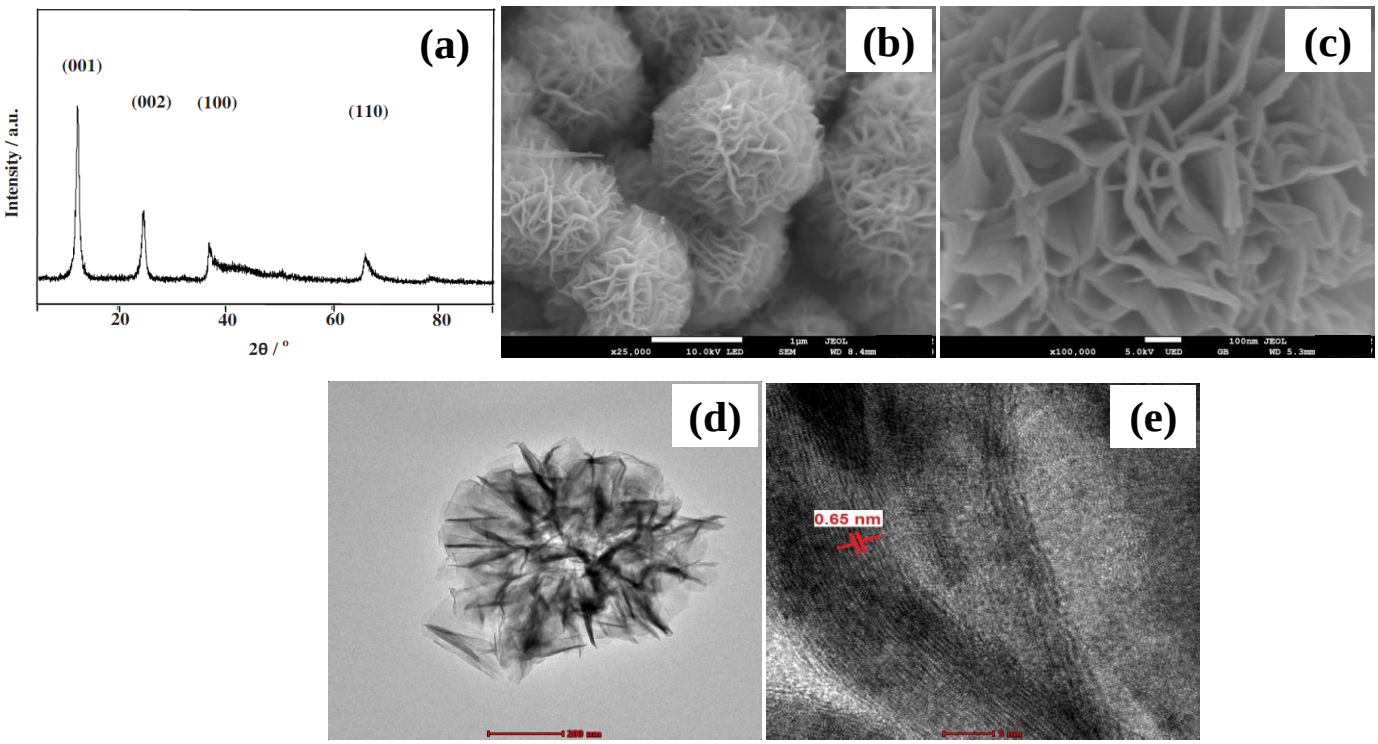

Fig. 1. (a) XRD pattern of MnO_2; FESEM micrograph of flower shaped MnO_2 at (b) low and (c) high magnification; (d) TEM and (e) HRTEM image of MnO_2.

D. 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 Netherland) 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, Ω) and coulombic efficiency (η, %) were calculated according to the following Eqs. (1)–(6):

$$C_S(CV) = \frac{1}{mv(\Delta V)} \int_{Va}^{V_b} i(V)dV \qquad (1)$$

$$C_S(CV) = 4\frac{it}{m\Delta V} \qquad (2)$$

$$E_D = \frac{1}{2} C_S (\Delta V)^2 \qquad (3)$$

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

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

$$\eta = \frac{t_d}{t_c} x100 \qquad (6)$$

where m (g) is active mass, v (mV/s) is scan rate, ΔV (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.

III. Results and Discussion

A. Physicochemical Properties of MnO_2

The XRD pattern of hydrothermal reaction product of MnO_2 is shown in Fig. 1a. The XRD pattern is indexed to the monoclinic potassium birnessite (JCPDF No 43-1456) structure with *C2/m* space group (No. 12) [10]. The (001) and the (002) planes are typical of the layered structure of δ–MnO_2 whereas the broadened (100) plane indicate crystallized water and formation of water-MnO_2 interlayer [11]. The basal plane spacing calculated from the (001) plane is ~0.73 nm, which is the characteristic of the birnessite MnO_2 due to water molecule and intercalated potassium ion.

The FESEM images of MnO_2 at low magnification (Fig. 1b) shows uniform flower-like morphology of MnO_2. Using Image J software measurement, the average diameter of the flowers was ~1.23 µm. A higher magnification FESEM image in Fig. 1c clearly shows that the curly and folded thin nanosheets of thickness ~20 nm are branched out from one

central zone.

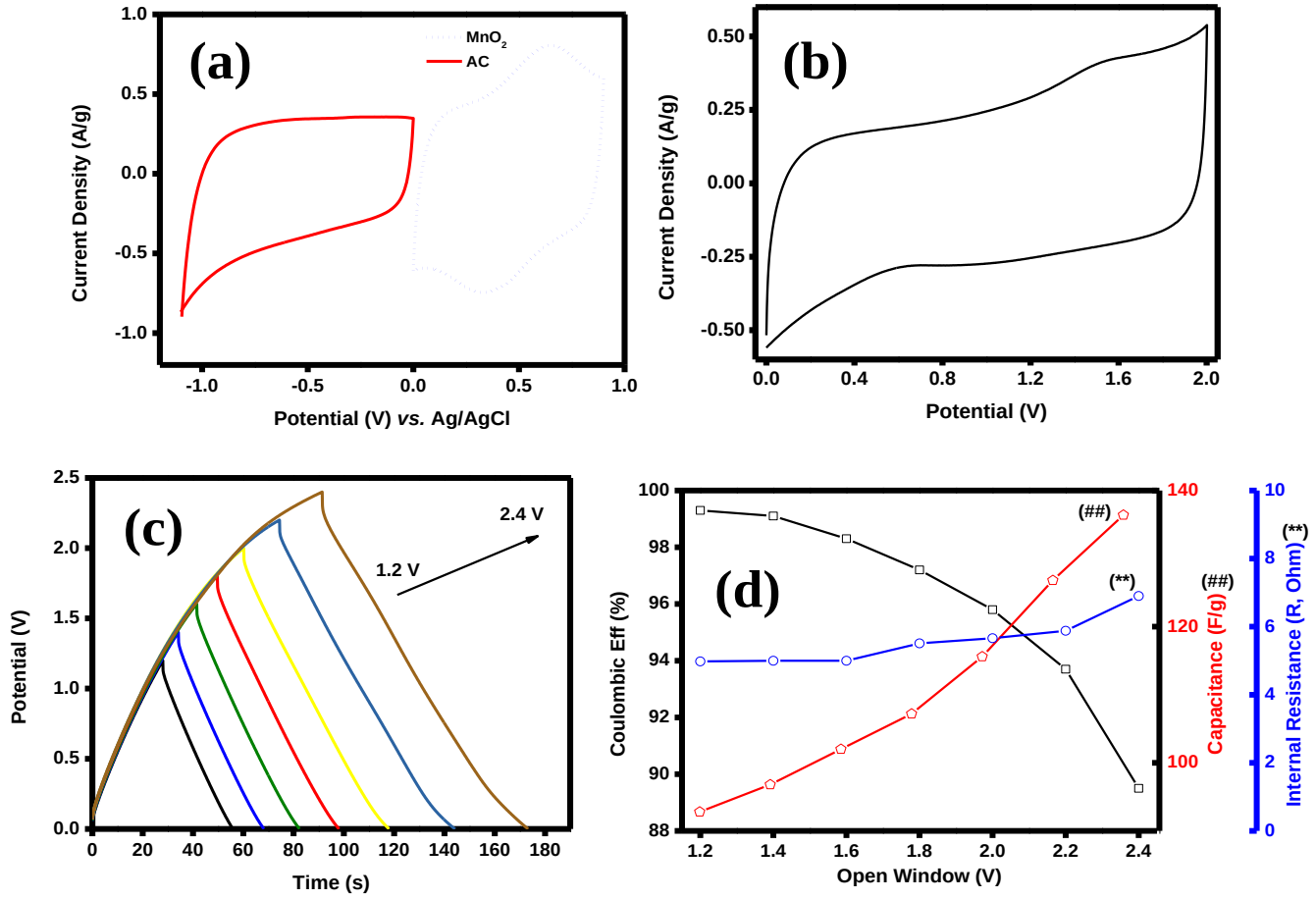

Fig. 2. (a) CV curve for MnO_2 and AC electrode; (b) CV curve for MnO_2//AC supercapacitor at 10 mV/s; (c) CDC curve at current density of 1 A/g for potential range 1.2 – 2.4 V; (d) Variation of η, C_S and I_R for different potential.

The bright field TEM image of the MnO_2 is shown in Fig. 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 Fig. 1e. The measured spacing along the (001) plane is ~ 0.65 nm in HRTEM, which is lower than that observed in the XRD pattern (~0.73 nm). This lowering is due to the evaporation of interlayer water molecules under the high energy electron beam irradiation [12].

B. Determination of MnO_2//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 MnO_2 and AC is shown in Fig. 2a. The 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 MnO_2 to AC electrode is 0.89, calculated according to Eq. (7).

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

C. Supercapacitor Performance Analysis

The MnO_2//AC asymmetric supercapacitor CV curve at scan rate 10 mV/s is shown in Fig. 2b. It shows that near rectangular CV shape in 2.0 V potential range. The calculated C_S at this scan rate is 54 F/g.

To understand the maximum open potential of MnO_2//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 Fig. 2c. The curve shows symmetric triangle of charge and discharge; indicate that the optimum reversibility during charging and discharging. The relation of η, C_S and I_R is shown in Fig. 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_S and I_R, however, increase respect to increasing open potential. The C_S is increased from 93 to 137 F/g and the I_R increased from 4.98 to 6.90 Ω. The optimize supercapacitor should having higher η and C_S but minimum I_R. Thus, open potential of 2.0 V is the most promising for MnO_2//AC system.

Then, the performance of MnO_2//AC was tested at different current densities ranging from 3 to 0.1 A/g and the CDC curve is shown in Fig. 3a. Near triangle shape for each CDC test indicate that high reversibility of the supercapacitor for each current density. Clearly, as the current desnsity decrease, the discharge time was also increased. This phenomenon related to the higher fraction of active surfaces are invove in 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 η, C_S and I_R for CDC analysis at different current density was shown in Fig. 3b. Similar to analysis in Fig. 2d, the η 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 Ω. 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 Fig. 3c.

The MnO_2//AC supercapacitor was tested for cell stability test for 850 cycles and the evidence was shown in Fig. 3d. the device show promising electrochemical stability with the C_S retention ~ 95% after the end of cycle. The η is unchanged at the end of the stability cycle and shows ~94% throughout the test.

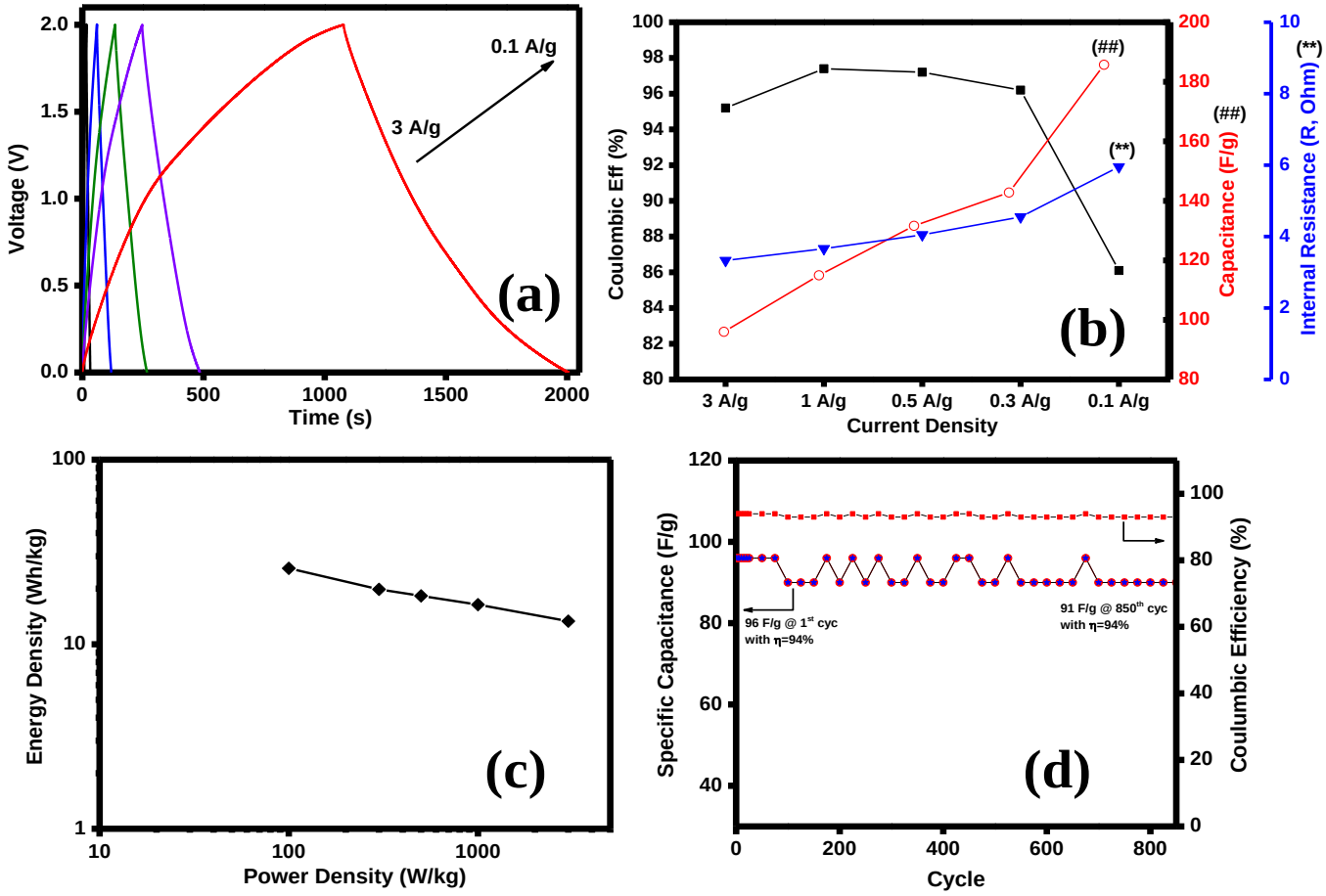

Fig. 3: (a) CDC curve at current densities range from 3 – 0.1 A/g; (b) Variation of η, C_S and I_R for different current densities; (c) Ragone plot of MnO_2//AC supercapacitor; (d) Cycle stability test of MnO_2//AC supercapacitor.

Table 1: Comparison of MnO_2 based ASC device.

Positive electrode	**Negative electrode**	**Electrolyte**	**Open Potential**	**C_S (F/g) @ rate behavior**	**Power (kW/kg)**	**Energy (Wh/kg)**	**R_S**	**Ref.**
MnO_2 (amorphous)	AC	0.1M K_2SO_4	0 – 2.2 V	31 (0.55 A/g)	0.605	17.3		[13]
(Y-α-MnO_2	AC	1M LiOH	0.5 – 1.5 V	62.4 (100 mA/g)		19.5	~0.02	[14]
α-MnO_2	AC	0.1M K_2SO_4	0 – 2.0 V	21 (2.5 mA/cm^2)	-	11.7	1.3	[15]
MnO2 nanorod	AC	0.5M K_2SO_4	0 – 1.8 V	53.7 (2C)	2	17	-	[16]
α-MnO_2	AC	0.5M Na_2SO_4	0 – 1.8 V	23.1 (12.74 mA/cm^2)	14.7(P_{max})	10.4		[17]
MnO_2-NF	Graphene Hydrogel	0.5M Na_2SO_4	0 – 2.0 V	41.7 (1 A/g) 26.8 (10 A/g)	1 (1 A/g) 10 (10 A/g)	23.2 (1 A/g) 14.9 (10A/g)	4.9	[18]
δ-MnO_2	AC	1M Na_2SO_4	0 – 1.6 V	-	0.4 4.0	20.9 8.0	-	[19]
MnO_2 (amorphous)	AC	2M $MgCl_2$ 2M $CaCl_2$ 2M KCl	0 – 1.8 V 0 – 2.0 V 0 – 2.0 V	45 (10 mV/s) 40 (10 mV/s) 35 (10 mV/s)	1.0	20 22.5 18	1.08 1.08 0.59	[20]
α-MnO_2/CNT	AC	2M KNO_3	0 – 2.0 V	35 (2 mV/s)	123 (P_{max})	21	0.54	[21]
δ-MnO_2	AC	0.5 M K_2SO_4	0 – 2.0 V	32.9 F/g (1A/g) 54 F/g (10mV/s)	0.3 24(P_{max})	19.8 25.79	0.76	This work

Table 1 summarize recently published MnO2 and AC based ASC. The performance shown by this study shows that the device is comparable and most cases is superior with previous report. Finally, the Nyquist plot from EIS measurement of the MnO_2//AC supercapacitor device is shown in Fig. 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.

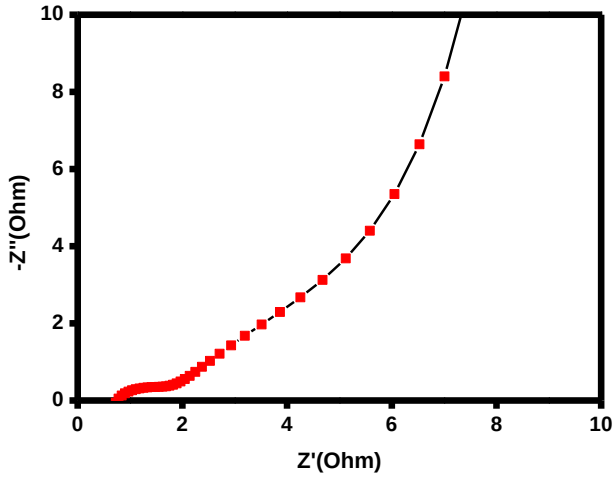

Fig 4: Nyquist plot of MnO_2//AC supercapacitor device.

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 Ω. 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 Ω, result from kinetic transfer of combination of MnO_2 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 [22]. The R_d arises from the ions diffusion resistance into the porous (micropores and mesopores) network of MnO_2//AC supercapacitor device. The calculated R_d value for the device is 0.72 Ω.

D. Conclusion

In conclusion, we have synthesis flower shaped MnO_2 and fabricated MnO_2//AC ASC device in aquesous electrolyte. The performance of the device is studied and shows the E_D of 25.79 Wh/kg at P_D 100 W/kg. The stability of the device has been study and shows ~ 95% C_S retention, promising to build energy storage device in the proposed system.

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