The Effect of Concentration Nanoparticles MnO$_2$ DOPED in Activated Carbon as Supercapacitor Electrodes

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Abstract

A symmetric supercapacitor has been fabricated using activated carbon adopted different concentration the nanoparticle manganese dioxide (MnO$_2$)-activated carbon (AC) composite as the electrode materials. The composite electrodes were prepared by mechanically mixing the activated carbon, MnO$_2$, and PVDF polymeric solution as a binder. The concentration of MnO$_2$ was varied from 0% until 20%. The charge storage mechanism in MnO$_2$ electrode, used in the aqueous electrolyte, was investigated by cyclic voltammetry and the impedance testing was done on two electrodes system. The result clearly showed that the low concentration of nanostructured MnO$_2$ has improved the specific capacitance of supercapacitor via pseudocapacitive charge storage mechanism and the increased of surface area. However, further increasing the MnO$_2$ content in the electrode decreased the capacitive performance and deteriorated the specific surface area of the electrode, mainly due to the aggregation of the MnO$_2$ particles within the composite. Structural analysis of the nanocomposite electrodes was characterized by scanning electron microscopy (SEM) and Brunauer-Emmett-Teller (BET) analysis. Additionally, the electrochemical properties are evaluated through cyclic voltammetry, electrochemical impedance spectra, and galvanostatic cycling measurements. The results demonstrate this MnO$_2$/AC composite owes homogeneous particle size of nanometer dimension. The experimental results showed that the highest specific capacitance of 372 F/g at the scanning rate of 10 m/V is achieved with a fairly low MnO$_2$ nanomaterials loading (5 wt. %) in 3 M KOH. The maximum cycle life of the supercapacitors 4500 cycles. Besides, the impedance tests results show that the charge transfer resistance of this composite is 0.88 Ω.

Keywords: Supercapacitor, Activated Carbon, Capacitance, Manganese Dioxide

INTRODUCTION

Supercapacitors as energy store components have been used widely in the fields of electronics and transportation, such as digital telecommunications systems, computer, and pulsed laser systems, hybrid electrical vehicles, etc [1].

Supercapacitor have many advantages compared with other energy storage devices such as batteries. From the technical side, supercapacitors have a relatively large number of cycles (> 100,000 cycles), high energy density a great ability to save energy, the principle is simple and convenient construction [2]. In terms of user-friendliness, supercapacitor improve security because of no corrosive materials and fewer toxic materials. Currently, the electrode material of commercial supercapacitor uses a porous carbon made from natural materials, namely coconut shell [3]. The porous carbon can be prepared by carbonization of natural materials such as coal, coconut shells, corn stalks, wood, bamboo, paper waste [4]. Porous carbon potential to be used as supercapacitor electrode material because it has the potential for high energy density, pore good accessibility and relatively low manufacturing costs [5]. To increase the capacitance of supercapacitor energy can be done by preparing porous carbon material which has the mesoporous fraction and high surface area [6]. The material used for the manufacture of a supercapacitor electrode including graphene, carbon nanotubes, carbon aerogel, a porous carbon and minerals-carbon composites [7].

Based supercapacitor electrode material, it is divided into two groups: (i) carbon material with a high surface area, such as activated carbon, carbon aerogel, etc.; (ii) metal oxides such as Ru, Ni, Co, Zn, etc., and the addition of the polymer [8].

Manganese oxides (MnO$_x$) are a class of transition metal oxides, including MnO, MnO$_2$, Mn$_3$O$_4$, Mn$_2$O$_3$, which is endowed with rich oxidation states and chemistry. The electron transfer of MnO$_x$ structures, along with the fast development of versatile structures controlled during the growth, has offered substantial potentials in many application

fields, including catalysis, chemical/biological sensing, and energy storage [9].

A major disadvantage of packing MnO_2 powders is the low electronic conductivity to sustain high rate charge-discharge processes. Hence, in a typical MnO_2 powder electrode, an electrically conductive enhancer, most commonly a high surface area graphitic carbon, must be incorporated into the powder electrode to improve its performance and a polymeric binder for mechanical stability. The total amount of carbon and the organic binder (''inactive'' components) ranges from 10 to 35% in weight and up to 70% of the total electrode volume, which will undoubtedly sacrifice the gravimetric and volumetric energy densities of the MnO_2 powder electrode. The volumetric capacity is of interest for manufacturers as those materials are studied with the aim of compact applications [10].

The research efforts focused on compounds providing high cyclability and capacitance. On the other mechanisms were proposed to explain the MnO_2 charge storage behavior. The first one implies the intercalation of protons (H+) or alkali metal cations (C+) such as Li+ in the bulk of the material upon reduction followed by deintercalation upon oxidation [11] :

$$MnO_2 + H^+ + e^- \longrightarrow MnOOH \qquad (1)$$

Or

$$MnO_2 + C^+ + e^- \longrightarrow MnOOC \qquad (2)$$
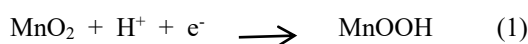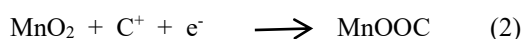
The second mechanism is based on the surface adsorption of electrolyte cations (C+) on MnO_2 [11] :

$$(MnO_2)_{surface} + C^+ + e^- \longrightarrow (MnO_2^- C^+)_{surface} \qquad (3)$$
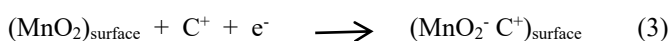
where $C^+ = Na^+, K^+, Li^+$. This mechanism was proposed following the observation of significant difference of the cyclic voltammogram and the capacitance of MnO_2 in the presence of various metal alkali cations in the Electrolyte.

In order to improve the conductivity, the approach to incorporate nanostructured MnO_2 into carbonaceous materials is great effectiveness and significance, which provide high electroactive surface area and reliable electrical connection for a maximum utilization of MnO_2. Relative to the formers, the activated carbon (AC), one of the promising carbonaceous materials for supercapacitor, is selected because of its relatively high power density, high specific surface area, and low cost. The combination of MnO_2 and AC may take advantage of the excellent electrical conductivity.

The general requirements for metal oxides are (1) The electrons in the metal oxide to be conductive, (2) the metal can exist in two or more oxidation states that coexist over a continuous range with no phase changes involving irreversible modifications of a 3-dimensional structure and (3) the protons can freely intercalate into the oxide lattice on reduction, allowing facile interconversion of $O2- \leftrightarrow OH-$ [11]. The nanostructured metal oxide is a good material to achieve a high specific capacitance because has pseudocapacitance behavior [12]. Wang et all has research MnO_2 /activated carbon (AC) composite, where use variation AC. Because that we try to made variation percentage MnO_2 [13].

For this purpose, various metal oxides are cheap and abundant have been investigated, MnO_2 as the alternative to metal oxides. MnO_2 is a good dielectric material and exhibits faradaic capacitance. Activated carbon has a high specific surface area, good electrochemical stability, good conductivity and high supercapacitor cycle life [14]. Therefore, the combination of the surface area of activated carbon with a capacitance of MnO_2 nanoparticles is expected to form composite materials with both the faradaic capacitance of the metal oxide and the double layer capacitance of the activated carbon.

MATERIALS AND METHOD

Materials

The materials used are coconut shell waste as precursors, KOH as the chemical activator, HCL 0.5 M, PVDF, DMAC, distilled water, electrolyte 3M KOH, MnO_2 nanoparticles (20 nm) Sigma-Aldrich and separator.

Method

A.   Synthesis Nanoporous Carbon

Synthesis of nanoporous carbon was done begins with the carbonization of coconut shell that has been destroyed. Carbonization performed at a temperature of 800 °C for 4 hours by using furnace without the aid of gas. This process produces carbon charcoal which is then crushed and screened to obtain the fine carbon powder size of 200 mesh. The charcoal is then mixed with KOH with variations in the mass ratio of carbon to KOH include 1: 3. The mixture stirred for 2 hours to ensure the continuity of the process of diffusion into the inside of the pores of charcoal, dry in open air for 24 hours at room temperature. Next process was the carbonizing process in N2 gas atmosphere at a temperature of 700 °C for 1 hour. The last process is washing the charcoal with 0.5M HCl and distilled water repeatedly. Nanoporous carbon dried at a temperature of 100 °C to evaporate off the water contained. The surface morphology of the composite was observed using a field-emission scanning electron microscope (FESEM, X-Mex Horbia). Surface area measurement using Brunauer-Emmett-Teller (BET) by adsorption analyzer NOVA 4200 (Quantachrome) at 77 K surface area analyzer under N2. Morphology study and the size of the crystals were analyzed by XRD Rigaku SmartLab type 3KW.
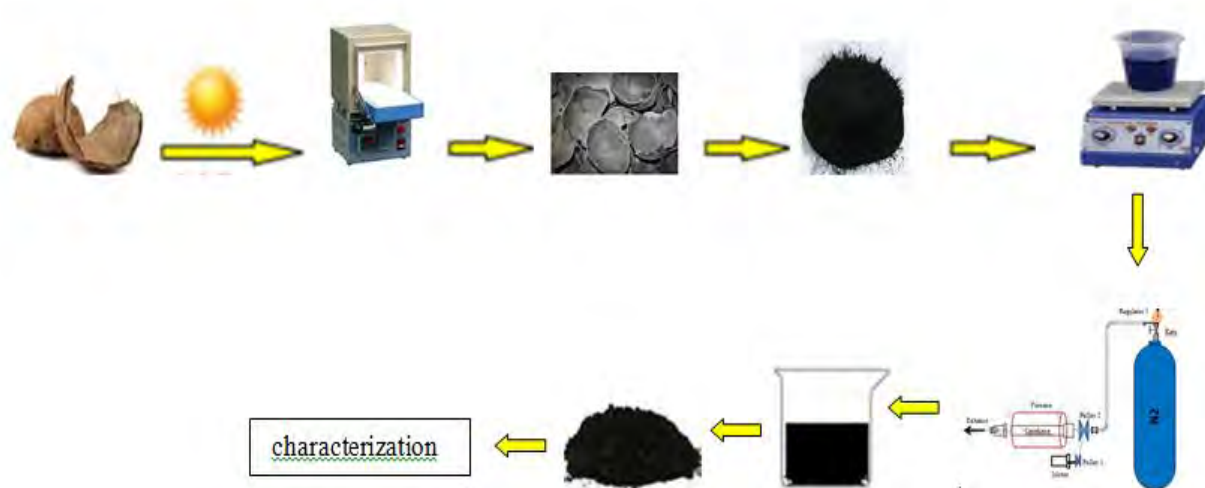
Figure 1: Schematic preparation Activated Carbon

B. *Preparation of Electrodes*

Manufacture of sheet electrodes

The mixture of polyvinylidene difluoride (PVDF) and Dimethylacetamide (DMAC) was stirred at 80 °C for 1 hour. In this solution added activated carbon and super-P. Next MnO_2 nanoparticles with the concentration is 0%, 5%, 10%, 15% and 20% and stirred for 3 hours to reach homogeneous condition. We then paste the sludge on the aluminum sheet using Dr. Blade method and dry it on open air to make the electrode. They are then dried in the oven at a temperature of 80 °C for 1 hour.

C. *Assembly the supercapacitors cells*

The capacitor cells were constructed with an electrolyte-impregnated polypropylene separator sandwiched between two symmetrical MnO_2/AC composite electrodes. The electrodes were pre-wetted with electrolyte before used. The supercapacitors performance was tested using a cyclic voltammogram, Electrochemical Impedance Spectroscopy, and galvanostatic instrument test. We testing as to two electrodes system of symmetric supercapacitors.
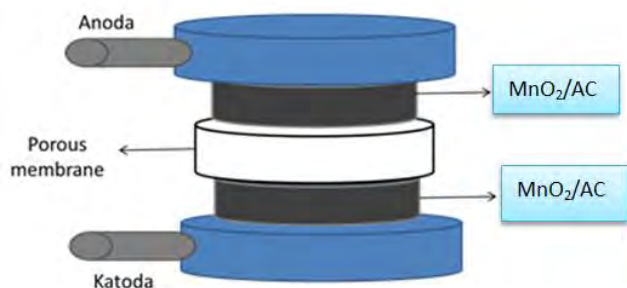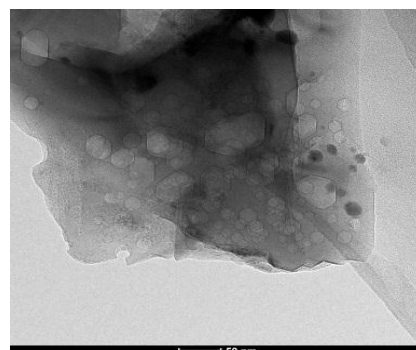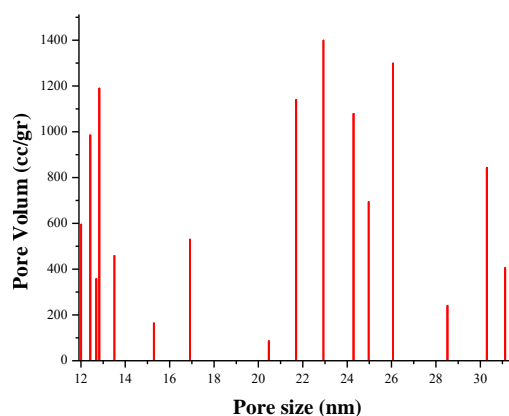

Figure 2: Assembly Sel Supercapacitor

RESULT AND DISCUSSION

A. *Morphology observation Activated Carbon*

(b)

(b)

Figure 3: (a) TEM Activated Carbon, (b) Pore size distribution

Fig. 3 shows the Transmission Electron Microscope (TEM) image of the Activated carbon sample. It can be seen from the TEM photograph that the sample belongs to superfine powders with average pore size 12-30 nm, the morphology of porous activated carbon and composite morphology of MnO_2/AC, it can be seen that the MnO_2 particle size of approximately 20 nm is almost uniform and unevenly distributed on the surface of the carbon. The results obtained BET surface area of 1469 m^2g^{-1} with an average pore size of 26 nm.

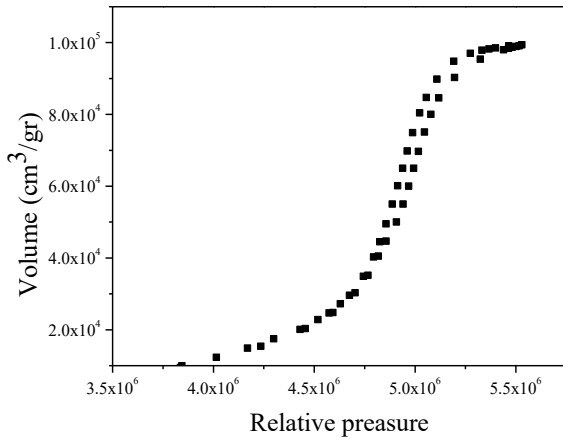
Figure 5: SEM EDX composites MnO_2/AC

Figure 4: Isotherm fisisorption and pore size distribution

High mesoporous rate is suitable for electrolyte ion to transport inside the porous structure of the activated carbon. More inner-surfaces of pores inside the AC can be wetted by the electrolyte. Therefore, the conductivity of activated carbon electrode is enhanced. When an electrode (electronic conductor) comes into contact with an electrolyte (ionic conductor), it shows some potential and attracts ions with the opposite sign, forming an "electrical double-layer" at the electrode/electrolyte interface [6].

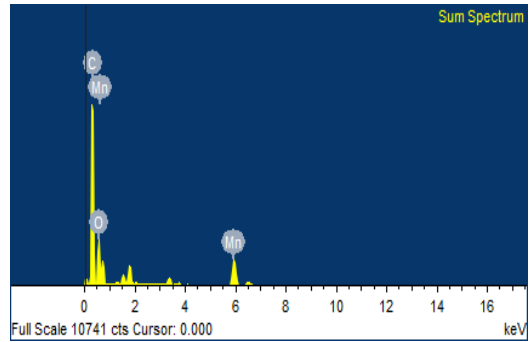*B.   Composites MnO_2/AC characterization*

Fig. 5 shows the morphology of porous activated carbon and composite morphology of MnO_2/AC, it can be seen that the MnO_2 particle size of approximately 20 nm is almost uniform and unevenly distributed on the surface of the carbon. Fig. 5 shows Mn particles are in the carbon pores. This uneven distribution is caused by the heat treatment during the process of the composite, where MnO_2 grow on the carbon surface quickly and has been reduced, but the growth was limited by the size of the pores of the carbon until the size of Mn is larger than the pores in the activated carbon. In smaller concentration, the presence of Mn may form new pores so that the increase the composite electrode surface area. This will accelerate the formation of an electrochemical double layer between the carbon surface and the electrolyte [14]. The existence of MnO_2 crystalline in the activated carbon matrix was supported by its XRD data in Fig. 6.

c. The structural analysis of MnO_2/AC

The XRD patterns of MnO2/AC show at Fig. 3. The MnO_2 peaks corresponding to Mn (111, 311, 222, 200) were observed (JCPDS 04-0836). The composite MnO_2/AC indicates peak intensity wider and higher. We estimated the crystallite size of 20 nm MnO_2.These results were fairly confirmed by the FESEM results shown in Fig. 6.
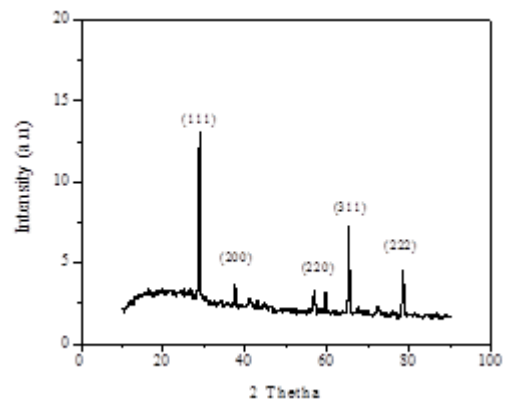

Figure 6: XRD composited MnO_2/AC

D. Electrochemical properties of MnO₂/AC composite electrodes

The supercapacitor was made of symmetric composite electrode MnO₂/AC and 3M KOH as electrolyte. The capacitance was determined using Equation :

$$C_e (F) = \frac{\int I dv}{\Delta v.vs} \qquad (4)$$

$$Csel = \frac{2Ce}{m} \qquad (5)$$

Where C_e is the electrode capacitance, I is the current, ΔV is potential, vs is scan rate, C_{sel} is the specific capacitance of the supercapacitors cell and m is the mass of the material active electrode [15].

The CV curves of the composite electrodes reveal that the mechanism of electrochemical storage could be described by the electrical double layer theory. Energy storage in these electrodes is the accumulation of ionic charge in the double layer at the electrode/electrolyte interface and this may be due to high surface area and the porosity of the activated carbon. The high capacitance achieved in these may be due to effective electrical and ionic conductivity. *C-V* tests for the variation percentage MnO₂ at a scan rate of 10mV/s are shown in Fig. 7.
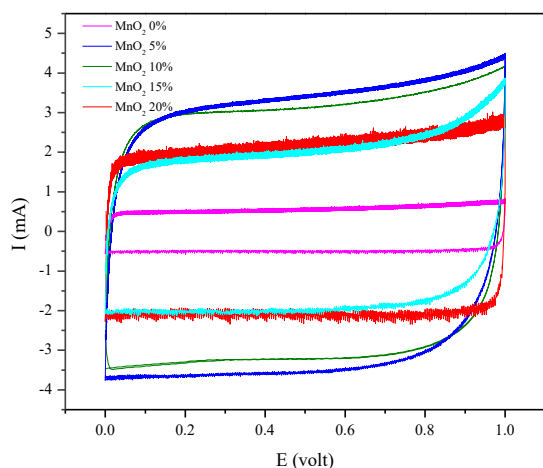

Figure 7: CV curves at different percentage of MnO₂/AC composition at 10 mVm⁻¹

The *C-V* curves display shapes with one pair of well-defined redox peak centered at 0 V and nearly same peak currents, which indicates the good reversibility of the redox the electrolyte. The redox peak corresponds to the redox transformation of MnO₂/AC electrode/electrolyte interface [16]. However, the *C-V* curves display a quasi-rectangle shape without apparent redox peak, implying an ideal electric double layer capacitor [17]. Besides, the capacitances are proportional to the areas of *C-V* shapes [18], and the

appearance of bumps means that the capacitances have been improved about, which is attributed to the pseudocapacitances produced by redox reactions. On the basis of *C-V* tests, the good performance of 5% MnO₂ is due to the capacity-storage mechanism of the electrical double layer capacitance and Faradic pseudocapacitance produced by the redox reaction of MnO₂/AC electrode/electrolyte interface.
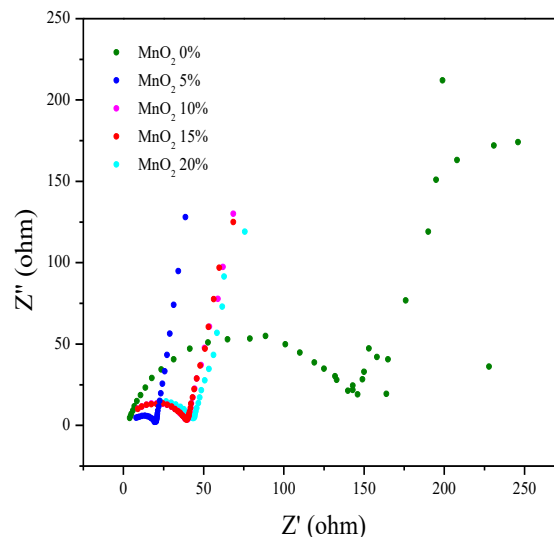

Figure 8: Nyquist plot composites MnO₂/AC

Fig. 8. shows the Nyquist plots of supercapacitors. The supercapacitors exhibit ideal electrochemical capacitance behaviors. In the high-frequency region, 5% MnO₂ not only has lower inner resistance, calculated from the point of intersecting with the *x*-axis, but also has smaller charge transfer resistance (5.72Ω for 0%, 0.881Ω for 5%, 0.982Ω for 10%, 1.32Ω for 15% and 1.77Ω for 20% respectively), which was counted from the span of the single semi-circle along the *x*-axis. It can be inferred that the introduction of MnO₂ decreases the inner resistance and accelerates the transfer of ions. Subsequently, the quick charge-discharge ability of the supercapacitors was improved. Furthermore, in the low-frequency region, the imaginary part of MnO₂ is more perpendicular to the real part. In brief, the introduction of 5%MnO₂ improves the impedance performance of the supercapacitors.

Fig. 9. shows the galvanostatic charge-discharge test of fabricating supercapacitors confirms. The device has a coulomb efficiency and cycle life. The Specific capacitance of supercapacitors is stable up to 4500 cycles at a current density of 2 mA/cm2.
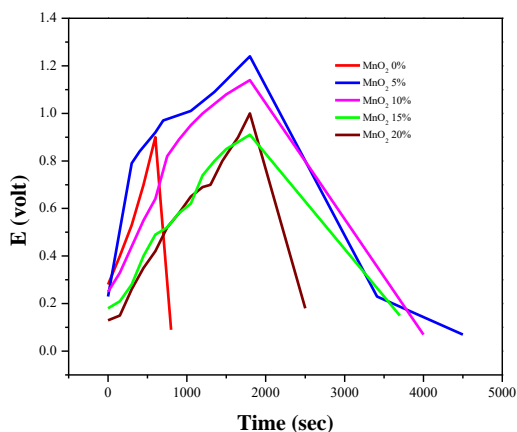
Figure 9: Profile charge-discharge galvanostatic composites MnO_2/AC on i = 1 mAcm^{-2}

CONCLUSION

A symmetric supercapacitor has been successfully fabricated by the sandwich method. Fabrication of having a composite electrode of $xMnO_2/AC$ shows maximum specific capacitance 372 F/g at x= 5%. This supercapacitor fairly stable during charge-discharge which can be retained for 4500 cycles. The dopant of MnO_2 nanoparticles in composite electrodes increases the specific capacitance due to the increase the exhibition of a pseudocapacitive mechanism in addition to double layer.

ACKNOWLEDGMENT

The result of the calculation of the specific capacitance of all carbon used as material written in Table 1 and fig 10. Table-specific capacitance calculation shows that the EDLC excellent performance obtained by the addition of 5% MnO_2. The increase in the capacitance of the composite due to the addition of MnO_2 due to the combined effects of a faradaic capacitance of metal oxides and double layer capacitance of activated carbon [19]. The high surface area of the nanostructured MnO_2 may also serve as a good support for the activated carbon particles to facilitate the electrochemical processes leading to higher capacitance.

Table 1: Specific Capacitance symmetry Supercapasitors MnO_2/AC

% MnO_2	Cs (F/gr)
0	100
5	372
10	361
15	226
20	191
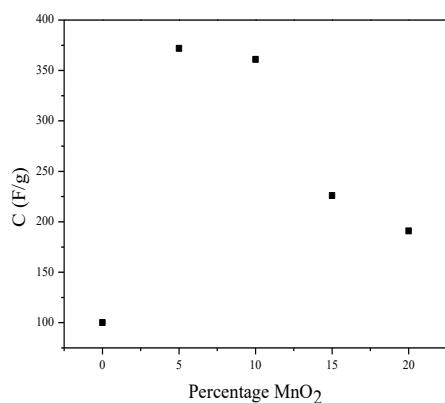
Figure 10: Profile % MnO_2 versus capacitance

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