

# Study on the Effect MnO<sub>2</sub>-Deposited Carbon Nanofiber Mat and Their Electrochemical Performance

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**Keywords:** MnO<sub>2</sub>, Carbon nanofibers, Electrospinning, Relative humidity, Capacitors

**Abstract:** Electric energy storage technology has evolved along with the increasing of the human need for portable electronic devices and the development of electric-powered vehicles, one of which is capacitors. Material that is often used for capacitors is activated Carbon and requires a binder, but the binder reduces the performance of activated carbon as an electrode. An alternative material that can be used as a substitute for activated Carbon is carbon black. One type of carbon black is acetylene black (AB). AB has been widely used as an additive for conductive additives in the electrode preparation process because it has a large and low-density specific area. Poly (vinyl alcohol) (PVA) has the physical properties of hydrophilic and semi-crystalline polymers. Some of the advantages of PVA are having good thermal stability, chemical resistance, good physical property, and excellent biocompatibility. Based on this, PVA is very interesting to be developed as an electroactive composite matrix containing acetylene black. PVA/AB composite carbon nanofiber is made using electrospinning techniques. Further development of carbon nanofiber as an electrode material needs modification with the addition of MnO<sub>2</sub> through immersion techniques. The results of the SEM and XRD test showed that MnO<sub>2</sub> was deposited on the carbon nanofiber surface area. The effect of adding MnO<sub>2</sub> can increase the capacitance of the PVA/AB composite CNF.

## 1. INTRODUCTION

Electric energy storage technology has developed a lot with the increasing human need for portable electronic devices and the development of electric-powered vehicles. One of them is a capacitor, which is an innovation in the world of energy storage devices that have large energy and power density, large charge storage capacity, fast charge/discharge process (Zhang and Zhao, 2009). These advantages have been widely used in various fields such as digital technology, electrical machinery, additional power units, and energy storage equipment (Pech et al., 2010). The material often used for capacitors is activated Carbon because it has high cost-effectiveness and performance efficiency (Gamby et al., 2001). Activated carbon electrodes still need binders such as organic material/polymers to bind particles, but the presence of binders reduces the performance of activated carbon as an electrode.

One alternative material that can be used as a substitute for activated Carbon is carbon black. Because carbon black has amorphous properties and

has several advantages, such as the price is relatively low and has availability in various types and sizes. Based on the process, black carbon consists of furnace black, thermal black, channel black, and acetylene black. Acetylene black (AB), prepared by the thermal decomposition technique of acetylene, whose electrical conductivity is known. In addition, AB has been widely used as an additive to conductive additives in the electrode preparation process because it has a large specific area and low density (Gamby et al., 2001). Previous research has made composites of polyurethane (PU)/CB, polyaniline (PANI)/CB, and Polyvinyl alcohol (PVA)/CB (Xiong et al., 2015).

Poly (vinyl alcohol) (PVA) has the physical properties of hydrophilic and semi-crystalline polymers. Some of the advantages of PVA are having good thermal stability, chemical resistance, good physical property, and very good biocompatibility (DeMerlis and Schoneker, 2003; Koski, Yim, and Shivkumar, 2004). Based on this, PVA is very interesting to be developed as an electroactive composite matrix containing carbon black. PVA/CB composites have been carried out in the form of fiber

using electrospinning techniques, because they can be applied in a variety of fields, have a wide specific area and high porosity.

In recent years, the electrospinning technique has been widely using to develop nanoscale diameter fibers. Although the electrospinning easy to use, the jet formation of the spinning dope is affected by the electrospinning condition. There is a parameter process that is influencing various fiber formation and fiber properties. Moreover, to get form fiber from the electrospinning with good characteristics, the ambient condition surrounds the chamber has to be controlled carefully during the electrospinning process. Fundamental processing condition have already reported which include applied voltage (Demir et al., 2002; Lee et al., 2004; Zhao et al., 2004), viscosity (Mit-uppatham, Nithitanakul and Supaphol, 2004; Shenoy et al., 2005), surface tension (Zheng et al., 2014) and conductivity and dielectric constant (Choi, Xue,) (Choi et al., 2004; Xue et al., 2014). Among the ambient parameter such as temperature and relative humidity also the most important influence the fiber formation. There is a Polymer such as polystyrene fibers resulted in larger diameter at higher humidity (Kim et al., 2004; Fashandi and Karimi, 2012) and polyetherimide (Ogulata and İçoğlu, 2013). Various of humidity also generate porous fibers by electrospinning polycaprolactone (PCL), poly L-lactic acid (PLLA) and polyvinylpyrrolidone (PVP) (Yazgan et al., 2017).

Manganese dioxide (MnO<sub>2</sub>) has many applications in industrial fields, including reagents in organic synthesis, as inorganic pigments in ceramics, and as electrodes in batteries. The use of MnO<sub>2</sub> as an electrode has several advantages, including inexpensive and environmentally friendly (Yu et al., 2011). Recently, there are several combination between Carbon with MnO<sub>2</sub> including carbon nanofiber (CNF)/MnO<sub>2</sub> with redox reaction of KMnO<sub>4</sub> solution (Ma et al., 2016), CNT/MnO<sub>2</sub> with hydrothermal reaction of KMnO<sub>4</sub> solution (Xia et al., 2012) and ACNF/MnO<sub>2</sub> (Wang et al., 2013).

Here, we reported the electrodes prepared via electrospinning of PVA/AB into nanofiber mats, which were heat treated. Before that, polyvinyl alcohol (PVA) was examined at various relative humidity conditions to obtain fiber shape, fiber surface, and fiber diameter. MnO<sub>2</sub> crystals were deposited on the surface of the CNFs by the immersing of aqueous KMnO<sub>4</sub>. The effect of MnO<sub>2</sub> crystal on the surface morphology with a varied mass ratio of CNFs versus KMnO<sub>4</sub> and electrochemical properties were investigated.

## 2 EXPERIMENTAL

### 2.1 Materials

Polyvinyl alcohol (PVA) technical grade and acetylene black (AB) were purchased from SAP chemicals and were used directly without further purification. Potassium permanganate (KMnO<sub>4</sub>) was purchased from Sigma Aldrich. All of the chemicals or materials were used directly without further purifications.

### 2.2 Synthesis of Carbon Nanofiber

The synthesis procedure for PVA/Acetylene Black (AB) could be explained as the following. PVA powder was mixed with distilled water under stirring for about an hour at 80 °C. Then, Acetylene Black was added to the PVA solution under constant stirring for 30 min. The mixture was sonicated at 50 °C for 4 hours to achieve the solution. Then the solution was injected into a 50 ml plastic syringe, which was fitted in an electrospinning apparatus to start spinning the PVA/AB solution. The spinning parameters were high voltage 10 kV (positive) was applied to the tip of syringe to achieve polymer jets, and negative was applied to the rotating cylinder, nozzle inside diameter 0.6 mm (23G), temperature in chamber 25 °C and relative humidity (RH) in chamber hold on 60 % where RH conditions were precisely regulated using dried silica and dehumidifier. The feed rate of the solution was controlled by means of a Cole Parmer Scientific syringe pump at 1 mL/h. The products were placed in a dry cabinet for 24 hours, previously further characterization.

Samples of 50 mm × 30 mm of electrospun nanofiber mats were placed into a sealed glass jar for iodine treatment in a muffle furnace (Themolyne) at 80 °C for 24 h. The glassed jar was contained iodine crystal with mass ratio iodine crystal versus mats of 1:2 to vaporize the iodine. After that, the sample was removed from the oven and naturally cooled down to room temperature. Iodine treatments are necessary for the preparation of carbon nanofiber with the desired morphological and structure.

The nanofiber mats were thermostabilized and carbonized in a Lindberg tubular furnace with heating procedures as follows: (1) The temperature was increased from 30 to 200 °C; (2) 200 to 400 °C; (3) 400 to 600 °C, each step the temperature was holding for 15 minutes. (4) The temperature was increased from 600 to 800 °C; (5) the temperature remained at 800 °C for an hour; and (6) the sample was cooled down to room temperature. During the carbonization

process, constant nitrogen flow was maintained through the tube.

### 2.3 MnO<sub>2</sub> deposition on surfaces carbon nanofibers (CNFs)

MnO<sub>2</sub> was deposited on the surface of the carbon nanofibers by the simple method degradation of KMnO<sub>4</sub>, as represented in the literature (Ma *et al.*, 2016). Firstly, a certain amount of different KMnO<sub>4</sub> concentration was dissolved in 10 mL distilled water and stirred until the KMnO<sub>4</sub> was fully dissolved. Mass ratios for every two CNFs *versus* KMnO<sub>4</sub> were 1: 1 and 1: 2. The CNF was immersed in the KMnO<sub>4</sub> solution at 65 °C for 4 hours. During immersion, the color of the solution changed from purple into brown. The MnO<sub>2</sub>-deposited CNFs (CNFs-MnO<sub>2</sub>) were removed from the solution, rinsed with distilled water, and dried overnight in an oven at 80 °C. The MnO<sub>2</sub>-CNFs obtained under this condition using the KMnO<sub>4</sub> concentrations listed above are denoted to as CNF-MnO<sub>2</sub> (1:1) and CNFs-MnO<sub>2</sub> (1:2). Note that the mass ratio in here represents the mass ratio of CNFs mat to KMnO<sub>4</sub> during preparation.

## 3 RESULT & DISCUSSION

### 3.1 The effect of relative humidity on PVA nanofiber

Relative humidity (RH) is one of the parameters processes that affected morphology nanofiber. Temperature and humidity of the environment are very much influencing the physical characteristic due to the effect of solvent vaporization and solution sensitivity on the drying rate of the solution. This includes the performance of nanofiber forming i.e., smooth fiber, bead or beadless, and fiber diameter. Interaction between the solution and the surrounding water vapor should be considered on fiber diameter. In this study, the effect of RH on morphology nanofiber (diameter and shape) is investigated based on PVA polymer solutions with a concentration of 15 % w/v. As shown in Figure 1, smaller diameter PVA fibers spun from the higher humidity was found from the same concentration. A possible reason for this condition is due to slower solvent evaporation that water condensing on the surface of electrospinning was absorbed into the solution from the environment during the electrospinning process, and it was related to lower viscosity. Mean fiber diameter was shown to reduce from 300 nm at 50 % relative humidity to 250

nm at 70 % relative humidity. Nevertheless, the lower relative humidity may also be led to rapid solvent vaporization that may cause an increase in the solidification rate. Thus, the larger fiber diameter has resulted.

The chamber of electrospinning is not a vacuum, and there are many slots on the wall. Therefore in the next step, the relative humidity was held on at 60%, caused it is relatively simple to control with dehumidifier during the electrospinning process.

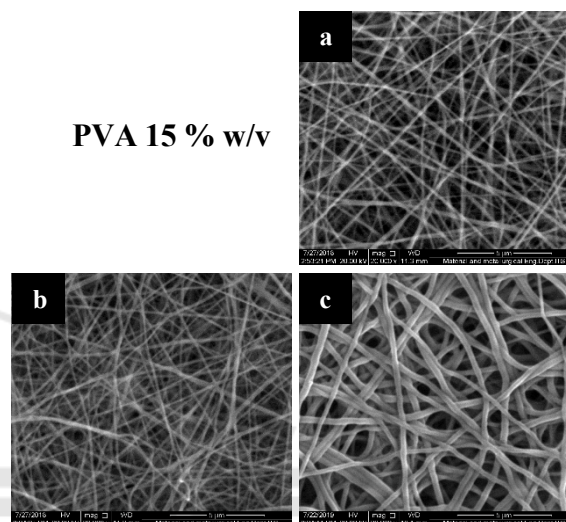


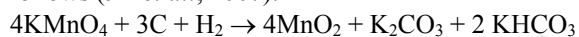
Figure 1 : SEM images of PVA 15 % w/v electrospun product at RH : (a) 70 % (b) 60 % (c) 50%

### 3.2 Synthesis Carbon Nanofiber/MnO<sub>2</sub>

MnO<sub>2</sub> was deposited by immersing Carbon Nanofiber (CNF) composites in the KMnO<sub>4</sub> solution. Carbon nanofibers were formed from the mixture between PVA and Acetylene black (AB) with AB concentration 10 and 15 wt. % based on PVA powder. In the previous study, AB concentration influenced the shape and diameter fibers (Yuniar *et al.*, 2019). The AB concentrations listed above are denoted to as 10CNFs-MnO<sub>2</sub> (1:1), 10CNFs-MnO<sub>2</sub> (1:2), 15CNFs-MnO<sub>2</sub> (1:1) and 15CNFs-MnO<sub>2</sub> (1:2).

Figure 4 shows the SEM images CNFs-MnO<sub>2</sub> composites where there are particles deposited on the surface of CNF, which indicate the presence of MnO<sub>2</sub>. After depositing MnO<sub>2</sub> by a redox reaction with KMnO<sub>4</sub> solution, the morphology of CNFs in contrast to that of CNFs from the previous study that CNFs before immersing was smooth fibers (Yuniar *et al.*, 2019). During the immersion of CNF in the KMnO<sub>4</sub> solution, the color changed from purple to dark brown that indicates MnO<sub>2</sub> had been formed (Fuenmayor *et al.*, 2013). For 10CNFs-MnO<sub>2</sub> (1:1)

and 15CNFs-MnO<sub>2</sub> (1:1), the surface area of CNFs became rough, and nanoparticles of MnO<sub>2</sub> can be exposed, as shown in Figures 1a and 1c. For 10CNFs-MnO<sub>2</sub> (1:2) and 15CNFs-MnO<sub>2</sub> (1:2), which is prepared in a higher mass ratio of KMnO<sub>4</sub>, the large-sized particle of MnO<sub>2</sub> are deposited on the fiber surface. Figures 1b and 1d show that the particles of MnO<sub>2</sub> appear uneven on the surface of the fiber and are more likely to form agglomerates around fiber nodes. It tends to make a layer above the fiber surface so that the fiber structure is covered by the layer above it. The previous study reported that smaller particles like microscale that have smooth texture on the surface, it takes adhesion of particle initially on the surface, and that means the particle MnO<sub>2</sub> (Chow, 2003). When the carbon fibers were immersed in a KMnO<sub>4</sub> solution at 65 °C, CNFs was directly reduced the KMnO<sub>4</sub>. The overall reaction is described as follows (Jin *et al.*, 2007):



Carbon fibers provided not only as a reagent. Based on the redox reaction of KMnO<sub>4</sub>, carbon fibers not only as a reagent but also as substrate and agent collector of the current. The rough surfaces of carbon fibers, it is becoming the new of surfaces carbon fibers, and it causes the carbon fibers are intrinsically less positive (Chi *et al.*, 2014). During the process of nucleation and MnO<sub>2</sub> nanoparticle, the more enough nucleation area, the more area can wipe out the essence of creating a new surface (Chi *et al.*, 2014).

The structure of the MnO<sub>2</sub> particle on the surface carbon nanofibers was analyzed by XRD analysis (X'pert PRO PANalytical). As shown in Figure 3, the XRD patterns of CNFs-MnO<sub>2</sub> shows the two broad diffractions approximately 17.5° and 25.3°. The spectrum of the carbon nanofibers (CNFs) can be indexed (002), which represented the graphite carbon structures. Broad peak diffraction revealed that the size of graphite might be in the nanometer scale and the degree of graphitic relative low (Zhou *et al.*, 2010). The diffraction peak at 36.6° associated with the (101) crystallographic planes of ramsdellite-type of MnO<sub>2</sub> (JCPDS 39-375) (Ghodbane, Pascal and Favier, 2009). Nevertheless, the peak just appeared in 10CNFs-MnO<sub>2</sub> (1:1). Consequently, CNFs-MnO<sub>2</sub> was reheated on tubular furnace at 300 °C for 1 h under constant nitrogen flow. It might be removed impurities of the CNFs-MnO<sub>2</sub>.

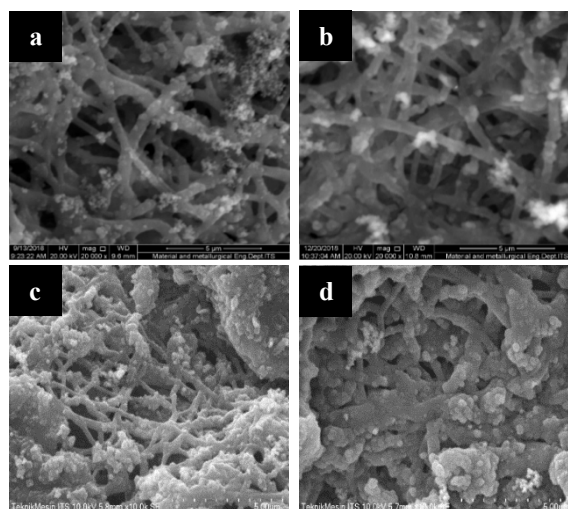


Figure 2 : SEM images after immersing KMnO<sub>4</sub> solution and dried at 80 °C : (a) 10CNFs-MnO<sub>2</sub> (1:1) (b) 10CNFs-MnO<sub>2</sub> (1:2) (c) 15CNFs-MnO<sub>2</sub> (1:1) (d) 15CNFs-MnO<sub>2</sub> (1:2)

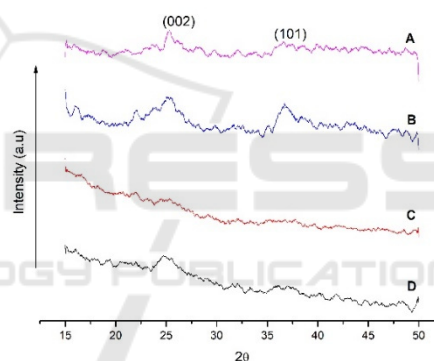


Figure 3 : XRD patterns after immersing KMnO<sub>4</sub> solution and dried at 80 °C : (a) 10CNFs-MnO<sub>2</sub> (1:2) (b) 10CNFs-MnO<sub>2</sub> (1:1) (c) 15CNFs-MnO<sub>2</sub> (1:2) (d) 15CNFs-MnO<sub>2</sub> (1:1)

Figure 4 shows the XRD patterns of CNFs-MnO<sub>2</sub> that reheated at 300 °C. The two broad diffractions approximately at 36.6° and 44.4° in the spectrum can be indexed (101) and (210), respectively, represent the presence of ramsdellite-type MnO<sub>2</sub> at all the samples (JCPDS 39-375) (Ghodbane, Pascal and Favier, 2009). All of the peaks in the spectrum are broad (poor crystallinity), and weak intensity, due to typically adhesive MnO<sub>2</sub> nanoparticle (Ma *et al.*, 2016) yet the peaks from XRD analysis proved the presence of MnO<sub>2</sub> in four samples. XRD pattern of 15CNFs-MnO<sub>2</sub> (1:2) has sharper peaks than those of 15CNFs-MnO<sub>2</sub> (1:1), 10CNFs-MnO<sub>2</sub> (1:2) and 10CNFs-MnO<sub>2</sub> (1:1), indicating that MnO<sub>2</sub> on the surfaces of 15CNFs-MnO<sub>2</sub> (1:2) might have a higher

degree of crystallinity. Nevertheless, the nanofiber structure is lost when reheated at 300 °C. As shown in Figures 5a and 5b, the 10CNFs-MnO<sub>2</sub> (1:1) and 10CNFs-MnO<sub>2</sub> (1:2) surface fiber became rough. The structure nanofibers were completely gone.

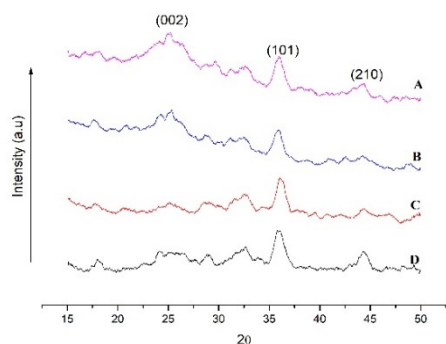


Figure 4 : XRD patterns after immersing KMnO<sub>4</sub> solution and dried at 300 °C : (a) 10CNFs-MnO<sub>2</sub> (1:1), (b) 10CNFs-MnO<sub>2</sub> (1:2), (c) 15CNFs-MnO<sub>2</sub> (1:1), and (d) 15CNFs-MnO<sub>2</sub> (1:2)

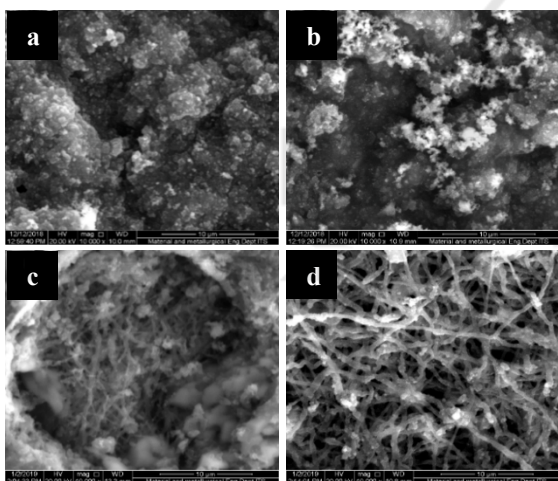


Figure 5 : SEM images of samples (a) 10CNFs-MnO<sub>2</sub> (1:1), (b) 10CNFs-MnO<sub>2</sub> (1:2), (c) 15CNFs-MnO<sub>2</sub> (1:1), and (d) 15CNFs-MnO<sub>2</sub> (1:2) after immersing KMnO<sub>4</sub> solution and dried at 300 °C

To evaluate the electrochemical performance of CNFs-MnO<sub>2</sub> as electrodes in capacitors, cyclic voltammetry (CV) measurements (Autolab PGSTAT 302N) were used on the CNFs-MnO<sub>2</sub> in a two split electrode system while using 1 M Natrium thiosulfate (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>) as an electrolyte. The CV curve was performed from -1 to 1 volt at scan rates of 100 mV.s<sup>-1</sup>. The capacitance was estimated from the results of CV curves using the equation  $C = (\int I dv) / (m s R)$ , where the I is the current, v is applied potential, m is the mass of the CNFs-MnO<sub>2</sub> electrode,

s is the scan rate, and R is the potential delta window for the measurement of CV. In the two split electrode, the aluminum band was sharpened circular with diameter 12 mm and used nanocellulose paper that soaked in the electrolyte solution for 24 hours as the separator for CV measurements. This measurement was operated without a binder.

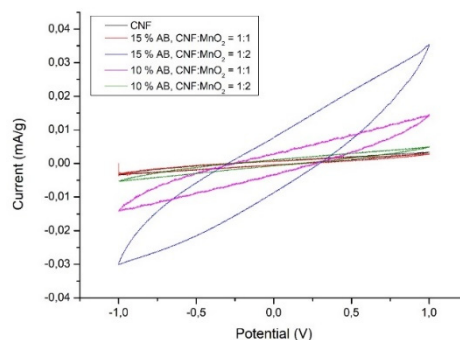


Figure 6: CV curves of the CNF-MnO<sub>2</sub> that dried at 300 °C

As shown in Figure 6, CV plots revealed the area of 15CNFs-MnO<sub>2</sub> (1:2) is larger than others. It might be 15CNFs-MnO<sub>2</sub> (1:2) acquired higher crystalline than others with uniform distribution of that would facilitate for reversible ion phenomenon, which is proved by XRD pattern as shown in Figure 4. It is showed that the CNF after immersing KMnO<sub>4</sub> solution that growth MnO<sub>2</sub> particle on the surfaces of fibers able to increase the capacitance. The high capacitance can be associated with the existence of MnO<sub>2</sub> among porous structures that able to cut off the electron diffusion path to provide ion and electron exchange. That means the redox reaction can be increased. Nevertheless, these capacitance values were relatively low compared to other capacitors' electrodes. It is caused the relatively poor electrical conductivity of the MnO<sub>2</sub> decorated on the surface of CNFs. MnO<sub>2</sub> possess with low crystalline was resulted in low concentration KMnO<sub>4</sub> that used for immersing carbon nanofiber. The capacitances of CNFs-MnO<sub>2</sub> are shown in Table 1.

Table 1 : Capicatanse of CNF and CNFs-MnO<sub>2</sub>

Variable	Capacitance (µF/g)
CNF	27
15CNFs-MnO <sub>2</sub> (1:1)	32
15CNFs-MnO <sub>2</sub> (1:2)	231
10CNFs-MnO <sub>2</sub> (1:1)	36
10CNFs-MnO <sub>2</sub> (1:2)	29

## 4. CONCLUSIONS

The study showed that during electrospinning, the diameter of nanofibers could be arranged by relative humidity. MnO<sub>2</sub> nanocrystals were successfully deposited on the surfaces of CNFs by the redox reaction of immersing the KMnO<sub>4</sub> solution. The electrochemical performance of CNFs-MnO<sub>2</sub> designated might be capable of electrodes in a capacitor with optimization.

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## REFERENCES

- Chi, H. Z. et al. (2014) 'Direct growth of MnO<sub>2</sub> on carbon fiber cloth for electrochemical capacitor', *JOURNAL OF ALLOYS AND COMPOUNDS*. Elsevier B.V., 587, pp. 354–360.
- Choi, J. S. et al. (2004) 'Effect of organosoluble salts on the nanofibrous structure of electrospun poly(3-hydroxybutyrate-co-3-hydroxyvalerate)', *International Journal of Biological Macromolecules*, 34(4), pp. 249–256.
- DeMerlis, C. C. and Schoneker, D. R. (2003) 'Review of the oral toxicity of polyvinyl alcohol (PVA)', *Food and Chemical Toxicology*, 41(3), pp. 319–326.
- Demir, M. M. et al. (2002) 'Electrospinning of polyurethane fibers', *Polymer*, 43(11), pp. 3303–3309.
- Fashandi, H. and Karimi, M. (2012) 'Pore formation in polystyrene fiber by superimposing temperature and relative humidity of electrospinning atmosphere', *Polymer*, 53(25), pp. 5832–5849.
- Fuenmayor, C. A. et al. (2013) 'Encapsulation of R-(+)-limonene in edible electrospun nanofibers', *Chemical Engineering Transactions*, 32, pp. 1771–1776.
- Gamby, J. et al. (2001) 'Studies and characterisations of various activated carbons used for carbon/carbon supercapacitors', *Journal of Power Sources*, 101(1), pp. 109–116.
- Ghodbane, O., Pascal, J. L. and Favier, F. (2009) 'Microstructural effects on charge-storage properties in MnO<sub>2</sub>-based electrochemical supercapacitors', *ACS Applied Materials and Interfaces*, 1(5), pp. 1130–1139.
- Jin, X. et al. (2007) 'Nanoscale microelectrochemical cells on carbon nanotubes', *Small*, pp. 1513–1517.
- Kim, G. T. et al. (2004) 'Effect of Humidity on the Microstructures of Electrospun Polystyrene Nanofibers', *Microscopy and Microanalysis*. 2004/08/01. Cambridge University Press, 10(S02), pp. 554–555.
- Koski, A., Yim, K. and Shivkumar, S. (2004) 'Effect of molecular weight on fibrous PVA produced by electrospinning', *Materials Letters*, 58(3), pp. 493–497.
- Lee, J. S. et al. (2004) 'Role of molecular weight of atactic poly(vinyl alcohol) (PVA) in the structure and properties of PVA nanofabric prepared by electrospinning', *Journal of Applied Polymer Science*. John Wiley & Sons, Ltd, 93(4), pp. 1638–1646.
- Ma, X. et al. (2016) 'Electrospun lignin-derived carbon nanofiber mats surface-decorated with MnO<sub>2</sub> nanowhiskers as binder-free supercapacitor electrodes with high performance', *Journal of Power Sources*. Elsevier B.V, 325, pp. 541–548.
- Mit-uppatham, C., Nithitanakul, M. and Supaphol, P. (2004) 'Effects of Solution Concentration, Emitting Electrode Polarity, Solvent Type, and Salt Addition on Electrospun Polyamide-6 Fibers: A Preliminary Report', *Macromolecular Symposia*. John Wiley & Sons, Ltd, 216(1), pp. 293–300.
- Ogulata, T. and İçoğlu, H. (2013) 'Effect of Ambient Parameters on Morphology of Electrospun Polyetherimide (PEI) Fibers', *Tekstil ve Konfeksiyon*, 23, pp. 313–318.
- Pech, D. et al. (2010) 'Ultrahigh-power micrometre-sized supercapacitors based on onion-like carbon', *Nature Nanotechnology*, 5(9), pp. 651–654.
- Pelipenko, J. et al. (2013) 'The impact of relative humidity during electrospinning on the morphology and mechanical properties of nanofibers', *International Journal of Pharmaceutics*, 456(1), pp. 125–134.
- Shenoy, S. L. et al. (2005) 'Role of chain entanglements on fiber formation during electrospinning of polymer solutions: good solvent, non-specific polymer–polymer interaction limit', *Polymer*, 46(10), pp. 3372–3384. doi: <https://doi.org/10.1016/j.polymer.2005.03.011>.
- Wang, J.-G. et al. (2013) 'A high-performance asymmetric supercapacitor based on carbon and carbon–MnO<sub>2</sub> nanofiber electrodes', *Carbon*, 61, pp. 190–199. doi: <https://doi.org/10.1016/j.carbon.2013.04.084>.
- Xia, H. et al. (2012) 'Hydrothermal synthesis of MnO<sub>2</sub>/CNT nanocomposite with a CNT core/porous MnO<sub>2</sub> sheath hierarchy architecture for supercapacitors', *Nanoscale Research Letters*, 7(1), p. 33.
- Xiong, Z. et al. (2015) 'Poly ( ethylene terephthalate ) / Carbon Black Composite Fibers Prepared by Electrospinning', *Chinese Journal of Polymer Science*, 33(9), pp. 1234–1244.
- Xue, N. et al. (2014) 'Rapid Patterning of 1-D Collagenous Topography as an ECM Protein Fibril Platform for Image Cytometry', *PLOS ONE*. Public Library of Science, 9(4), p. e93590.
- Yazgan, G. et al. (2017) 'Steering surface topographies of electrospun fibers: understanding the mechanisms', *Scientific Reports*, 7(1), p. 158.
- Yu, G. et al. (2011) 'Enhancing the Supercapacitor Performance of Graphene/MnO<sub>2</sub> Nanostructured

- Electrodes by Conductive Wrapping', Nano Letters. American Chemical Society, 11(10), pp. 4438–4442.
- Yuniar, R. ayu et al. (2019) 'Formation of Carbon Fibres From Polymer Poly ( vinyl alcohol )/ Acetylene Black using Electrospinning Method Formation of Carbon Fibres From Polymer Poly ( vinyl alcohol )/ Acetylene Black using Electrospinning Method', IOP Conf. Ser.: Mater.Sci.Eng, 543, p. 012030.
- Zhang, L. L. and Zhao, X. S. (2009) 'Carbon-based materials as supercapacitor electrodes', Chemical Society Reviews, 38(9), p. 2520.
- Zhao, S. et al. (2004) 'Electrospinning of ethyl–cyanoethyl cellulose/tetrahydrofuran solutions', Journal of Applied Polymer Science. John Wiley & Sons, Ltd, 91(1), pp. 242–246.
- Zheng, J. et al. (2014) 'The Effect of Surfactants on the Diameter and Morphology of Electrospun Ultrafine Nanofiber', Journal of nanomaterial, 687298, pp. 1–9.
- Zhou, Z. et al. (2010) 'Graphitic carbon nanofibers developed from bundles of aligned electrospun polyacrylonitrile nanofibers containing phosphoric acid', Polymer, 51(11), pp. 2360–2367.

