I.A.U
Karaj branch

Cost Effective and Scalable Synthesis of MnO₂ Doped Graphene in a Carbon Fiber/PVA: Superior Nanocomposite for High Performance Flexible Supercapacitors

Mohammad Javad Taghizadeh[*1], Behzad Poorbadiei[2], Esmail Soholi[1]

[1]Department of Chemistry, School of Sciences University of Imam Hossein, Tehran, Iran

[2]Faculty of Chemistry, University of Sharif, Tehran, Iran

Abstract

In the current study, we report new flexible, free standing and high performance electrodes for electrochemical supercapacitors developed througha scalable but simple and efficient approach. Highly porous structures based on carbon fiber and poly (vinyl alcohol) (PVA) were used as a pattern. The electrochemical performances of Carbon fiber/GO-MnO₂/CNT supercapacitors were characterized using cyclic voltammetry, galvanostatic charge/discharge and impedance spectroscopy techniques. The porosity of the electrode material was determined by scanning electron microscopy. The electrode specific capacitance was calculated to be 68Fcm-150 mv/s from cyclic voltammetry. The prepared films could be directly used as flexible supercapacitor electrodes and exhibited a highly specific capacitance and good cycle stability. The porous structures of films pavethe way for emission without blocking for electrolyteions and increase the specific area of the material. The electrochemical analysis confirms that the Carbon fiber/GO-MnO₂/CNT has improved particular capacitance compared to Carbon fiber/GO-MnO₂ and Carbon fiber/MnO₂. This study offers a new extremely light, conductive, inexpensive and environmentally friend electrode material that are promising for future flexible and efficient electrochemical supercapacitors.

Keywords:Supercapacitors, Superior Nanocomposite, Graphene, Carbon Fiber/PVA.

Corresponding author: *Mohammad Javad Taghizadeh, Department of Chemistry, School of Sciences University of Imam Hossein, Tehran, Iran, E-mail:* mohammadjavadtaghizadeh31@yahoo.com.

Introduction

The growing demand for the energy and environmental challenges facing the world leading to use ofrenewable energy sources such as batteries and supercapacitors (SPs). Over the past few years, SPs have paid close attention to wide range of applications including power utility applicationsand as back up energy storage due to their superior properties such asfast charging/discharging rates, high power performance, long cycle life and excellent environmental safety [1,2]. Today, flexible energy storage devices are widely considered to be usedin portable and wearable electronic systems in varied fields. SPs are classified into two groups: electrochemical double layer capacitors (EDLC) and pseudocapacitors. Pseudocapacitors can possess higher capacitance per gram than EDLCs. Therefore, it has been attempted to makelightweight, low cost and large-scale manufacturing of materials with pseudocapacitance properties [3,4].

Recently, many efforts have been made to investigatenew electrode materials to enhance cyclic stability and increasing the capacitance of the SPs. There are three major types of electrode materials: 1) carbon source materials such as CNT, graphene, activated carbon, nanodiamonds with high specific surface area based on double layer capacitance mechanism; 2) conducting polymers and 3) metallic oxides transmittedwith pseudocapacitance or Faradic process. Nowadays, hybrid capacitors are designed using both high-surface area carbonaceous materials and pseudocapacitance materials comprehensively in a single electrode. Rapid replacement of inherent redoxswitching and low weight. Among these, MnO_2 has received much research attention due toits facile synthesis, low cost, high specific capacitance and long-term stability [5,6]. At present, there is an increasing demand for low - cost, environmentally friend and renewable electronic devices derived to fabricating biobased as well as flexible, scalable and efficient energy storage devices such as SPs [7-9]. For instance, Dominko and his co-workers, developed low surface area graphene/cellulose composite a host matrix for Li/S batteries[10]. Shao and his co-workers used cellulose nanofibers paper as the SP substrate [11]. In the other related study, Deng et al. made solid-state and flexible PANI/Ag/cellulose aerogel supercapacitors [12]. It is worth noting that the drawback associated with metal oxides is its poor conductivity. Therefore, different approaches have been developedto achieve high performance, lightweight and conductivity composites of metal oxides.Polyvinyl alcohol (PVA), has been widely used as the gel electrolyte of SPs due toits availability, hydrophilicity, chemical resistance properties as well as excellent mechanical properties and good film forming [13,14].

Herein, we report a simple strategy for producing Carbon fiber/GO-MnO_2/CNT ternary hybrid nanocomposite with potential application as electrode for SPs (scheme 1). The porous and paper-like carbon fiber was used to support the MnO_2 nanoparticles. PVA was used as the polymer matrix

and stabilizer of GO-MnO$_2$ and CNT on the carbon fiber sheets. To the best of our knowledge, a flexible electrode material based on carbon fiber has not been studied yet. The ternary composite material exhibited excellent specific capacitance up to 168 F/cm^2 and good cycling stability. It has been observed that the porous structure and addition of CNT increase the electrochemical capacitance of the electrode. Therefore, excellent mechanical properties of PVA, the high specific surface area of carbon based materials and pseudocapacitance of MnO$_2$ prepared low cost and scalable electrode in potential energy storage devices.
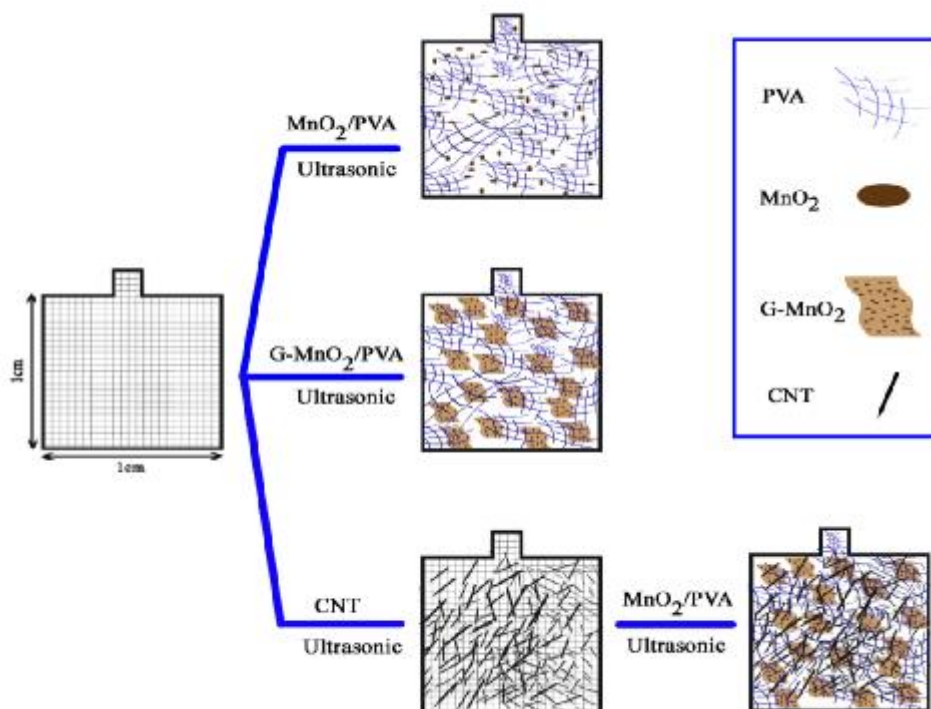
Scheme 1. producing Carbon fiber/GO-MnO$_2$/CNT ternary hybrid nanocomposite.

Experimental

Materials and Methods

Poly (vinyl alcohol) with molecular weight of 145000, Carbon fiber(CF)(from china), natural graphite powder, potassium permanganate (KMnO$_4$) (from Merck) sulfuric acid (H$_2$SO$_4$, 98%), hydrochloric acid (HCl, 37%), phosphoric acid (H$_3$PO$_4$, 85%) and hydrogen peroxide (H$_2$O$_2$ 30%) were purchased from Merck Company and used without further purification, NaOH, Mn(OAc)$_2$, Citric acid, NH$_3$, CNT(from Merck).

Fabrication of the nanocomposite

Purification of graphite

10g impure graphite was dissolved in NaOH 25% (5g NaOH was loaded into a beakerand thenH_2O was added to a total mass of 20 g). Then, impure graphite was poured into porcelain crucible and NaOH solution was added, following it the solution was stirred to obtain homogeneous solution. Porcelain crucible was placed in furnace at 300 °C for 1 h, then obtained lump was milled by a mortar. The Resulting graphite was washed with H_2O and HCl 5% several times to obtain a neutral pH and was dried at 60 °C.

Synthesis of GO

GO was synthesized by modified hummer method[15,16]. First of all, 3g purified graphite was poured into a flask containing 360 mL H_2SO_4 (98%). Then 40 mL H_3PO_4 was added, following 18g $KMnO_4$was added for 30 min. The resulted solution was stirred for 12 h at 55 °C. Then 150 mL distilled water was added and temperature of the solution was reduced to 4 °C byan ice bath. Next, 4 mL H_2O_2 (30%) was added dropwise to the solution until there is no bubbles. Following stage, the solution was washed with HCl (5%) and water then it was centrifuged and dried at 40 °Cfor 24 h.

Synthesis of manganese oxide nanoparticles

1g Mn(OAc)$_2$ and 1.74g acid citric was dissolved in deionized water then pH was fixed in 6 by NH_3 and stirred at 80 °C for 2 h. The obtained gel was heated at 380 ° C for 12 h in the furnace toform manganese oxide nanoparticles.Next, for the purification, it was stirred in H_2SO_4 2M, for 1h. After filtration and washing, the resulted sediment was dried at 100 °C to obtain brown sediment.

Synthesis of GO doped to manganese oxide nanoparticles

200 mg resulted graphene oxide was stirred in the aqueous solution of 0.02 M $KMnO_4$ under reflux conditions for 12 h. Then it was washed several times with water and was dried at 55 °C.

Preparation of PVA solution

At the first, 0.3g PVA was weighed and was poured in 10 mL deionized water then it was stirred at 95 °C under reflux conditions for 2 h to obtain homogenous solution of PVA 3%.

Preparation of carbon fiber-manganese oxide fiber (CF/MnO$_2$)

10 ml of 3% PVA solution was loaded onto a 25 ml baker and then 0.1 g of MnO nanoparticles were dispersed in PVA solution by sonication for 2 h. Then, a carbon fiber (1 × 1 cm2, 0.001 g) was immersed in the solution.After drying of the fiber the same procedure was done tow time again and

at last, it was completely dried at 60 0C for 20 h.Preparation of carbon fiber-manganese oxide-graphene oxide (CF/G-MnO_2). This electrode was also prepared by the previous method.

Preparation of carbon fiber - manganese oxide – graphene oxide - carbon nanotube (CF/CNT/G-MnO_2)

First 0.05 g CNT was dispersed in 20 mL ethanol solution for2 h under ultrasonication. Then carbon fiber (1×1 cm2, 0.001 g) was immersed in the solution then it was dispersed for other 30 min until CNT is dispersed on yarn.0.1 g of G-MnO_2 was added to the 10 mL of PVA solution (3 wt%) and then dispersed via ultrasonic irradiation in 30 min. CF/CNT papers were immersed in the above solution and dried in room temperature. this process was repeated three times. The sample preparation method was used for electrochemical analysis of silver paste to attach each of the electrodes to a thin copper wire and dried overnight at 40 ° C.

Characterization

In order to verify the the chemical structure of the products, FTIR spectra over a frequency range of 500–4000 cm^{-1} obtained at room temperature using a FTIR spectrometer (ABB Bomem MB-100). The thermal properties of samples were conducted using a thermogravimetricanalyzer (TGA-DSC1/Mettler Toledo) ranging from room temperature to 700˚C at a rate of 15˚C/ min under N_2atmosphere. The surface morphology of the fibers was observed by scanning electron microscope (SEM) of model Vegall-Tescan. Cyclic voltammetry (CV) was performed using a standard three-electrode electrochemical cell utilizing an Autolab/GPES interface (Metrohm) with the sample as the working electrode, a platinum wire as the counter electrode and a 3 M KCl-saturated Ag/AgCl electrode as the reference electrode in a 0.5M Na_2SO_4electrolyte. The specific capacitance (C) of the active electrode materials was also determined from the charge/discharge curves using the equation:

$$C=(i×\Delta t)/(m×\Delta V)$$

where i is discharging current, Δt is the discharging time, m the mass of active electrode materials ona single side, and ΔV is the voltage drop upon discharging.

Results and discussion

FTIR is a powerful tool for characterization of chemical structure of materials. FTIR spectra of GO, MnO_2 and GO/MnO_2 composite are shown in Figure 1.FTIR spectrum of GO demonstrates C=O stretching band of carboxylic acid groups in 1716 cm^{-1}. The main peak of MnO_2 nanoparticleshas

appeared at 500 cm^{-1} corresponding to the Mn-O stretching vibration. The main peak of MnO$_2$ at 500 cm^{-1} in FTIR spectrum of GO/MnO$_2$ nanocomposite indicates that MnO$_2$ nanoparticles have been synthesized on the surface of GO.
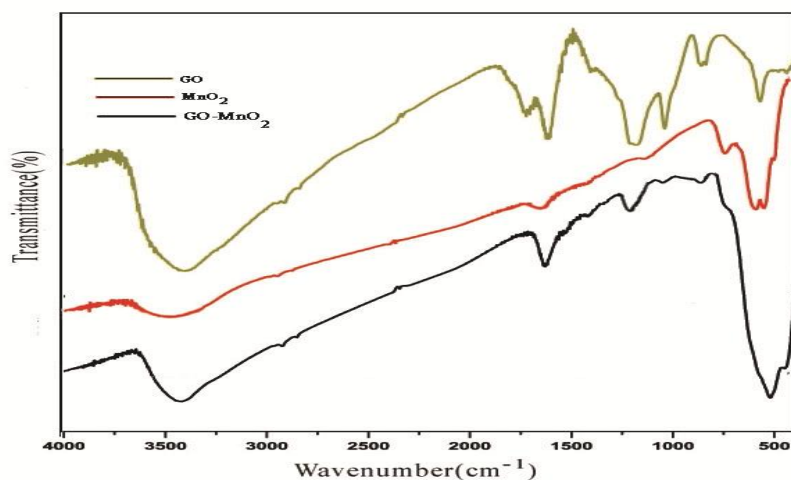
Figure 1. FT-IR of GO, MnO$_2$, GO-MnO$_2$.

The TGA curves of the synthesized materials in the temperature range between 30 to 750 ºC are shown in Figure 2. The adsorbent water molecules were removed to 150 ° C in all samples. The decomposition of PVA and carboxylate groups of GO take place from 150 to 500 ºC. It has been observed that there areapproximately 10 %of MnO$_2$ in CF/MnO$_2$ composite by comparing with TGA curve of CF at temperature rangeof 500-750 ºC. Addition of CNT increased the thermal stability of the CF/G-MnO$_2$/CNT nanocomposite.
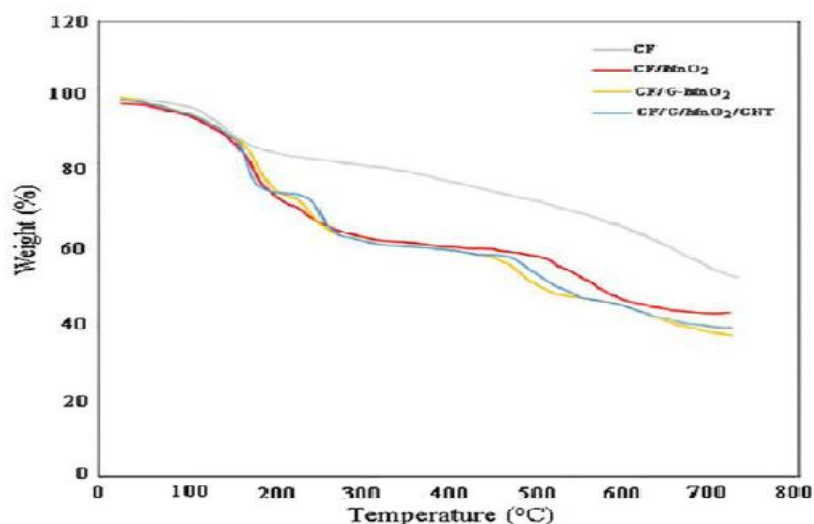
Figure 2. TGA curves of the CF, CF/MnO$_2$, CF/G-MnO$_2$, CF/G-MnO$_2$/CNT.

SEM images of the synthesized MnO$_2$ nanoparticles are shown in Figure 3a. The rodshapednanoparticles with 25 nm in diameter and 300 nm in length have completely covered the

surface of GO (Figure 3b). The filament of bare CF and functionalized CF with GO/MnO$_2$ are shown in Figure 3c and d respectively. It is observed that CFs have successfully functionalized with GO/MnO$_2$ as shown in section SEM image with 500 nm resolution.
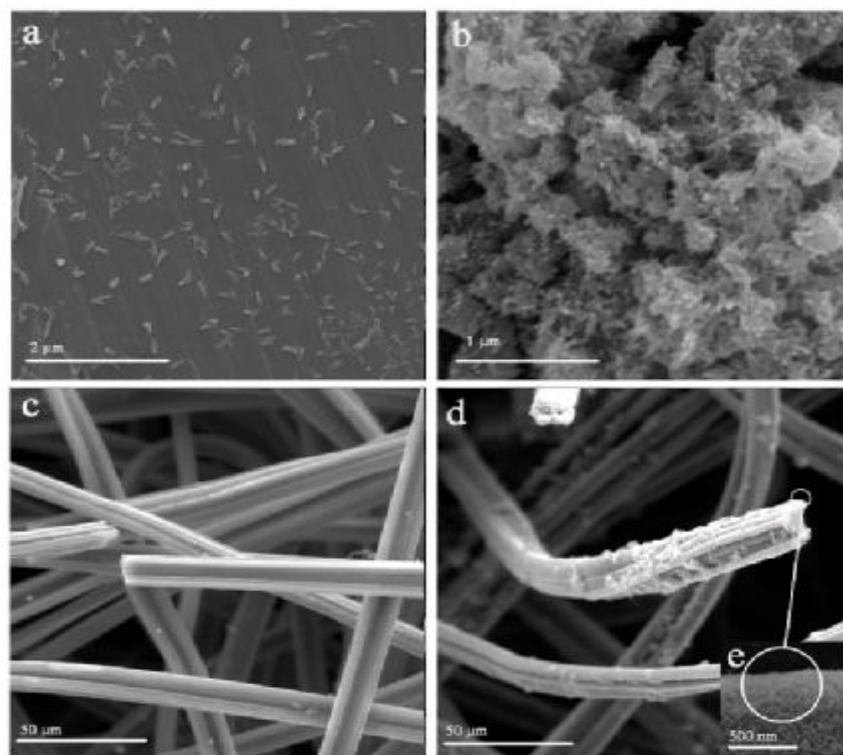
Figure 3. (a) SEM images of MnO$_2$ nanoparticles, (b) GO/MnO$_2$, (c) CF, (d) CF/GO/MnO$_2$.

Figure 4 shows the cyclic voltammograms (CV) of three different electrodes in 1M KOH electrolyte at the scan rate of 100 mV/s. Calculated specific capacitance are 17.8, 20.7 and 40.6 F/g for MnO$_2$, GO/MnO$_2$ and GO/MnO$_2$/CNT electrodes respectively. The curves clearly show that the redox currents increasewith the addition of G-MnO$_2$ instead of MnO$_2$ alone. CNT help to enlarge the area of the curves enclosed in CV curves because of improving the conductivity of the electrode.
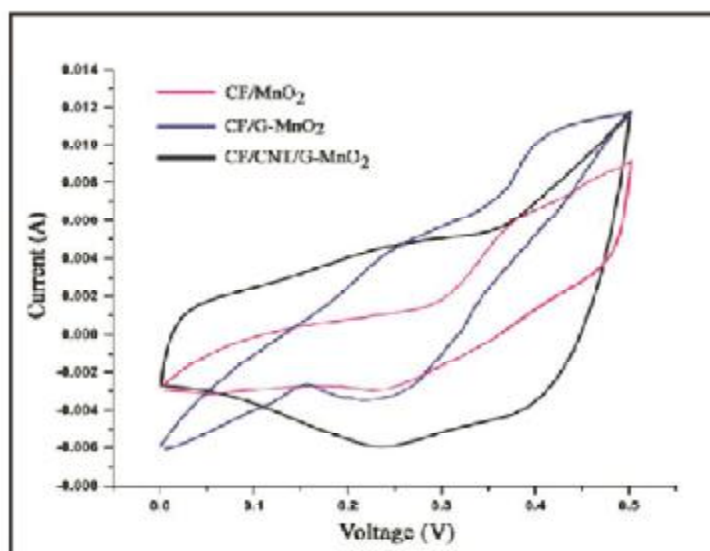
Figure 4. Cyclic voltammograms (CV) of for MnO_2, GO/MnO_2 and $GO/MnO_2/CNT$.

TheCyclic stability of the electrode was tested as illustrated in Figure 5a. After 500 consecutive cycles, the specific capacitance of the electrode decreases from 40.6 F/g at first cycle to 28.5 F/g, with retention of 70% specific capacitance. The electrochemical impedance spectroscopy (EIS) measurements were evaluated with the frequency ranging from 100 kHz to 100 mHz in KOH 1M aqueous as electrolyte.

Nyquist plots of the EIS data for the three prepared electrodes are shown in Figure 5b. The EIS of the MnO_2 and $G-MnO_2$ electrodes indicate well resolved semicircles in the high frequency range indicates same charge transfer resistance at both electrode/electrolyte interface. No distinct semicircle in the $G-MnO_2$ / CNT sample curveindicates a very low charge transfer resistance in this electrode which could be attributed to the conductive nature of the CNT that enclose with $G-MnO_2$. The straight line observed in the lower frequencies represents the Warburg impedance resulting from diffusive resistance of the electrolyte in the electrode materials. It is evident that $G-MnO_2$ and $G-MnO_2/CNT$ plots at low frequency area demonstrate straight line indicates that these electrodes have low diffusion resistance compared with MnO_2 alone. Galvanostatic charge/discharge is a very important procedureto evaluate the electrochemical capacitance of the material under controlled current conditions. Galvanostatic charge/discharge experiments, with current density from 0.5 to 10 mA are shown in Figure 5d. These curves show a small IR drop once discharging began, indicating internal resistance between $G-MnO_2$ and CF. The specific capacitance is calculated to be 166 and 71 F/g at 0.5 and 5 mA/g for the electrode normalized by MnO_2 weight. This result is in good accordance with the CV tests. At lower current, the electrolyte ions can be diffused sufficiently into

the interior electrode. Therefore, due to the limitation of emission, decrease in specific capacity is caused by increasing current density.
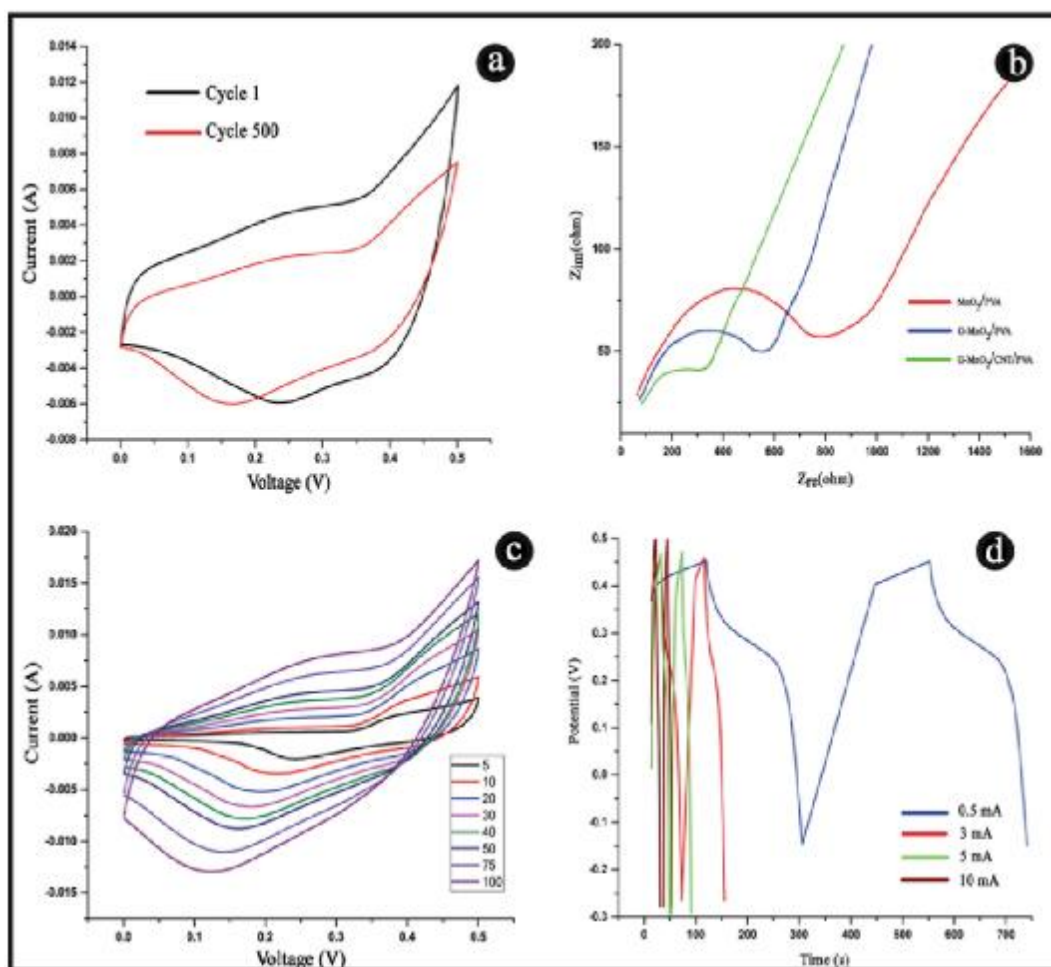
Figure 5. (a) Cyclic stability of the electrode, (b) The EIS data for the three prepared electrodes, (c) electrochemical properties of the G-MnO$_2$/CNT/PVA electrode, (d) Galvanostatic charge/discharge experiments.

To evaluate the electrochemical properties of the G-MnO$_2$/CNT/PVA electrode, Cyclic voltammetry was performed at different scan rates in KOH 1M, see Figure 5c which shows the first scans. This electrode representsCV curves of a nearly rectangular shapethat exhibits atypical capacitive behavior under the measured scan rates. Specific capacitance calculated from CV curves was 8 F/g at scan rate of 5 mV/s. The value gradually declined to 40.6 F/g when scan rate increased to 100 mV/s. The high electrochemical activity of MnO$_2$ and conductivity of CNT results in high capacitance at the electrode. The presence of graphene oxide in the composite provides high surface area for electrochemical reactions. There is a redox peak in 0.24 V observed a scan rate of 5 mV/s which gradually decreased to the 0.12 V at100 mV/s. The specific capacitance decreases as potential scan increases because at higher scan rate electrolyte ionscannot diffuse completely into the inner active sites of material hence, electrochemical reactions could not perform completely.

Table 1 summarizes the Carbon fiber/GO-MnO$_2$/CNT supercapacitors with those of other previously reported GO-MnO$_2$ materials in the literature. Comparison of the Carbon fiber/GO-MnO$_2$/CNT with other proposed methods clearly shows that the Specificcapacitance at the carbon fiber/GO-MnO$_2$/CNT used is higher than other electrodes.

Table 1. Comparison of the Specificcapacitance of GO/MnO$_2$ materials.

Currentcollector	working electrode	Electrolyte (M)	Specificcapacitance (F/g)	References
nickel foam	GO/MnO$_2$	0.5M Na$_2$SO$_4$	145.7	[17]
nickel foam	GO(3D)/MnO$_2$	0.5M Na$_2$SO$_4$	130	[18]
nickel foam	GR/MCNTs/MnO$_2$	0.5M Na$_2$SO$_4$	126	[19]
stainless steel	GO/MnO$_2$	0.5M Na$_2$SO$_4$	127	[20]
nickel foam	GO/MnO$_2$ precursor	0.5M Na$_2$SO$_4$	81.25	[21]
nickel foam	MnO$_2$/MnCO$_3$/rGO	0.5M Na$_2$SO$_4$	123.6	[22]
Carbon fiber	GO-MnO$_2$/CNT	0.5M Na$_2$SO$_4$	168	This work

Conclusion

In summary, we have successfully investigated the efficiency of carbon fibers membranes as flexible electrode materials for high performance supercapacitors. In this approach, MnO$_2$ nanoparticles were prepared and mixed with PVA solution to attachment into the carbon fibers. In order To improvement of the electrode, two different flexible thin film supercapacitors with G-MnO$_2$ and G-MnO$_2$/CNT composition were successfully fabricated. The proper electrochemical analysis was performed and it was concluded that the later nanocomposite (i.e. G-MnO$_2$/CNT) presented high specific capacitance and good cycling stability after 500 cycles. Furthermore, the proposed electrode showed great potential for the development of effective and low-cost flexible electrodes in energy storage devices.

References

[1] Q. Tang, M. Sun, S. h. Yu, G. Wang, *Electrochim. Acta*. 125, 488 (2014).

[2] Y. Huang, J. Liang, Y. Chen, *Original Research Article*, 8(12), 1805 (2012).

[3] W. Li, Y. J. Yang, *J Solid State Electrochem*. 18(6), 1621 (2014).

[4] L. X. Peng, B. Peng, Y. Xie, G. Yu, *Nano Lett.*, 13(5), 2151 (2013).

[5] X. Wang, K. Gao, Z. Shao, X. Wua, X. Wang, *J. Power Sources.*, 249, 148 (2014).

[6] W. Ouyang, J. Sun, J. Memon, C. H. Wang, J. Geng, Y. Huang, *Carbon.*, 62, 501 (2013).

[7] X. Jiang, Y. Cao, P. Wei, J. Wang, K. D. Wu, H. Zhu, *Mater.*, 140, 43 (2015).

[8] G. Zhu, Zh. He, J. Chen, J. Zhao, X. Feng, Y. Ma, Q. L. Wang, W. Huang, *Nanoscale.*, 6, 1079 (2014).

[9] L. Maa, X. J.Shen, Z. h. Zhu, G. H. Zhou, *Chem Eng J.,* 252, 95 (2014).

[10] M. U. M. Patel, N. D. Luong, J. Seppälä, E. R. Dominko, *J. Power Sources.*, 254, 55 (2014).

[11] Q. Niu, K. Gao, Z. Shao, *Nanoscale.*, 6, 4083 (2014).

[12] X. Zhang, Z. Lin, B. Zhang, W. Sharma, S. Gu, W. Deng, *J. Power Sources.*, 246, 283 (2014).

[13] M. Sathish, S. T. Tomai, I. Honma, *J. Mater.Chem.*, **21**, 16216 (2011).

[14] H. Fei, Ch. Yang, H. Bao, G. Wang, *J. Power Sources.*, 266, 488 (2014).

[15] H. Yu, B. Zhang, C. Bulin, R. Li, *Sci. Rep.*, 6, 36143 (2016).

[16]N.I.Zaaba, K.L.Foo, U.Hashim, S.J.Tan, W. Liu, C.H.Voon, *Procedia Eng.*,184, 469-477 (2017).

[17] S. Chen, J. Zhu, X. Wu, Q. Han, X. Wang, *ACS nano.*, 4, 2822 (2010).

[18] Y. He, W. Chen, X. Li, Z. Zhang, J. Fu, C. Zhao, E.Xie, *ACS nano*, 7, 174 (2012).

[19] L. Deng, Z. Hao, J. Wang, G. Zhu, L. Kang, Z. Liu, Z. Wang, *Electrochim. Acta*, 89, 191 (2013).

[20]Y. Duana, X. Sunb, H. Y. Zhaoc, Z. B. Liu, *Adv. Mater. Res.,*936, 607 (2014).

[21] F. Ding, N. Zhang, C. Zhang, C. Zhang, *Mater. Trans.*, 56, 1857 (2015).

[22] Y. Liu, D. He, H. Wu, J. Duan, Y. Zhang, *Electrochim. Acta*, 164, 154 (2015).