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NANOSTRUCTURED CNT-MnO₂ ELECTRODE PREPARED BY ELECTROPHORETIC DEPOSITION METHOD FOR SUPERCAPACITORS

RINGKASAN: Komposit Nanotub Karbon (CNTs)-manganese dioksida (MnO₂) telah disediakan sebagai elektrod positif untuk kapasitor lampau melalui kaedah Pemendapan Elektroporetik (EPD). Komposit elektrod tersebut mempamerkan kelakuan kapasitan-pseudo melalui tindakbalas elektrokimia antara MnO₂ dan ion OH untuk menghasilkan MnOOH di dalam elektrolit KOH. Nilai kapasitan spesifik yang dicapai adalah dalam julat 60-210 F/gm, melalui analisa kitaran volumetri dengan kadar imbasan 5 hingga 100 mV/s bergantung kepada jisim dan komposisi elektrod.

ABSTRACT: Carbon nanotubes (CNTs)-manganese dioxide (MnO₂) composite as positive electrode for supercapacitor has been prepared by Electrophoretic Deposition (EPD). The composite electrodes exhibited pseudocapacitance reactions in a 6 M KOH electrolyte resulting from the reaction of MnO₂ with OH ions to form MnOOH. Specific capacitance values ranging from 60-210 F/g were obtained by means of cyclic voltammetry scanning within a scan rate of 5 mV/s to 100 mV/s from electrodes of different mass and composition.

INTRODUCTION

MnO₂ has been considered as a promising electrode material for electrochemical supercapacitors because of its low cost and excellent capacitive performance. Many types of manganese dioxides have been investigated including crystalline and amorphous phase. However, MnO₂ exhibited low specific capacitance, because of high resistivity of bulk manganese oxide. One way of overcoming this is by adding the conductive materials such as carbon (Malak-Polaczyk *et al.*, 2010; Zhao *et al.*, 2014), carbon nanotubes (Wang *et al.*, 2013; Wang *et al.*, 2012; Li *et al.*, 2013; Wang *et al.*, 2011; Yang *et al.*, 2012; Sivakkumar *et al.*, 2007; Zou *et al.*, 2011; Teng, Santhanagopalan & Meng 2010; Teng, Santhanagopalan, Wang, *et al.*, 2010), graphene (Deng *et al.*, 2013;

Wu & Fu 2013; Yang *et al.*, 2014; Lim *et al.*, 2014; Jafta *et al.*, 2013; Tang *et al.*, 2014) and polymers (Yan *et al.*, 2014; Yoon & Kim 2013) to form a composite.

Concerning the materials issues, MnO₂ is one of the most studied materials as a low-cost alternative to RuO₂. It has a very high theoretical capacitance of ~1380 F/g but suffers from poor conductivity, hence lower than 30 % of the value was obtained. To further improve the performance of MnO₂-based supercapacitor, it is necessary to design MnO₂ materials into nanoarchitectures with desirable physicochemical features or composites with other materials, such as carbon derivatives or conductive polymer (Lei *et al.*, 2012; Li *et al.*, 2012; Sen *et al.*, 2013).

Composites of CNT-MnO₂ also have been investigated by various researchers for improving the performance of the composite electrode (Wang *et al.*, 2012; Li *et al.*, 2012). Generally, it has been found that by introducing CNTs into the matrix composite improves the electrochemical performance of the MnO₂ by lowering the electrical resistivity of the electrode. The conventional method for fabricating electrode from CNTs or metal oxides or the composite of both is by a paste coating method. In this method, the active material is mixed together with a certain amount of binder and acetylene black to form a paste before coating. Binder is used to improve adhesion between the particles and the substrate; while acetylene black is added to improve electrical conductivity (Kiamahalleh *et al.*, 2010; Cottineau *et al.*, 2006; Hassan *et al.*, 2014; Pandolfo *et al.*, 2006). However, these two materials lacked capacitive properties; hence can be considered 'dead weight'; which effectively reducing the specific capacitance of the electrode. To alleviate this, we propose a method to produce electrode material without usage of binder and acetylene black. The method is known as an electrophoretic deposition (EPD). Various researchers have applied this method to produce CNTs coating on various substrate for different applications. The CNTs are first charged with positive manganese ions (Mn²⁺), whereby during the deposition process the CNTs and manganese oxide are being deposited electrophoretically. This simultaneous reaction of the electrophoretic and electrochemical deposition of CNTs and manganese oxide/hydroxides is the novelty of this study.

MATERIALS AND METHODS

The carbon nanotubes in this study was supplied by Shenzhen Nanoport (NTP), China. The properties are shown in the Table 1.

Table 1. Properties of the supplied CNTs

| | |
|------------------|--------------|
| Diameter | 20-50 nm |
| Length | 5 microns |
| Purity | At least 95% |
| Synthesis Method | CVD |

10 gm of the CNTs was refluxed with concentrated nitric acid for 8 hrs. The nanotubes were then repeatedly washed with distilled water and filtered, followed by drying at 80° C for 24 hours. This process apart from purifying the CNTs, would functionalize the CNTs with carboxylic groups (-COOH). During refluxing process, the oxygen-containing groups are introduced to the ends and sidewalls of the tubes. These groups, which are chemically attached to the tubes, are mostly represented by -COOH groups, less by -C=O, and -OH groups (Datsyuk *et al.*, 2008; Yang *et al.*, 2007). 5 mg of the refluxed CNTs were then dispersed ultrasonically in 100 ml ethanol, by ultrasonic equipment (VCX 500, Sonics USA) with 50 % amplitude for 2 hours. In order to charge the carbon nanotubes, three different concentrations of Mn(NO₃)₂·6H₂O were added into the suspension at different concentrations of 1.0 x 10⁻⁵ mol/l, 5.5 x 10⁻⁵ mol/l and 1 x 10⁻⁴ mol/l, respectively. Nickel foils with the size of 3 x 5 cm were used as electrophoretic deposition (EPD) electrodes, and were put in parallel at 2 cm distance facing each other into the suspension.

An electric field of 100 V was applied across the two electrodes using high voltage DC power supply (KENWOOD Regulated DC power supply, model PD110-5AD). The deposition duration was 5 minutes for each charger salt concentration. The weight of the substrate before and after deposition were measured and recorded. The microstructure of the CNTs coated electrodes were investigated by high resolution Scanning Electron Microscopy (LEO 1525). Transmission Electron Microscope (TEM) analysis was performed on TECHNAI Phillips equipment. Effects of different concentration of charger salt on the chemical composition of CNT films were analysed by EDX. The XPS data collection was also performed on the coated samples using Omicron XPS system. The analysis of the XPS results was performed using CASA software. The cyclic voltammetry tests were performed using Autolab PGSTAT 30 system utilizing Ag/AgCl and platinum foil as a reference and counter electrode respectively.

RESULTS AND DISCUSSION

SEM observation on the coated surface revealed the deposition of the CNTs on the nickel substrate. The CNTs were observed to cover the entire nickel surface without recess or voids. The typical representation of uniform coatings was observed from coatings deposited of -the suspensions containing the charger salt within concentration range of 1×10^{-5} to 1×10^{-4} mol/l. It can be observed from Figure 1 that the coatings produced have a nanoporous structure because of the entanglement of the CNTs among each other. This is highly desirable as the porous electrode would provide clear pathways for ions diffusion into the electrode, hence, better materials utilization. TEM images in Figure 2 exhibits the formation of MnO₂ nanoparticles attached to the surface of the CNTs particles

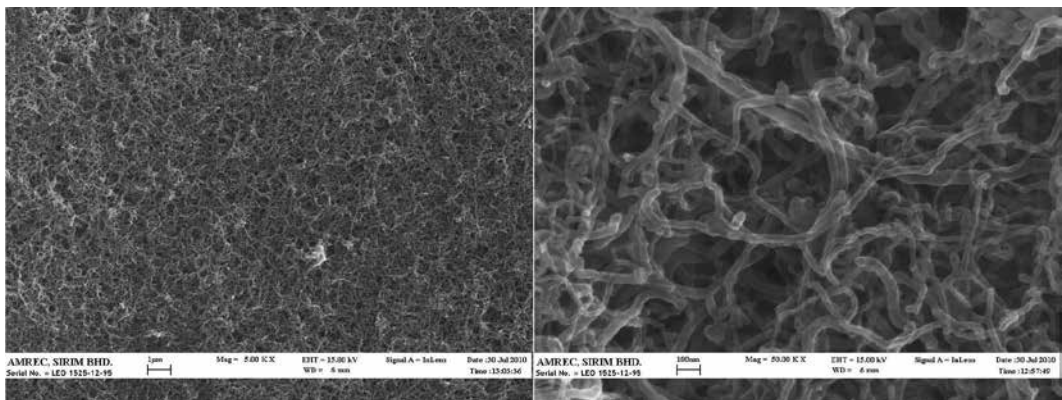


Figure 1. Surface morphology of CNTs-MnO₂ electrode at (a) 5 K magnification and (b) 50K magnification

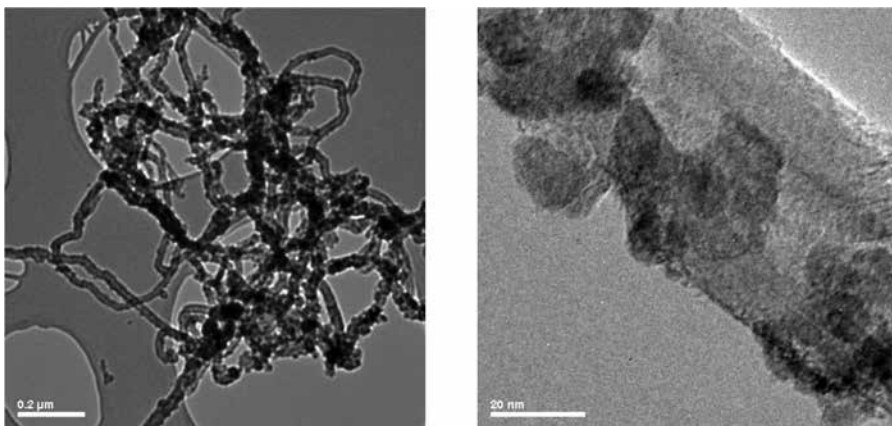


Figure 2. TEM images of CNT-MnO₂ composite electrode showing MnO₂ nanoparticles on (left) CNTs bundles and (right) individual CNT

It can also be seen that higher concentration of charger salt in the suspension always produced a coating with higher weight. The weight of the coating of 0.3, 0.5 and 0.7 mg/cm² was obtained for the deposition from CNTs suspension containing charger salt concentration of 1×10^{-5} , 5.5×10^{-5} and 1×10^{-4} mol/l respectively. EDS analyses performed on the deposited samples, as shown in Figure 3 revealed elemental presence of C, Mn and O respectively. It was also found that at the charger salt concentration of 1×10^{-5} mol/l, the numbers of Mn atoms detected were only 6 per 100 C atoms. This value increases to 24 per 100 C atoms for coating deposited from 5.5×10^{-5} mol/l charger salt containing bath, and subsequently, for coating deposited from 1×10^{-4} mol/l charger salt containing bath, gave the highest count of Mn atoms of about 46 per 100 C atoms. This was translated to weight percentage of approximately 12 %, 45 % and 67 % of MnO₂ in the CNTs-MnO₂ composite coating respectively.

Elemental mapping of Mn, C and O showed uniform distribution of respective element on the electrode surface, as shown in Figure 4, indicated by the presence of Mn and O elements together with the C element, suggesting the uniform distribution of MnO₂ on the surface of carbon nanotubes.

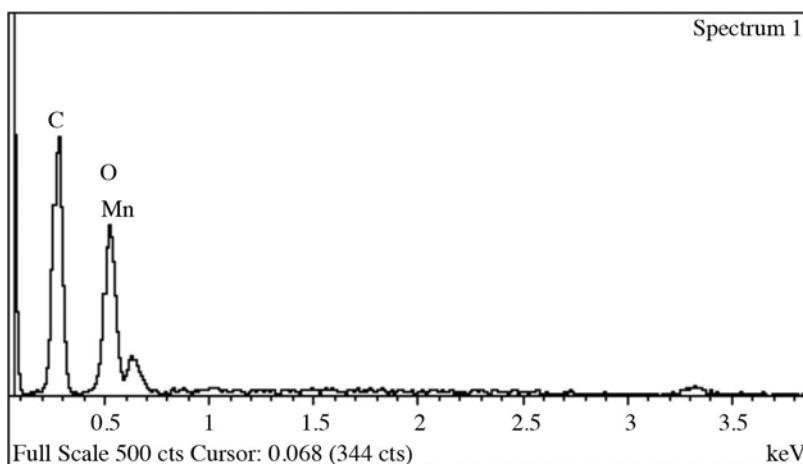


Figure 3. EDS spectra of CNTs-MnO₂ electrode

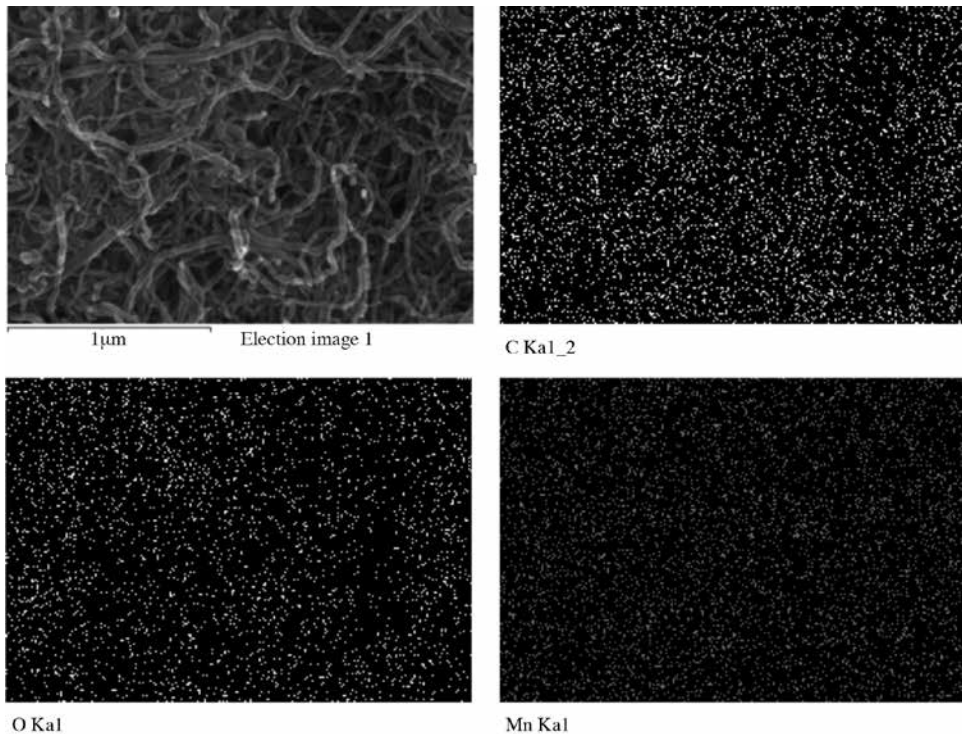
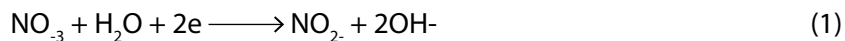
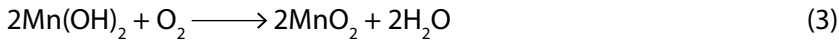


Figure 4. EDS mapping showing elemental distribution of C, O and Mn

XPS analysis by curve fitting on Mn 2p^{3/2} peak as shown in Figure 6(a) revealed the existence of two peaks at 641.9 eV and 644.2 eV respectively. Peak at 641.9 eV is related to the MnO₂, while binding energy of 644.2eV and 657.5 can be attributed to existence of unconverted Mn(OH)₂. Deconvolution of O region, shown in Figure 6(b), yielded three O related components. Binding energy at 529.6 eV relates to MnO₂ and higher values of 531.1 and 532.8 eV corresponds to the binding energies of OH (manganese hydroxides) and H-O-H (adsorbed water) respectively (Pang *et al.*, 2000). During the application of voltage across the electrodes in electrophoretic process; these reactions took place at the cathode surface:



Mn(OH)₂ would be deposited simultaneously with the CNTs to form a composite coating on the cathodic substrate. However, Mn(OH)₂ is unstable in the air, and upon contact with the air, it will turn into manganese dioxide through the following reaction (Liu *et al.*, 2009; Tomandl *et al.*, 2004)



The mechanism for the deposition of CNTs-MnO₂ composite material can be depicted in Figure 5 below.

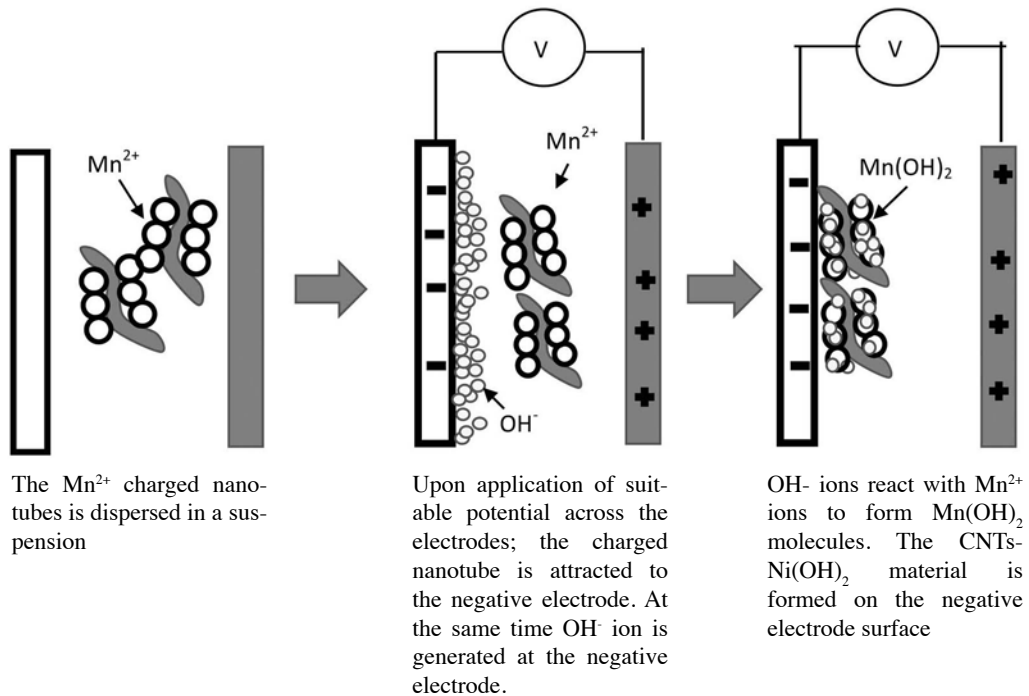
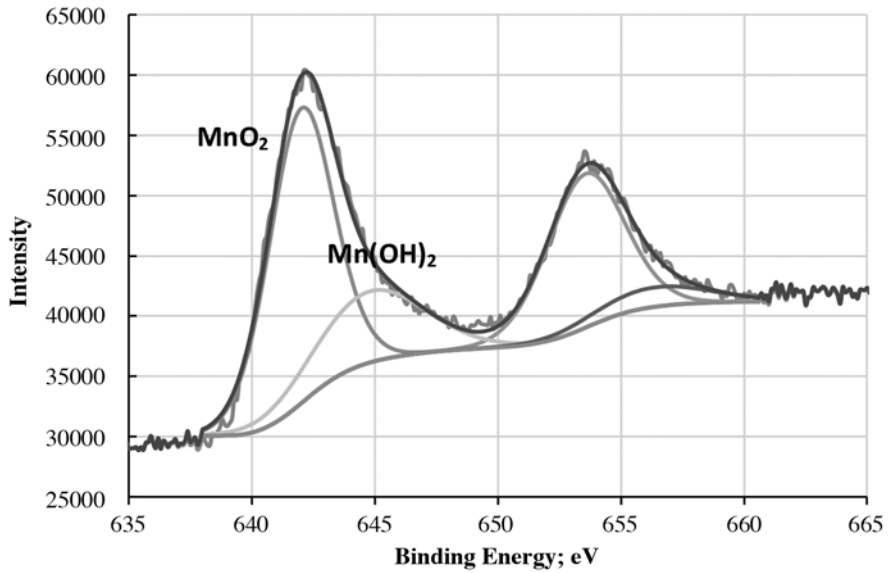
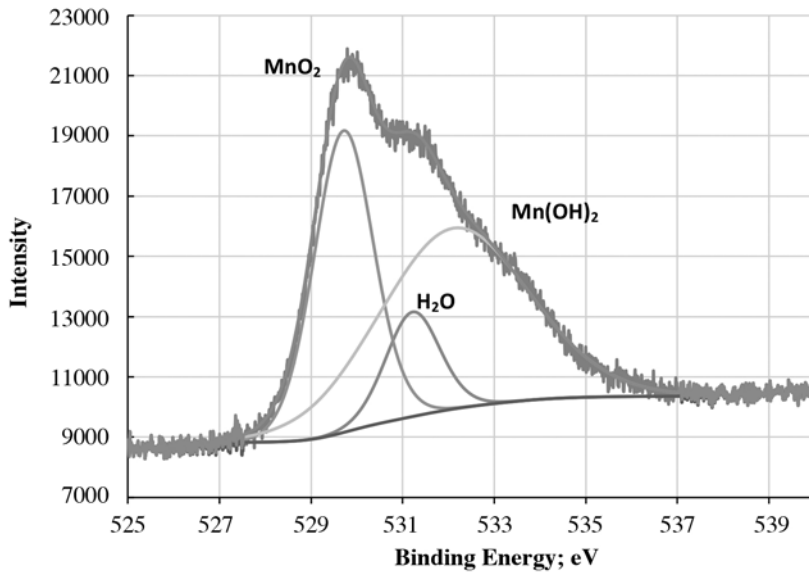


Figure 5. Schematic diagram of deposition mechanism of CNTs-Mn(OH)₂ by electrophoretic deposition process

In Figure 6(c), it can be seen that the dominant carbon peak is observed at 284.9 eV of C=C(sp²) binding energy, related to the carbon structure in the CNTs, C-C. Binding energy at 285.5 is assigned to sp³ or C-C bonding and binding energy of 289.5 eV is for -COOH (Okpalugo *et al.*, 2005). The COOH bonding at binding energy of 288.3 eV is related to CNT functionalization occurring during refluxing process. The refluxing process would functionalize the CNTs with carboxylic groups (-COOH). During refluxing process, the oxygen-containing groups are introduced to the ends and sidewalls of the tubes. These groups, which are chemically attached to the tubes, are mostly represented by -COOH groups, less by -C=O, and -OH groups (Datsyuk *et al.*, 2008; Yang *et al.*, 2007).



(a)



(b)

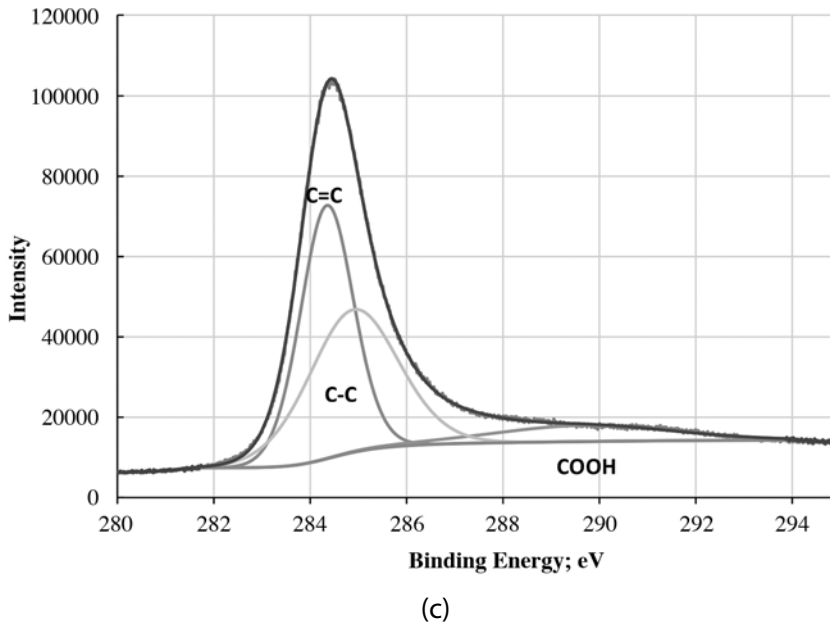


Figure 6. Deconvolution of elemental components in XPS analysis; (a) Mn (b) O and (c) C

The electrochemical reaction of MnO₂ in KOH solution is described below (Wang *et al.*, 2015; Deng *et al.*, 2011):



It was observed that the charge accumulation was greater in electrodes with higher mass loading with higher MnO₂ concentration, as shown in Figure 6. The electrode of 67 % MnO₂ shows the highest charge storage capacity followed by 45 % and 12 % respectively. Higher storage capacity of the 67 % electrode is due to the higher mass loading and MnO₂ content of the electrode; which effectively increase the availability of the active material to store charge through redox reactions.

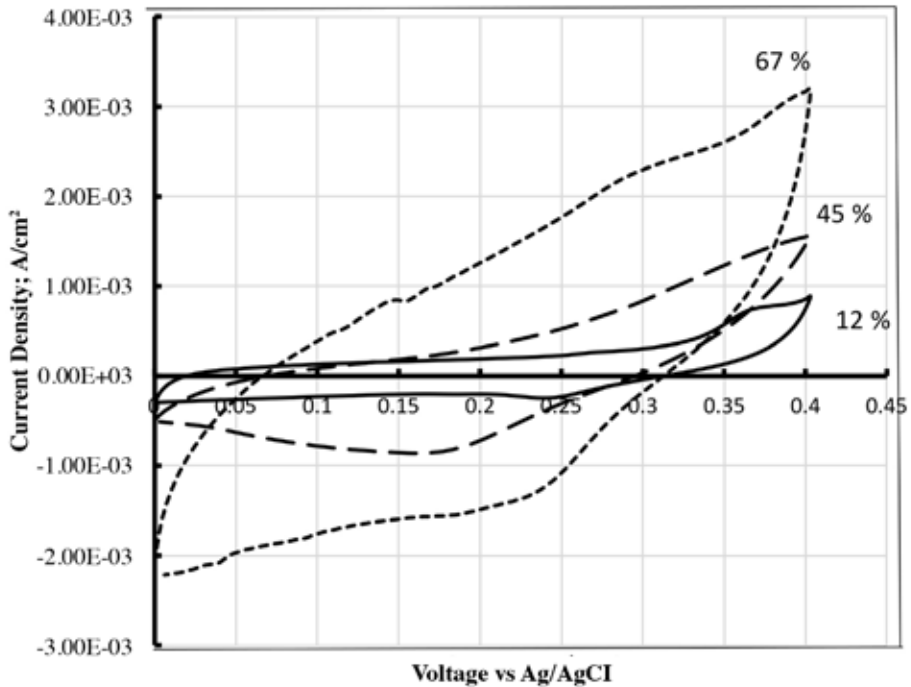


Figure 7. Cyclic voltammometry profile of the electrodes of different mass and composition

From the graph of specific capacitance Figure 7, it can be seen that the highest specific capacitance value of 210 F/gm was obtained at the scan rate of 5 mV/s from the electrode with MnO₂ content of 45 %, followed by 195 F/gm for electrode of 67 % and 177 F/gm for electrode with 12 % respectively. However, with increasing scan rate, electrode with the highest weight and MnO₂ content exhibited the highest specific capacitance drop of 66 % at 100 mV/s, followed by electrodes with 45 % and 12 % MnO₂ at 54 % and 40% respectively. This is a common observation regarding the electrode with higher mass loading electrode. This is because at higher scan rate (faster charging/discharging rate), the ions (K⁺) did not penetrate the electrode pores completely, thus, giving a lower materials utilization for reduction-oxidation reaction; hence the lower specific capacitance was obtained. It also demonstrated the ability to fast charge and discharge of higher mass loading and MnO₂ content is poor compared to electrodes with less mass loading. One of the factors which contributes to this was the material utilization is seen to be more efficient in thin film structure, because of the shorter diffusion path of ions travelled, which effectively contributed to low resistance of the electrode. Furthermore, the specific capacitance values decrease sharply, indicating the effect of high resistivity of MnO₂ present in the respective electrode.

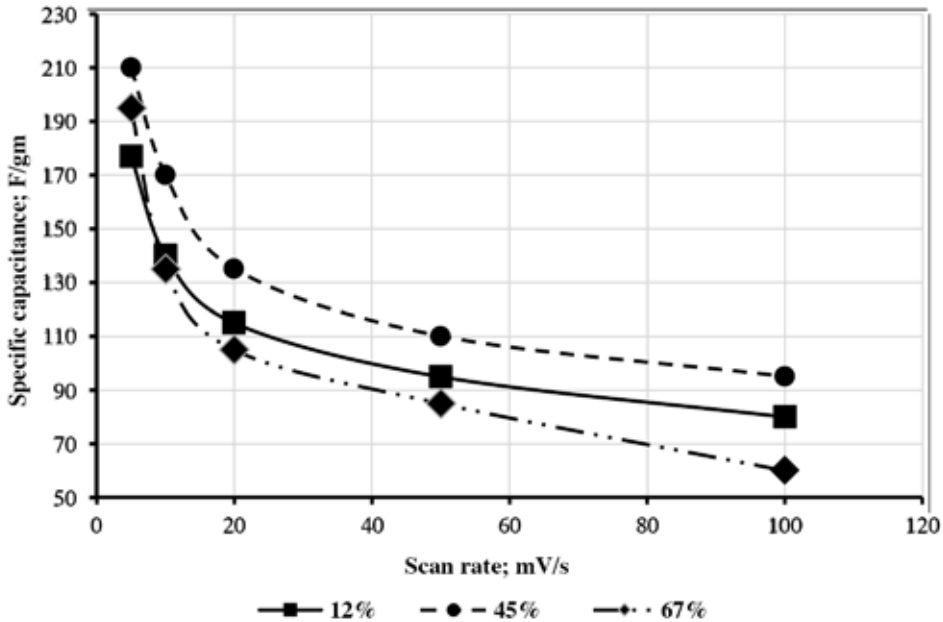


Figure 8. Specific capacitance of CNTs-MnO₂ electrodes of different mass and composition

CONCLUSION

The composite electrode of CNTs and MnO₂ was successfully produced through a novel method of combining electrophoretic deposition of CNTs and chemical/electrochemical deposition of metal oxides, to form a composite coating of CNTs/MnO₂ on the nickel current collector. This is an effective approach to produce a composite coating of CNTs- MnO₂ composite electrode without any binder. The role of CNTs in the composite is primarily to provide a porous template and structural network for the manganese oxide particles which will in turn provide the electrode with charge storage properties through faradaic reactions with the electrolyte. The result showed the potential of the electrodes to be used in energy storage application; especially supercapacitor.

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REFERENCES

- Cottineau, T., Toupin, M., Delahaye, T., Brousse, T., & Bélanger, D. (2006). Nanostructured transition metal oxides for aqueous hybrid electrochemical supercapacitors. *Applied Physics A: Materials Science and Processing*, 82, 599–606.
- Datsyuk, V., Kalyva, M., Papagelis, K., Parthenios, J., Tasis, D., Siokou, A., Galiotis, C. (2008). Chemical oxidation of multiwalled carbon nanotubes. *Carbon*, 46(6), 833–840.
- Deng, S., Sun, D., Wu, C., Wang, H., Liu, J., Sun, Y., & Yan, H. (2013). Synthesis and electrochemical properties of MnO₂ nanorods/graphene composites for supercapacitor applications. *Electrochimica Acta*, 111, 707–712.
- Deng, W., Ji, X., Chen, Q., & Banks, C. E. (2011). Electrochemical capacitors utilising transition metal oxides: an update of recent developments. *RSC Advances*, 1(7), 1171.
- Hassan, S., Suzuki, M., Mori, S., & El-Moneim, A. A. (2014). MnO₂/carbon nanowalls composite electrode for supercapacitor application. *Journal of Power Sources*, 249, 21–27.
- Jafta, C. J., Nkosi, F., le Roux, L., Mathe, M. K., Kebede, M., Makgopa, K., Ozoemena, K. I. (2013). Manganese oxide/graphene oxide composites for high-energy aqueous asymmetric electrochemical capacitors. *Electrochimica Acta*, 110, 228–233.
- Kiamahalleh, M. V., Najafpour, G., Abd, S. S., Buniran, S., & Zein, S. H. S. (2010). Multiwalled carbon nanotubes filled with transition metal oxides as supercapacitor materials. *World Appl. Sci. J.*, 9, 1–7.
- Lei, Z., Shi, F., & Lu, L. (2012). Incorporation of MnO₂-coated carbon nanotubes between graphene sheets as supercapacitor electrode. *ACS Applied Materials & Interfaces*, 4(2), 1058–64.
- Li, J., Que, T., & Huang, J. (2013). Synthesis and characterization of a novel tube-in-tube nanostructured PPy/MnO₂/CNTs composite for supercapacitor. *Materials Research Bulletin*, 48(2), 747–751.
- Li, Q., Anderson, J. M., Chen, Y., & Zhai, L. (2012b). Structural evolution of multi-walled carbon nanotube/MnO₂ composites as supercapacitor electrodes. *Electrochimica Acta*, 59(0), 548–557.
- Lim, Y. S., Tan, Y. P., Lim, H. N., Huang, N. M., Tan, W. T., Yarmo, M. A., & Yin, C.-Y. (2014). Potentiostatically deposited polypyrrole/graphene decorated nano-manganese oxide ternary film for supercapacitors. *Ceramics International*, 40(3), 3855–3864.
- Liu, D., Garcia, B. B., Zhang, Q., Guo, Q., Zhang, Y., Sepelari, S., & Cao, G. (2009). Mesoporous hydrous manganese dioxide nanowall arrays with large lithium ion energy storage capacities. *Advanced Functional Materials*, 19(7), 1015–1023.
- Malak-Polaczyk, A., Matei-Ghimbeu, C., Vix-Guterl, C., & Frackowiak, E. (2010). Carbon/λ-MnO₂ composites for supercapacitor electrodes. *Journal of Solid State Chemistry*, 183(4), 969–974.
- Okpalugo, T. I. T., Papakonstantinou, P., Murphy, H., McLaughlin, J., & Brown, N. M. D. (2005). High resolution XPS characterization of chemical functionalised MWCNTs and SWCNTs. *Carbon*, 43(1), 153–161.
- Pandolfo, A. G., & Hollenkamp, A. F. (2006). Carbon properties and their role in supercapacitors. *Journal of Power Sources*, 157(1), 11–27.

- Pang, S.-C., & Anderson, M. A. (2000). Novel electrode materials for electrochemical capacitors: Part II. Material characterization of sol-gel-derived and electrodeposited manganese dioxide thin films. *Journal of Materials Research*, 15(10), 2096–2106.
- Sen, P., De, A., Chowdhury, A. D., Bandyopadhyay, S. K., Agnihotri, N., & Mukherjee, M. (2013). Conducting polymer based manganese dioxide nanocomposite as supercapacitor. *Electrochimica Acta*, 108, 265–273.
- Sivakkumar, S. R., Ko, J. M., Kim, D. Y., Kim, B. C., & Wallace, G. G. (2007). Performance evaluation of CNT/polypyrrole/MnO₂ composite electrodes for electrochemical capacitors. *Electrochimica Acta*, 52(25), 7377–7385.
- Tang, Q., Sun, M., Yu, S., & Wang, G. (2014). Preparation and supercapacitance performance of manganese oxide nanosheets/graphene/carbon nanotubes ternary composite film. *Electrochimica Acta*, 125, 488–496.
- Teng, F., Santhanagopalan, S., & Meng, D. D. (2010). Microstructure control of MnO₂/CNT hybrids under in-situ hydrothermal conditions. *Solid State Sciences*, 12(9), 1677–1682.
- Teng, F., Santhanagopalan, S., Wang, Y., & Meng, D. D. (2010). In-situ hydrothermal synthesis of three-dimensional MnO₂-CNT nanocomposites and their electrochemical properties. *Journal of Alloys and Compounds*, 499(2), 259–264.
- Tomandl, A., Wolpers, M., & Ogle, K. (2004). The alkaline stability of phosphate coatings II: in situ Raman spectroscopy. *Corrosion Science*, 46(4), 997–1011.
- Wang, H., Peng, C., Peng, F., Yu, H., & Yang, J. (2011). Facile synthesis of MnO₂/CNT nanocomposite and its electrochemical performance for supercapacitors. *Materials Science and Engineering: B*, 176(14), 1073–1078.
- Wang, H., Peng, C., Zheng, J., Peng, F., & Yu, H. (2013). Design, synthesis and the electrochemical performance of MnO₂/C@CNT as supercapacitor material. *Materials Research Bulletin*, 48(9), 3389–3393.
- Wang, J.-G., Kang, F., & Wei, B. (2015). Engineering of MnO₂-based nanocomposites for high-performance supercapacitors. *Progress in Materials Science*, 74, 51–124.
- Wang, J.-G., Yang, Y., Huang, Z.-H., & Kang, F. (2012). Synthesis and electrochemical performance of MnO₂/CNTs-embedded carbon nanofibers nanocomposites for supercapacitors. *Electrochimica Acta*, 75(0), 213–219.
- Wu, M.-S., & Fu, Y.-H. (2013). Tubular graphene nanoribbons with attached manganese oxide nanoparticles for use as electrodes in high-performance supercapacitors. *Carbon*, 60, 236–245.
- Yan, D., Liu, Y., Li, Y., Zhuo, R., Wu, Z., Ren, P., Geng, Z. (2014). Synthesis and electrochemical properties of MnO₂/rGO/PEDOT:PSS ternary composite electrode material for supercapacitors. *Materials Letters*, 127(0), 53–55.
- Yang, J., Zou, L., & Song, H. (2012). Preparing MnO₂/PSS/CNTs composite electrodes by layer-by-layer deposition of MnO₂ in the membrane capacitive deionisation. *Desalination*, 286(0), 108–114.
- Yang, Q., Li, Q., Yan, Z., Hu, X., Kang, L., Lei, Z., & Liu, Z.-H. (2014). High performance graphene/manganese oxide hybrid electrode with flexible holey structure. *Electrochimica Acta*, 129, 237–244.

Yang, W., Thordarson, P., Gooding, J. J., Ringer, S. P., & Braet, F. (2007). Carbon nanotubes for biological and biomedical applications. *Nanotechnology*, 18(41), 412001.

Yoon, S., & Kim, K. B. (2013). Effect of poly(3,4-ethylenedioxythiophene) (PEDOT) on the pseudocapacitive properties of manganese oxide (MnO₂) in the PEDOT/MnO₂/multiwall carbon nanotube (MWNT) composite. *Electrochimica Acta*, 106(0), 135–142.

Zhao, Y., Meng, Y., & Jiang, P. (2014). Carbon/MnO₂ core–shell nanospheres for flexible high-performance supercapacitor electrode materials. *Journal of Power Sources*, 259, 219–226.

Zou, M., Ai, D., & Liu, K. (2011). Template synthesis of MnO₂/CNT nanocomposite and its application in rechargeable lithium batteries. *Transactions of Nonferrous Metals Society of China*, 21(9), 2010–2014.