Open Journal of Energy Efficiency, 2021, 10, 73-80
https://www.scirp.org/journal/ojee
ISSN Online: 2169-2645
ISSN Print: 2169-2637

MnO_2 Nanosheets Anchored on a Biomass-Derived Porous Carbon for High-Performance Supercapacitors

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How to cite this paper: Ding, X.Y. and Wu, G.J. (2021) MnO_2 Nanosheets Anchored on a Biomass-Derived Porous Carbon for High-Performance Supercapacitors. *Open Journal of Energy Efficiency*, **10**, 73-80.
https://doi.org/10.4236/ojee.2021.103005

Received: August 5, 2021
Accepted: September 7, 2021
Published: September 10, 2021

Abstract

Considering the great potential of composite electrode with carbon and transition metal oxides as a future ideal form of electrode for future energy storing system, many efforts have been devoted into such aspect of research. Sweet potato-derived carbon framework with nanosheet form of MnO_2 anchored on it was carried out through the low-temperature solution grown technique, which is simple, low-cost, and applicable for large-scale commercial production. Such form of composite electrode can facilitate the inner transportation of electrons and ions, and offer high specific capacitance (309 F/g at 0.5 A/g) with comparable discharging rate capability (94 F/g at 20 A/g), which reasonably can be regarded as a superior form of composite electrode.

Keywords

Composite Electrode, MnO_2, Sweet Potato, Biomass, Supercapacitors

1. Introduction

With the rapid development of the modern society, the problems of global warming and resource shortage have undoubtedly become the most important factors that restrict further human development. In order to alleviate current situation, finding a green and effective storing system which can consistently provide low-carbon and sustainable energy becomes more and more important. Actually supercapacitor, a high-capacity capacitor with long working period, high power density and environmental friendliness, is an ideal solution [1] [2]. As is known to us all, supercapacitor mainly stores energy through either electrical double layer capacitors (EDLCs) with carbon-based materials [3] or pseudocapacitors which are based on transition metal oxide [4]. However, neither type of supercapacitor is perfect. For carbon-based EDLCs, though it can offer higher power density, short charging and discharging process, and good stability, the energy density is confined by the limited charge separation at electrode/electrolyte interface and available surface area of active materials [5]. For pseudocapacitors that rely on metal oxides, exclusively for MnO_2, it has high theoretical capacity, natural abundance, and environmental capability, but short cycle life and low power density [6]. As a result, the composite materials combining both carbon-based materials and MnO_2 will be the most optimal choice. Many efforts have already been devoted in such aspect. For instance, supercapacitors that are based on composite materials, say, graphene/MnO_2/carbon nanotubes (CNTs) [7], laser-scribed graphene-MnO_2 [8], and MnO_2@CNTs/CNTs [9], can all achieve high capability and offer higher power, but most of them are not likely put into large-scale commercial application for their high producing cost [10]. As a result, it's of importance to find a carbon material with high compatibility and low cost as the base of composite materials. Biomass precursors, natural elements that can produce activated carbons (ACs) with hierarchical porous structures and high surface areas, fulfill the previous requirements for its environmental friendliness and abundances in nature [11]. Nowadays, hydrothermal synthesis and electrodeposition method are the main methods to prepare bio-carbon/MnO_2 composites [12]. However, these methods are not suitable for large-scale production. In order to further decrease the producing cost to promote large-scale commercial application, one feasible method is to anchor nanostructured MnO_2 to the sweet potato-derived carbon framework (SPCF) through low-temperature solution growth technique to generate SPCF accompanied with the synchronous loading of MnO_2 nanoparticles. The generated composite material SPCF/MnO_2 shows improved electrical properties with a high specific capacitance (309 F/g at 0.5 A/g) and a good discharging rate capability (94 F/g at 20 A/g). These properties demonstrate the SPCF/MnO_2 composite material as a competitive electrode material for supercapacitors.

2. Materials and Methods

2.1. Reactants and Materials

All the chemicals were analytical grade purity and distilled water (DI water) was used throughout the study. Sweet potato powders were purchased from Rong-Fang flagship store (China). KOH crystals and HCl were purchased from Tianjin Fuqi Chemical Co., Ltd.

2.2. Preparation of SPCF

Firstly, carbonize the sweet potato powder through the tube furnace at a temperature of 500˚C for 1 hour in N_2 atmosphere. Then mix and grind the generated sample with KOH crystals at a mass proportion of 1:3. Activate the mixture through the tube furnace at a temperature of 800˚C with an increasing rate of

5˚C/min for 1 hour in N_2 atmosphere. Lastly, after cooling down, wash the obtained sample with dilute HCl solution and DI water, and dry the product in the oven at 80˚C for 12 hours. The generated product then is labeled as SPCF.

2.3. Synthesis of SPCF/MnO_2 Composites

Separately weigh 3 groups of SPCF, and each with same mass of 100 mg. Mix each group of SPCF with various concentration of $KMnO_4$ solution (1.5 mmol, 2.0 mmol, 3.0 mmol). Then heat the mixture at 60˚C for 5 hours with magnetic stirring simultaneously. Finally, filter and wash the resultant with DI water for 5 times. Dry the resultant in the oven at 80˚C for 12 hours, and label them as SPCF/MnO_2-1.5, SPCF/MnO_2-2.0, SPCF/MnO_2-3.0.

2.4. Preparation of the Working Electrode

The working electrode is prepared by mixing active material (SPCF or SPCF/MnO_2), carbon black, and polytetrafluoroethylene (PTFE) with a mass proportion of 8:1:1, and then cover the Ni foam with the mixture. Dry the resultants in the oven at the temperature of 80˚C for 12 hours. Finally, the Ni foam covered with mixture is cold compressed for 1 min under a pressure of 12 MPa to get the working electrode.

2.5. Characterization

Take morphology surface pictures via scanning electron microscopy (SEM, GeminiSEM 500). Detect the phase structure of samples through powder X-ray diffractometer (XRD, Cu Kα, 1.5418 Å).

2.6. Electrochemical Measurements

Cyclic Voltammetry (CV), Galvanostatic cha-discharging (GCD), and electrochemical impedance spectroscopy (EIS) were investigated through the electrochemical station (CHI660e). The working electrode's electrochemical characteristic is measured via a three-electrode system in a 6 mol KOH aqueous solution. The counter and reference electrodes are equipped with a Pt plate and an Ag/AgCl plate coordinately.

3. Results and Discussion

The crystal structures and phase compositions of SPCF and MnO_2/SPCF were measured through their XRD patterns. According to **Figure 1**, the SPCF shows two broad diffraction peaks at 24˚ and 43˚, coordinately corresponding to the (002) and (100) planes of carbon, which are related to the significantly small graphite domain [13]. Despite of the diffraction peaks from carbon, the XRD patterns of SPCF/MnO_2 composites exhibit other characteristic peaks at 12.3˚, 24.7˚, 36.5˚, and 65.4˚, which respectively correspond to the (001), (002), (111), and (020) planes of δ-MnO_2 [14].

As is known to us all, MnO_2 assemblies with various morphologies of nano-sized may show different electrochemical properties. Figure 2 shows the SEM micrographs of various SPCF/MnO_2 composites with different MnO_2 content. As Figure 2 showed, the SPCF/MnO_2-1.5 sample shows that a thin layer of small MnO_2 nanoparticles sparsely distribute to the SPCF surface because of the low MnO_2 content. The SPCF/MnO_2-2.0 sample shows that a dense layer of MnO_2 nanosheet uniformly covers the SPCF surface for greater amount of MnO_2. The SPCF/MnO_2-3.0 sample shows nanowires of MnO_2 comprised of nanosheets covered on the SPCF surface because of the abundant MnO_2 content.

In order to justify the merits of SPCF/MnO_2 composites and feasibility of combining EDLCs and pseudocapacitors, the electrochemical performance of

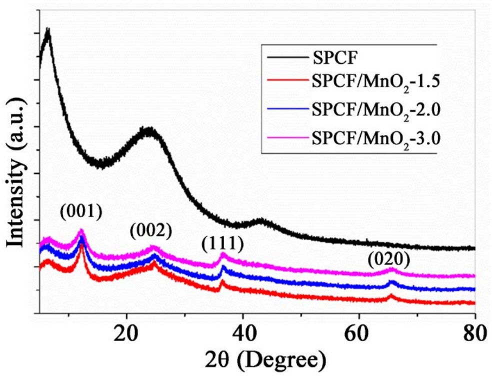

Figure 1. XRD patterns of SPCF and SPCF/MnO_2 composites.

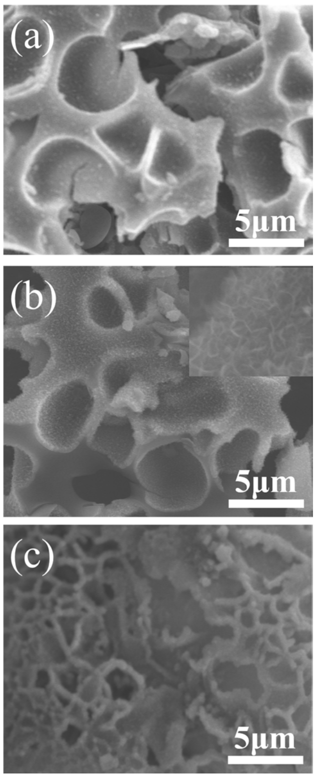

Figure 2. SEM images of SPCF/MnO_2-1,5 (a), SPCF/MnO_2-2.0 (b), and SPCF/MnO_2-3.0 (c).

these 3 materials were measured through CV, GCD, and EIS techniques. As shown in Figure 3(a), the CV curves of all 3 samples of composites possess larger encircling area and two apparent redox peaks, which can indicate the significant improvements of the capacitive performance and prove the feasibility of combining EDLCs and pseudocapacitors by comparing with the CV curve of bare SPCF. Figure 3(b) shows the result of GCD measurements. According to the plot, the composites apparently show longer discharging period compared with bare SPCF so that the specific capacitance was improved. The GCD curve of SPCF was almost symmetrical, because it represents EDLCs which has ideal

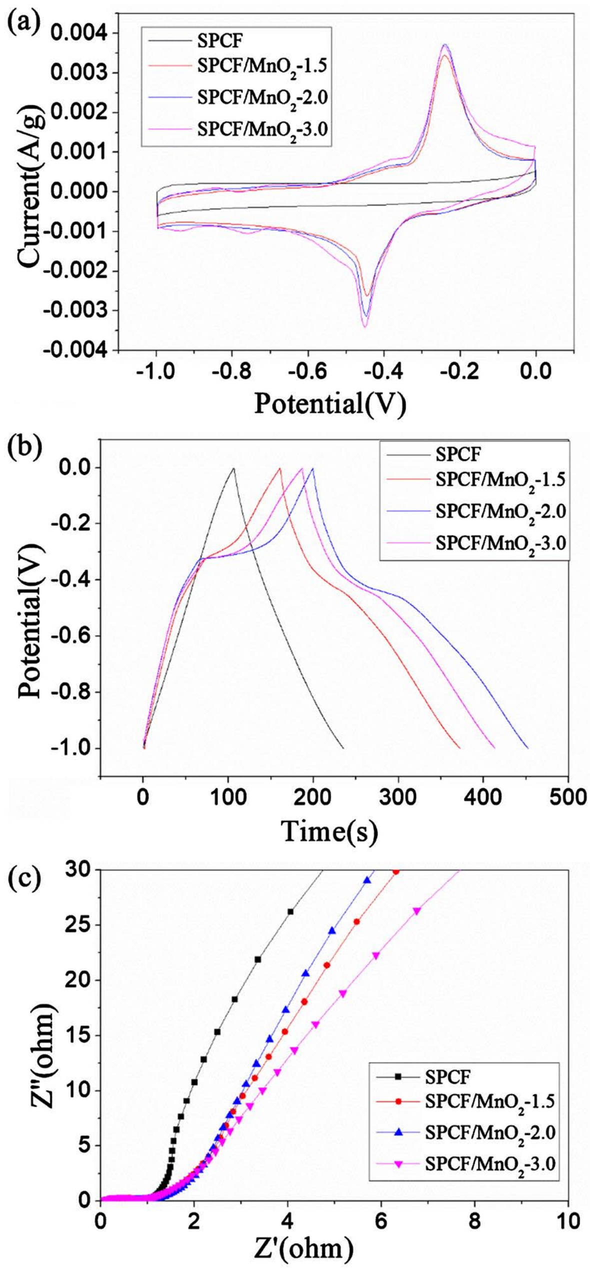

Figure 3. CV curves at scan rate of 5 mV/s (a), GCD curves at 1 A/g (b), and Nyquist plots (c) of SPCF and $SPCF/MnO_2$ composites.

electrical double-layer capacitive property. Meanwhile, the GCD curves of composites show the characteristics of pseudocapacitors with hybrid electrodes for the large deviation from isosceles triangular shape [15]. The result shown in GCD measurement is coincided with the result of CV curve. More importantly, both CV and GCD curve of SPCF/MnO_2 exhibit larger integrated area at the same scan rate, longer discharging period, and better electrochemical performance among all 3 composite materials. **Figure 3(c)** indicates the EIS measurements of SPCF and SPCF/MnO_2's electrochemical characteristics. According to the **Figure 3(c)**, all four samples' plots exhibit straight lines while at the low frequency region, which represents the diffusion-controlled process [16]. The straight line can be regarded as Warburg resistance, and the slope of the line is right proportional to the rate of ion diffusion into the active materials [17]. As shown in the **Figure 3(c)**, SPCF plot is the most vertical one, because carbon-based materials only represent EDLCs. Despite of SPCF, the plot of SPCF/MnO_2-2.0 is more vertical than those of the other two composites. The main reason for this is 2D nanosheets have demonstrated their merits due to the anisotropic structure and high surface-to-bulk ratio, which grant a shorter diffusion path for electrons and ions [18]. It is therefore SPCF/MnO_2-2.0 has better capacitive behavior and faster ion diffusion rate during the diffusion-controlled process. Such outcome is consistent with those of CV and GCD analysis.

Figure 4 specifically measures the property of SPCF/MnO_2-2.0 at current densities from 0.5 to 20 A/g through GCD technique. According to the GCD plots of SPCF/MnO_2-2.0 at various current densities, there is no apparent IR drop at 20 A/g, which shows that the electrochemical process of the sample has fast and reversible kinetics. It can also be observed that the discharge curve of SPCF/MnO_2-2.0 can reach a specific capacitance of 309 F/g at 0.5 A/g, which is much better than the common MnO_2-carbon composites. SPCF/MnO_2-2.0 electrode can achieve the specific capacitance of 94 F/g at a high current density of 20 A/g.

4. Conclusion

In summary, SPCF/MnO_2 composite electrode can be fabricated through

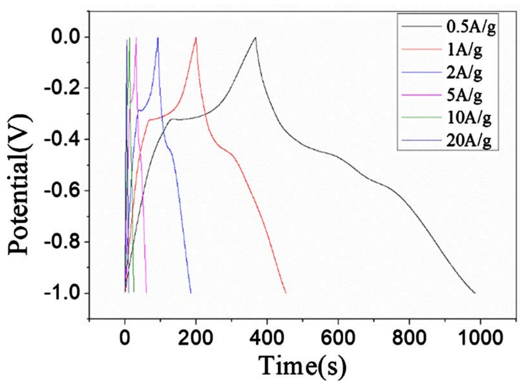

Figure 4. GCD curves of SPCF/MnO_2-2.0 at various current density.

low-temperature solution growth technique which is simple and environmental-friendly. The 3D interconnected porous structure of SPCF which uses sweet potato as precursor combines with the nanosheet of MnO_2 that anchors on the SPCF can offer higher electrons and ions' transportation within the whole system. Plus, the SPCF/MnO_2-2.0 electrode was achieved through the combination of EDLCs and pseudocapacitors. According to the GCD curves of SPCF/MnO_2-2.0 electrode at various current densities, it possesses a high specific capacitance of 309 F/g at 0.5 A/g. Considering the benefits of SPCF/MnO_2 composite materials, like the low cost, simple preparation process, environmental friendliness, and superior capacitance performance, it has great potential to be used as an ideal form of electrode for energy storing in the future. Moreover, the method has the potential to be applied to the manufacture of other bio-compound material.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

References

[1] Zhu, Q.C., Zhao, D.Y., Cheng, M.Y., Zhou, J.Q., Owusu, K.A., Mai, L.Q. and Yu, Y. (2019) A New View of Supercapacitors: Integrated Supercapacitors. *Advanced Energy Materials*, **9**, Article ID: 1901081. https://doi.org/10.1002/aenm.201901081

[2] Wang, G.P., Zhang, L. and Zhang, J.J. (2012) A Review of Electrode Materials for Electrochemical Supercapacitors. *Chemical Society Reviews*, **41**, 797-828. https://doi.org/10.1039/C1CS15060J

[3] Ji, H.X., Zhao, X., Qiao, Z.H., Jung, J., Zhu, Y.W., Lu, Y.L., Zhang, L.L., MacDonald, A.H. and Ruoff, R.S. (2014) Capacitance of Carbon-Based Electrical Double-Layer Capacitors. *Nature Communications*, **5**, Article No. 3317. https://doi.org/10.1038/ncomms4317

[4] Xiao, J.W., Wan, L., Yang, S.H., Xiao, F. and Wang, S. (2014) Design Hierarchical Electrodes with Highly Conductive $NiCo_2S_4$ Nanotube Arrays Grown on Carbon Fiber Paper for High-Performance Pseudocapacitors. *Nano Letters*, **14**, 831-838. https://doi.org/10.1021/nl404199v

[5] Ge, J., Yao, H.B., Hu, W., Yu, X.F., Yan, Y.X., Mao, L.B., Li, H.H., Li, S.S. and Yu, S.H. (2013) Facile Dip Coating Processed Graphene/MnO_2 Nanostructured Sponges as High Performance Supercapacitor Electrodes. *Nano Energy*, **2**, 505-513. https://doi.org/10.1016/j.nanoen.2012.12.002

[6] Jia, H.N., Cai, Y.F., Zheng, X.H., Lin, J.H., Liang, H.Y., Qi, J.L., Cao, J., Feng, J.C. and Fei, W.D. (2018) Mesostructured Carbon Nanotube-on-MnO_2 Nanosheet Composite for High-Performance Supercapacitors. *ACS Applied Materials & Interfaces*, **10**, 38963-38969. https://doi.org/10.1021/acsami.8b14109

[7] Cheng, Y.W., Lu, S.T., Zhang, H.B., Varanasi, C.V. and Liu, J. (2012) Synergistic Effects from Graphene and Carbon Nanotubes Enable Flexible and Robust Electrodes for High-Performance Supercapacitors. *Nano Letters*, **12**, 4206-4211. https://doi.org/10.1021/nl301804c

[8] El-Kady, M.F., Ihns, M., Li, M.P., Hwang, J.Y., Mousavi, M.F., Chaney, L., Lech,

A.T. and Kaner, R.B. (2015) Engineering Three-Dimensional Hybrid Supercapacitors and Microsupercapacitors for High-Performance Integrated Energy Storage. *Proceedings of the National Academy of Sciences of the United States of America*, **112**, 4233-4238. https://doi.org/10.1073/pnas.1420398112

[9] Wu, P., Cheng, S., Yang, L.F., Lin, Z.Q., Gui, X.C., Ou, X., Zhou, J., Yao, M.H., Wang, M.K., Zhu, Y.Y. and Liu, M.L. (2016) Synthesis and Characterization of Self-Standing and Highly Flexible delta-MnO_2@CNTs/CNTs Composite Films for Direct Use of Supercapacitor Electrodes. *ACS Applied Materials & Interfaces*, **8**, 23721-23728. https://doi.org/10.1021/acsami.6b07161

[10] Guo, W., Yu, C., Li, S.F., Wang, Z., Yu, J.H., Huang, H.W. and Qiu, J.S. (2019) Strategies and Insights towards the Intrinsic Capacitive Properties of MnO_2 for Supercapacitors: Challenges and Perspectives. *Nano Energy*, **57**, 459-472. https://doi.org/10.1016/j.nanoen.2018.12.015

[11] Zhou, X.L., Zhang, H., Shao, L.M., Lu, F. and He, P.J. (2021) Preparation and Application of Hierarchical Porous Carbon Materials from Waste and Biomass: A Review. *Waste and Biomass Valorization*, **12**, 1699-1724. https://doi.org/10.1007/s12649-020-01109-y

[12] Wang, X.H., Li, X.S., Ge, W.J. and Yang Y. (2019) Progress in Biomass-Derived Carbon Materials/MnO_2 Composite and Its Application in Supercapacitors. *Journal of Forestry Engineering*, **4**, 1-10.

[13] Xiao, K., Ding, L.X., Chen, H.B., Wang, S.Q., Lu, X.H. and Wang, H.H. (2016) Nitrogen-Doped Porous Carbon Derived from Residuary Shaddock Peel: A Promising and Sustainable Anode for High Energy Density Asymmetric Supercapacitors. *Journal of Materials Chemistry A*, **4**, 372-378. https://doi.org/10.1039/C5TA08591H

[14] Deng, X.C., Bai, X.J., Cai, Z.H., Huang, M.J., Chen, X.R., Huang, B. and Chen, Y.D. (2020) Renewable Carbon Foam/Delta-MnO_2 Composites with Well-Defined Hierarchical Microstructure as Supercapacitor Electrodes. *Journal of Materials Research and Technology*, **9**, 8544-8555. https://doi.org/10.1016/j.jmrt.2020.05.130

[15] Zhang, W.K., Peng, L., Wang, J.W., Guo, C.L., Chan, S.H. and Zhang, L. (2020) High Electrochemical Performance of Bi_2WO_6/Carbon Nano-Onion Composites as Electrode Materials for Pseudocapacitors. *Frontiers in Chemistry*, **8**, 577. https://doi.org/10.3389/fchem.2020.00577

[16] Zhai, T., Xie, S. L., Yu, M.H., Fang, P.P., Liang, C.L., Lu, X.H. and Tong, Y.X. (2014) Oxygen Vacancies Enhancing Capacitive Properties of MnO_2 Nanorods for Wearable Asymmetric Supercapacitors. *Nano Energy*, **8**, 255-263. https://doi.org/10.1016/j.nanoen.2014.06.013

[17] Zhou, W., Lei, S.J., Sun, S.Q., Ou, X.L., Fu, Q., Xu, Y.L., Xiao, Y.H. and Cheng, B.C. (2018) From Weed to Multi-Heteroatom-Doped Honeycomb-Like Porous Carbon for Advanced Supercapacitors: A Gelatinization-Controlled One-Step Carbonization. *Journal of Power Sources*, **402**, 203-212. https://doi.org/10.1016/j.jpowsour.2018.09.044

[18] Zhao, M.T., Wang, Y.X., Ma, Q.L., Huang, Y., Zhang, X., Ping, J.F., Zhang, Z.C., Lu, Q.P., Yu, Y.F., Xu, H., Zhao, Y.L. and Zhang, H. (2015) Ultrathin 2D Metal-Organic Framework Nanosheets. *Advanced Materials*, **27**, 7372-7378. https://doi.org/10.1002/adma.201503648