Science and Applications of Thin Films, Conference & Exhibition (SATF 2018)
Izmir Institute of Technology, Izmir, Turkey, September 17-21, 2018

Synthesis of $MnCo_2O_4$ nanowires on flexible carbon fiber cloth for high-performance supercapacitors

Yasar Ozkan Yesilbag[a,d,*] , Fatma Nur Tuzluca[a,d] and Mehmet Ertugrul[b,c,d]

[a]*Department of Physics, Erzincan Binali Yıldırım University, Erzincan 24100, Turkey*
[b]*Department of Electrical and Electronics Engineering, Ataturk University, Erzurum 25240, Turkey*
[c]*Department of Nanoscience and Nanoengineering, Ataturk University, Erzurum 25240, Turkey*
[d]*Nanoscience and Nanoengineering Application and Research Center, Ataturk University, Erzurum 25240, Turkey*

* Corresponding author. Tel.: +90 446 224 30 32; fax: +90 446 224 30 16
E-mail address: *oyesilbag@erzincan.edu.tr*

Abstract

$MnCo_2O_4$ nanowires (NWs) array is directly synthesized on carbon cloth using hydrothermal method. The structure, morphology and electrochemical performance of $MnCo_2O_4$ NWs arrays are systematically characterized by X-Ray Diffraction Spectroscopy (XRD), Field Emission Scanning Electron Microscopy (FESEM), Energy Dispersion X-Ray Spectroscopy (EDS), Cyclic Voltammetry (CV) and Galvanostatic Charge/Discharge (GCD). This electrode structure demonstrates good electrochemical performance with a maximum areal capacitance of 0.77 F cm^{-2} at 0.25 mA cm^{-2}. Areal capacitance value after a 4000 charge-discharge cycle, indicating excellent cycle stability 87.3%.

Keywords: $MnCo_2O_4$ nanowires; supercapacitor; carbon fiber cloth; hydrothermal method.

Introduction

Supercapacitors are a new generation of eco-friendly energy storage devices that do not require maintenance and repair, and also have the ability to charge-discharge hundreds of thousands of times, low internal resistance, high power density, extremely long operating life, safe running performance at low/high temperatures (Burke, 2000; Yu et al. 2015; Fic et al. 2018). In addition to prolonging the life of batteries when used with them, these devices optimize the system size and cost, increase the power efficiency in all electric and hybrid electric vehicles and also address a wide range of applications from renewable energy sources, automotive sector (Rolison ve Nazar 2011; Huang et al. 2013a). Supercapacitors store energy by means of ion adsorption at the electrode/electrolyte interface (Electric Double Layer Capacitor–EDLC) or by means of rapid and reversible redox reactions (pseudocapacitor) in the vicinity and the surface of the electrode materials. Pseudocapacitors usually offer much higher specific capacitance than supercapacitor made of carbonaceous materials based on double-layer charge storage (Huang et al. 2013b). Transition metal oxides and hydroxides are the most popular materials for the electrode of supercapacitors because of their high theoretical capacitance, low cost, and low toxicity (Zhang et al. 2015). However, transition metal oxides with low electrical conductivity reduce electrochemical performance after long charge/discharge processes. For this reason, transition metal oxides in the AB_2 spinel structure (two different transition metals A and B; Co, Mn, Ni, and Zn) with two different metal cation ions as the electrode material are preferred (Li et al. 2014; Yunyun et al. 2015; Waghmode and Torane 2017). On the other hand, metal substrate introduces comparable extra weight due to their large mass density, decreasing the actual specific capacitance to a great deal when

considering the substrate weight (Tang et al. 2015). Carbon fiber cloth (CFC), a network of micro-sized carbon fibers, has large surface area, high porosity, flexibility, good electric conductivity, low-weight structure and excellent chemical stability in a wide variety of liquid electrolytes (Huang et al. 2013a; Tang et al. 2015; Xiong et al. 2015). In this work, manganese cobaltite ($MnCo_2O_4$) nanowires were grown homogenously on carbon fiber cloth (CFC) to obtain a binder-free CFC@$MnCo_2O_4$ positive electrode through a simple hydrothermal method followed by calcination.

Materials and Methods

The carbon cloth was cleaned in ultrasonic cleaner for acetone, ethanol and de-ionized water 15 minutes respectively. In a typical synthetic process, 1 mmol of $Mn(NO_3)_2.4H_2O$, 2 mmol of $Co(NO_3)_2.6H_2O$ were dissolved 35 mL de-ionized water under magnetic stirring for 30 min. Then, 2 mmol of NH_4F and 5 mmol urea (CH_4N_2O) were added into the solution successively. The solution with carbon cloth was transferred into a teflon-lined stainless steel autoclave and heated at 100°C for 12 h. After reaction, the precursor electrode was taken out, cleaned with ethanol and deionized water and dried in air. The precursor electrode was then annealed in air at 300 °C and kept for 3 h to obtain $MnCo_2O_4$ nanowires (Figure 1).

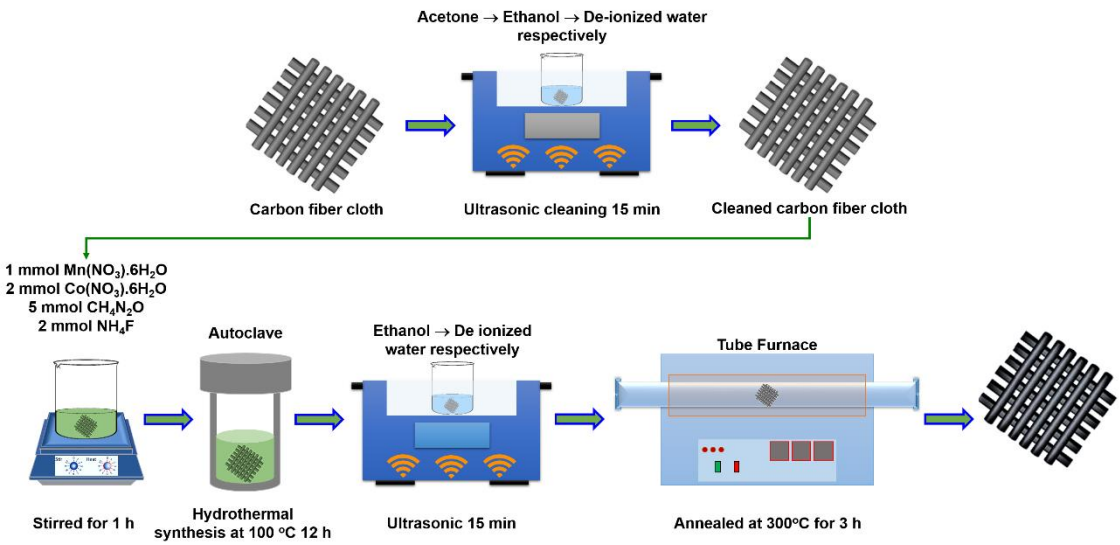


Fig. 1. Schematic illustration synthesis of $MnCo_2O_4$ NWs on CFC substrate.

The crystal structures and morphologies of the $MnCo_2O_4$ NWs were determined by using X-Ray Diffraction (PANalytical Empyrean, Cu-Ka, λ=1.54060 Å), Field Emission Scanning Electron Microscopy (FEI Quanta 450 FEG) and Energy Dispersion X-Ray Spectroscopy (EDAX, AMETEK Materials Analysis Division). The electrochemical performance were determined by Cyclic Voltammetry and Galvanostatic Charge Discharge analyses using a Gamry Reference 1010E potentiostat instrument.

The electrochemical measurements were performed using 1 M KOH aqueous electrolyte solution. Platinum foil (2 × 1 cm^2 in area) and the Ag/AgCl were used as the counter and reference electrodes, respectively. The

$MnCo_2O_4$ electrode (2×1 cm^2) were immersed in electrolyte and were used directly as a working electrode. The electrochemical measurements were performed in a three-electrode electrochemical cell at room temperature. The areal capacitance (C) was calculated by equation (1):

$$C = \frac{Ixt}{AxV} \tag{1}$$

where I is the constant discharge current, t is the discharge time, V is the potential window and A is the electrode area.

Results and Discussion

The crystal structures and morphologies of the $MnCo_2O_4$ nanowires were determined by using X-Ray Diffraction (PANalytical Empyrean, Cu-Kα, λ=1.54060 Å). The XRD diffraction patterns of the sample taken over a 15° to 80° (2θ) range are given in Figure 2. As seen in figure 2, there are 8 peaks – in addition to the 1 peak originating from the carbon cloth substrate – corresponding to the values of (111), (220), (311), (222), (400), (422), (511) and (440) that are the crystal planes of the $MnCo_2O_4$ nanowires according to JCPDS Card No: 23-1237.

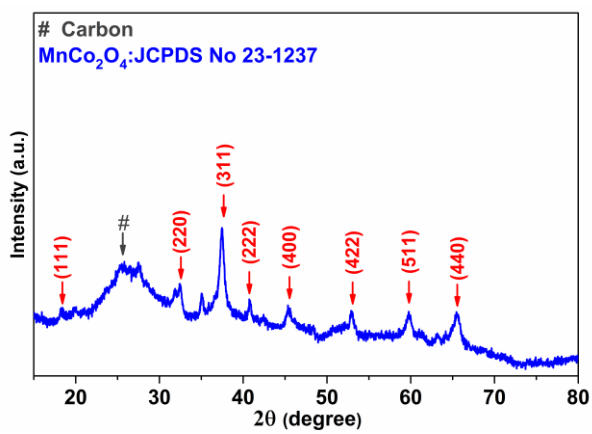


Fig. 2. XRD patterns of $MnCo_2O_4$ NWs.

Figure 3 and Figure 4 shows the FESEM images and EDS analyzes of the morphology of $MnCo_2O_4$ NWs arrays respectively. As seen in figure 3, high density of $MnCo_2O_4$ nanowires were formed and grown uniformly on the carbon cloth after calcination. The purity and composition of the $MnCo_2O_4$ NWs were further confirmed by EDS analysis shown in figure 4. EDS spectrum revealing the existence of C, O, Mn and Co elements in the electrode material and the atomic contents are 33.4%, 42.2%, 2.67% and 21.69%, respectively.

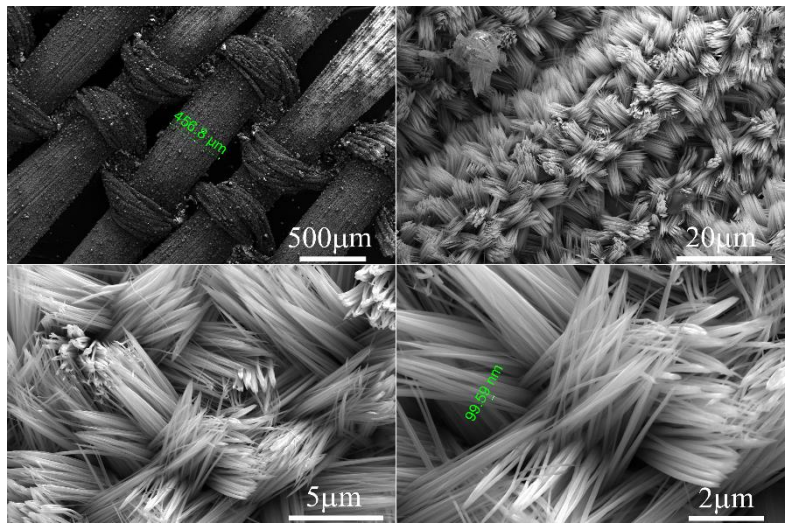


Fig. 3. Low and high magnification FESEM images of $MnCo_2O_4$ NWs.

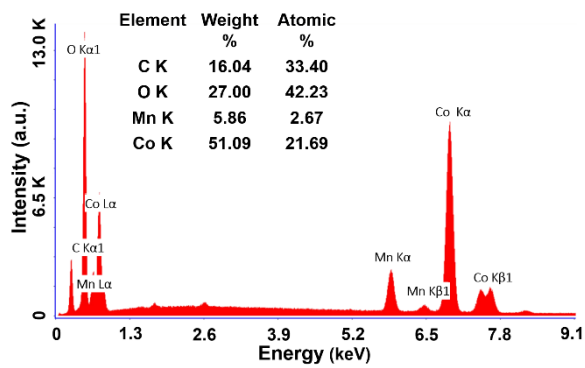


Fig. 4. EDS analyzes of $MnCo_2O_4$ NWs.

Electrochemical properties of $MnCo_2O_4$ electrode in 1 M KOH aqueous electrolyte are shown in Figure 5-7. CV measurements of the CFC@$MnCo_2O_4$ electrode were taken in the 0 to 0.5 V potential range with different scan rate (Figure 5a-b). In the CV curve taken at 5 mV s^{-1}, the contribution from the substrate material (carbon cloth) is negligible Figure 5a. The increase of scan rate allows access ions only on the external surface and, in this case, decreasing the charge storage values. The charge storage process for $MnCo_2O_4$ in a KOH aqueous electrolyte solution is expressed by the reactions in equation (2) and (3):

$$MnCo_2O_4 + OH^- + H_2O \rightarrow 2CoOOH + MnOOH + e^- \quad (2)$$

$$MnOOH + OH^- \rightarrow MnO_2 + H_2O + e^- \quad (3)$$

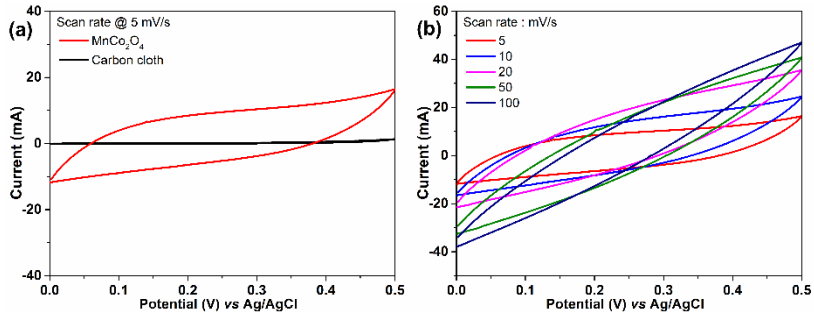


Fig. 5. CV measurements of (a) the bare CFC and CFC@$MnCo_2O_4$ electrode @ 5mV s^{-1}, (b) CFC@$MnCo_2O_4$ electrode @ 5-100 mV s^{-1}.

In order to evaluate the areal capacitance, GCD measurements were performed. The GCD curves of the $MnCo_2O_4$ electrode in the voltage range of 0 to 0.4 V at various current densities of 0.25 to 5 mA cm^{-2} are illustrated in Figure 6a. The areal specific capacitance of the CFC@$MnCo_2O_4$ electrodes are calculated to be 0.77, 0.67, 0.55, 0.43 and 0.25 F cm^{-2} at current densities of 0.25, 0.5, 1, 2 and 5 mA cm^{-2}, respectively, according to equation (1) (Figure 6b). The areal capacitance gradually decreased at higher current density due to the incremental voltage drop and insufficient active material involved in redox reaction at a higher current density. At the end of 4000 charge discharge cycles, the change in capacitance value was found as 87.3% and indicating excellent cycle stability (Figure 7a). Figure 7b shows the Nyquist plots of the EIS spectra for the $MnCo_2O_4$ electrodes and the inset shows equivalent circuit and values. At the high frequency, the intersection of the curve at the real part (Z') indicates the resistance of the electrochemical system which is about 1 Ω. In the low frequency area, the slope of the curve shows the constant phase element (CPE), which represents the electrolyte diffusion to the electrode surface. Experimental data and the expected equivalent circuit are consistent with each other. Equivalent series resistance (**R_s**) and charge transfer resistance (**R_{ct}**) values obtained from this circuit were found to be 0.7 and 7.6 Ω respectively.

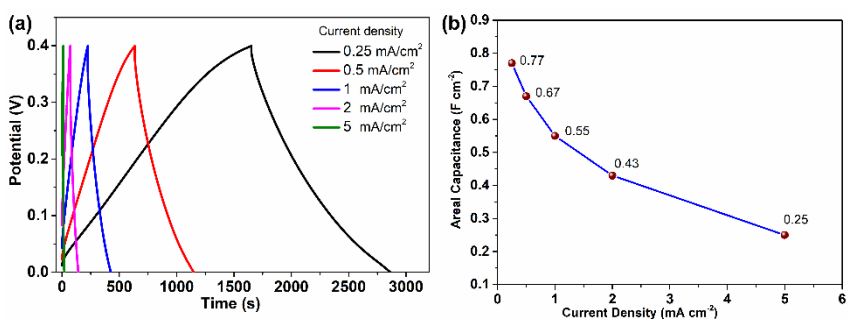


Fig. 6. (a) GCD curves and (b) the areal capacitances vs different current densities of $ZnCo_2O_4$ NWs.

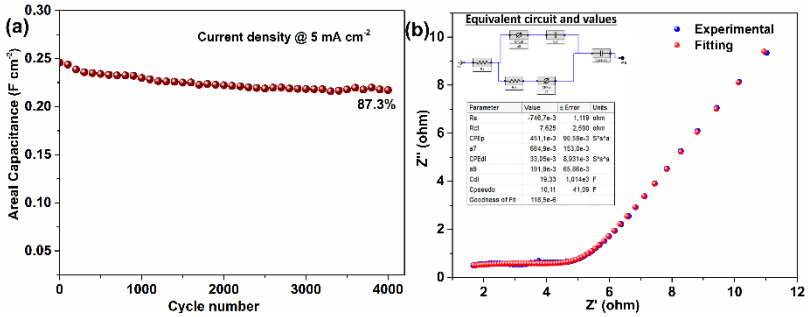


Fig. 7. (a) Long term cycling stability, (b) EIS measurement and inset the equivalent circuit and values.

Conclusion

In conclusion, $MnCo_2O_4$ NWs were synthesized on carbon cloth by hydrothermal method. According to GCD measurements at 0.25 mA cm^{-2} current density, areal capacitance were obtained 0.77 F cm^{-2} for $MnCo_2O_4$ NWs. Voltammetric and galvanostatic results indicate that the porous structure and large surface area of the carbon fiber cloth and also presence of the $MnCo_2O_4$ nanowires play are mainly responsible for obtaining optimum capacitance values and long cycle life. This electrode design can be extended to grow other mesoporous metal oxides on the substrate to fabricate high-performance supercapacitor electrode. Chemically precipitated $MnCo_2O_4$ nanowires on carbon fiber cloth were employed as the electro-active materials for the supercapacitor. This study also gives different point of view into the design of metal oxide heterostructure electrodes used in a various range of applications.

Acknowledgements

This research is partially supported by Erzincan Binali Yıldırım University Scientific Research Project Unit (Project number: FBA-2017-468).

References

Burke, A. (2000). Ultracapacitors: why, how, and where is the technology. Journal of power sources, 91(1), 37-50.

Fic, K., Platek, A., Piwek, J., & Frackowiak, E. (2018). Sustainable materials for electrochemical capacitors. Materials Today.

Huang, L., Chen, D., Ding, Y., Feng, S., Wang, Z. L., & Liu, M. (2013b). Nickel–cobalt hydroxide nanosheets coated on $NiCo_2O_4$ nanowires grown on carbon fiber paper for high-performance pseudocapacitors. Nano letters, 13(7), 3135-3139.

Huang, L., Chen, D., Ding, Y., Wang, Z. L., Zeng, Z., & Liu, M. (2013a). Hybrid composite $Ni(OH)_2$@$NiCo_2O_4$ grown on carbon fiber paper for high-performance supercapacitors. ACS applied materials & interfaces, 5(21), 11159-11162.

Li, L., Zhang, Y. Q., Liu, X. Y., Shi, S. J., Zhao, X. Y., Zhang, H., ... & Tu, J. P. (2014). One-dimension $MnCo_2O_4$ nanowire arrays for electrochemical energy storage. Electrochimica Acta, 116, 467-474.

Rolison, D. R., & Nazar, L. F. (2011). Electrochemical energy storage to power the 21st century. Mrs Bulletin, 36(7), 486-493.

Tang, Q., Chen, M., Wang, L., & Wang, G. (2015). A novel asymmetric supercapacitors based on binder-free carbon fiber paper@nickel cobaltite nanowires and graphene foam electrodes. Journal of Power Sources, 273, 654-662.

Waghmode, R. B., & Torane, A. P. (2017). Role of deposition time on synthesis of high-performance NiCo2O4 supercapacitors. Journal of Materials Science: Materials in Electronics, 28(13), 9575-9583.

Xiong, W., Hu, X., Wu, X., Zeng, Y., Wang, B., He, G., & Zhu, Z. (2015). A flexible fiber-shaped supercapacitor utilizing hierarchical $NiCo_2O_4$@polypyrrole core–shell nanowires on hemp-derived carbon. Journal of Materials Chemistry A, 3(33), 17209-17216.

Yu, Z., Tetard, L., Zhai, L., & Thomas, J. (2015). Supercapacitor electrode materials: nanostructures from 0 to 3 dimensions. Energy & Environmental Science, 8(3), 702-730.

Yunyun, F., Xu, L., Wankun, Z., Yuxuan, Z., Yunhan, Y., Honglin, Q., ... & Fan, W. (2015). Spinel $CoMn_2O_4$ nanosheet arrays grown on nickel foam for high-performance supercapacitor electrode. Applied Surface Science, 357, 2013-2021.

Zhang, Y., Li, L., Su, H., Huang, W., & Dong, X. (2015). Binary metal oxide: advanced energy storage materials in supercapacitors. Journal of Materials Chemistry A, 3(1), 43-59.