전기방사기법을 이용한 탄소-망간 복합 나노섬유 제조 및 슈퍼캐패시터 응용

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Preparation of Carbon/Manganese Hybrid Nanofiber Web by Electrospinning and Application of Supercapacitor

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1. Introduction

Electrochemical capacitors are charge-storage devices having the properties of high energy density, great power density and long cycle life [1]. Electrochemical capacitor can be divided into two types: redox supercapacitors (pseudocapacitors) and electrochemical double layer capacitors (EDLC). The EDLC utilized the formation of the electrical double layer at the interface between the electrolyte and the activated carbon [2]. Pseudocapacitor works on the basis of a faradaic charge exchange mechanism into the electrode material itself [3]. Hydrous ruthenium oxide has excellent pseudocapacitance, but it is not proper for wide application because of too much expensive. So many researcher look for the materials having both high capacitance and more low cost. Both manganese and nickel oxides has proposed as a candidate of pseudocapacitor among transition metal oxides. Presently, Many works has been progressed on the basis of electrospinning, sol-gel, electrodeposition or other aqueous chemistry approaches [4-8].

The electrospinning is a unique method that can prepare the nanofiber web because it use the difference of electromotive force between polymer solution and collector. The nanofber web offers as a crucial raw materials to electrical and electrochemical system by the enhancement of physical property. Recently, the polymers such as PAN, PBI were electrospun in the solvents like DMF and THF.

We focus on the preparation of PAN-based carbon/MnO_2 nanofiber composite web by a co-electrospinning and the examination as a potential electrode of pseudocapacitor. The physical properties of the carbon/MnO_2 composite nanofiber was characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), and energy dispersive X-ray spectroscopy (EDX).

2. Experimental

2. 1. Materials and co-electrospinning

Polyacrylonitrile (PAN), N,N-dimethylformamide (DMF) and manganese dioxide (MnO_2) were purchased from Aldrich Chemical Co. The 10 wt.% PAN polymer

solution was prepared by mixing in DMF. MnO_2 was to be dispersed completely in a PAN solution, and PAN/MnO2 solution is to be electrospun. The amount of MnO_2 is controlled with weight fraction of 5 ~ 20 wt.% and co-electrospun. The mixed solution was spun into fiber web through a positively charged capillary using an electrospinning apparatus (NT-PS-35K, NTSEE Co., Korea). The electrospun fiber was collected on an attached aluminum foil wrapped on a metal drum rotating at approximately 300 rpm.

2. 2. Stabilization, activation and characterization

The electrospun nanocomposite fiber web was stabilized by heating up to 280℃ at a rate of 1℃/min and holding for 1 hr under an air atmosphere. The stabilized fiber webs were heated up to 800 ℃ at a rate of 5 ℃/min and activated by supplying 30 vol.% steam for 1 hr in a nitrogen carrier gas. The micro-textural characterization of the nanostructured materials was performed by SEM. The increase of manganese's content corroborate by EDX and XRD.

2. 3. Electrochemical test

Two-electrode supercapacitor cells were fabricated with two 1.5 x 1.5 cm^2 electrodes, a polypropylene separator (Cellgard 3501, Scimat Co., UK), and a Ni 50 nm foil as a current collector soaked in 6 M KOH aqueous solution. The electrochemical characteristics were evaluated by a galvanostatic charge/ discharge and cyclic voltammetry (CV). The cell capacitance is calculated from the slope of the discharge on the basis of the equation (1)

$$C = i(t/V) \quad (1)$$

where C is the capacitance of the cell in farads; i is the discharge current in amperes (A); and t is the discharging time from 0.54 V to 0.45 V (about 50~60 % of the initial potential), V is the potential variation in the time range measured, the slope in volts per second (V/S). In a symmetrical system, the specific capacitance C_m in farads per gram of samples (F/g) is related to the capacitance of the cell C in terms of the equation (2)

$$C_m = 2C/m \quad (2)$$

where m is the weight (g) per electrode of samples.

The CV of the unit cells were performed in the potential range of 0 to 0.9 V at a scan rate ranging from 1 to 500 mV/sec.

3. Results and discussion

Fig. 1 is SEM images of carbon naonfiber composite web with various conditions. The diameter of PAN/MnO_2 electrospun fiber was distributed ranging from 100 to 500 nm as shown in Fig. 1(a)-(d). The nanocomposite fibers electrospun were partially aligned along the winding direction of the drum winder. Fig. 1(e)-(h) represent the SEM images of nanocomposite fibers stabilized at 280 ℃ for 60 min. The particles of MnO_2 was exposed on the surface of the stabilized fibers. Fig.

1(i)-(l) are the SEM images of nanocomposite fibers activated at 800 ℃ for 60 min. Much more micropores are to be formed throughout the surface of fiber at high activated temperature, and the particle of MnO_2 was widely distributed extending all regions to form as the round shapes. Fig. 2 is the XRD patterns of PAN-based carbon/MnO_2 naonfiber composite web with the contents of MnO_2. Two peaks of Θ = 24 and 42° is in existence in pure carbon as shown in Fig. 2(a). This mean the PAN-based carbon is crystallized. On the contrary, One peak of Θ = 37° exists in pure MnO2 as shown in Fig. 2(f). As the contents of MnO2 is increased as shown in Fig. 2(b)-(e), the carbon peaks is disappeared in carbon/MnO2 nanofiber composite web, while the MnO_2 peak is formed. Table 1 is the elemental analysis of EDX about PAN-based carbon/MnO_2 naonfiber composite web with the contents of MnO_2. The content of oxygen decreases with the increase of MnO_2 contents. This might bring out the crystallization of MnO_2 by the decrease of the excess oxygens. The cyclic voltammograms (CV) of nanostructured electrodes with various contents of MnO_2 is compared in Fig. 3, with keeping a potential window of 0 to 0.9 V. The voltametric curve of pure carbon show the typical double layer capacitance, but that of carbon/MnO2 looks like pure carbon without showing exact redox process. The reason for this that the redox peaks is covered under large double layer current. The range of current of MnO_2/carbon electrodes increased with increasing the content of MnO_2 to carbon fiber. Fig. 4 shows the specific capacitances of the nanocomposite samples as a function of the content of MnO_2. The capacitance of the nanostructured electrodes is determined from the dc discharge with a 0.9 V potential window of capacitor device. The specific capacitances of pure carbon is 140 F/g, while that of 20 wt% MnO_2/carbon electrodes increases up to 318 F/g. The ratio is increased up to 125%. The reasons for this that the pure carbon exhibits only the behavior of doble layer capacitance, while the electrode added MnO2 displays bot doble layer and pseudocapacitance. In addition, this leads to process of non-faradaic and faradaic.

4. Conclusions

The MnO_2/PAN-based fibers was prepared by a co-electrospinning technique. The PAN-based carbon/MnO_2 nanofiber composite web was prepared by the oxidative activation. It was demonstrated as a electrochemical capacitor to improve high capacitance. The specific capacitance increases as the content of MnO_2 increases. The capacitance of 20 wt% MnO_2/Carbon nanocomposite fiber webs increased up to 318 F/g.

Acknowledgements

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References

[1] K. Honda, M. Yoshimura, K. Kawakita, Electrochem. Soc, 151 A532 (2004).
[2] J.K. Chang, C.T. Lin, W.T. Tsai, Electrochem. Commun. 6 (2004).
[3] J.P. Zheng, T.R. Jow, J. Electrochem. Soc. 142 L6, (1995).
[4] J.N. Broughton., M.J. Brett, J. Electrochim Acta, 49, 4439 (2004).

[5] K.C. Liu, M.A. Anderson, J. Electrochem. Soc. 143, 124 (1996).
[6] C. Kim, K.S. Yang, W.J. Lee, Electrochem. Solid-State Lett., 7, A397 (2004)
[7] C. Kim, Y.O. Choi, W.J. Lee, K.S. Yang, Electrochim. Acta, 50, 883 (2004)
[8] C. Kim, S.H. Park, W.J. Lee, K.S. Yang, Electrochim. Acta, 50, 877 (2004)

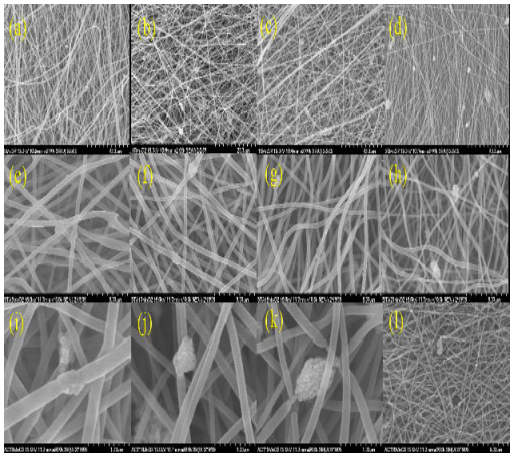

Fig. 1. SEM images PAN-based carbon/MnO_2 composite nanofibers with the contents of MnO_2.

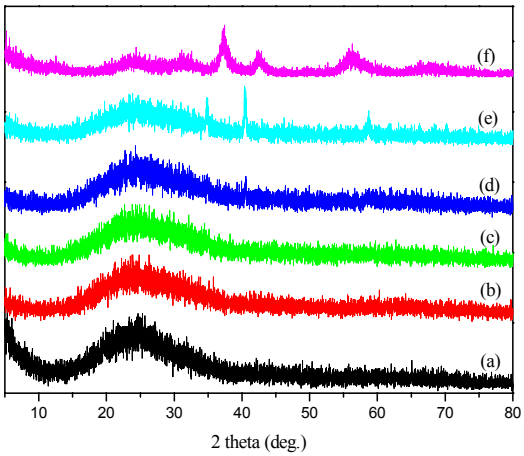

Fig. 2. XRD patterns of PAN-based carbon/MnO_2 composite nanofibers with the contents of MnO_2.

Table 1. Elemental analysis of EDX with the contents of MnO_2.

Sample / Element	Carbon web	5wt% MnO2 /carbon composite	10wt% MnO2 /carbon composite	15wt% MnO2 /carbon composite	20wt% MnO2 /carbon composite
C	89.7	80.44	87.44	87.85	86.56
O	10.3	16.94	8.42	6.61	6.43
Mn	·	2.62	4.23	5.54	7.01
Total	100.0	100.0	100.0	100.0	100.0

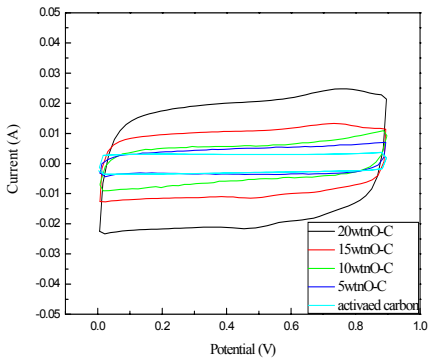

Fig. 3. Cyclic voltammograms of carbon/MnO_2 composite nanofibers with the contents of MnO_2.

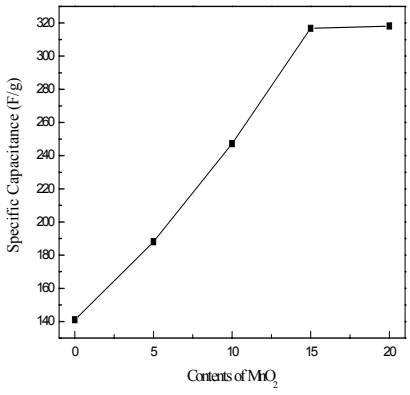

Fig. 4. Specific capacitance of carbon/MnO_2 composite nanofibers with the contents of MnO_2.