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Cobalt-Manganese Oxide/Carbon-nanofiber Composite Electrodes for Supercapacitors

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Composite electrodes consisting of Mn-Co oxide and high electrical conductive carbon nanofibers(vapor grown carbon nanofiber, VGCF)($CoMnO_2$/VGCF) were prepared by thermally decomposing manganese and cobalt nitrates directly onto the pore of a porous nickel foam substrate as a current collector to form manganese and cobalt oxides, and their supercapacitive properties were investigated using cyclic voltammetry in 1M KOH aqueous solution. The $CoMnO_2$/VGCF electrodes exhibited high specific capacitance value of 630 F/g at 5 mV/s and excellent capacitance retention of 95% after 10^4 cycles.

Keywords: Supercapacitor, Cobalt-manganese oxide, VGCF(vapor-grown carbon fiber), Nickel foam, Capacitance

1. INTRODUCTION

Electrochemical supercapacitors have attracted interest as an energy storage device with high power density, high charge/discharge cycle life and high energy efficiency[1-5]. There are two types of supercapacitor, electrical double-layer and redox supercapacitors. The charge-storage in double-layer supercapacitors is achieved by the formation of a double-layer on the surface of the electrode material, whereas, in redox supercapacitors, the charge is stored on both the electrode surface through a double-layer and the bulk of the material via Faradaic reaction. Hence, the charge stored in redox supercapacitors may be greater than that in double-layer counterparts[3-5].

Among the various metal oxides studied over the years, hydrous RuO_2 has been recognized as one of the most promising electrodes due to their high specific capacitance and good cycleability[2-5]. But the higher cost and poor abundance of RuO_2 pose problem for its commercial use. Hence, exploring and studying of other low-cost metal oxide instead of hydrous RuO_2 become a research trend[2]. Recently, cobalt-manganese oxide have been studied as alternative materials about the hydrous RuO_2 for supercapacitors[6-11]. It has been reported that the supercapacitive properties can be improved when metal oxides are composited with carbon based materials including carbon nanotube, fiber, and activated carbon powders[12-19]. Also, we reported that CoNi oxide/carbon-nanofiber composite electrodes showed excellent supercapacitive properties[18].

In the present work, the cobalt-manganese oxide/VGCF composite electrodes were prepared simply by thermally decomposing cobalt and manganese nitrates on the surface of the pore in the 3-dimensional porous nickel foam current collector and their supercapacitive properties were investigated by using cyclic voltammetry in 1M KOH. For comparison, the electrochemical properties of cobalt-manganese oxide electrode without VGCF were also investigated. Here, vapor grown carbon fiber(VGCF) used to make a composite electrode with metal oxides is expected to give good supercapacitive properties because it has higher electrical conductivity of 83.3 Scm^{-1} and fibrous nature[17]. In addition, a 3-dimensional porous nickel foam current collector used here has an advantage to keep dimensional stability of the electrode materials, compared to 2-dimensional planar substrates including metal or graphite foils[18].

2. EXPERIMENTAL PART

VGCF (Showa Denko K.K, Japan) used in this study had the specific surface area of 13 m^2g^{-1}, specific resistance of 0.012 Ω·cm, and aspect ratio of 67. All other chemicals were purchased from Aldrich and used as received. Triply distilled water of 18 MΩ obtained through aqua MAX water system (Younglin, Korea) was used to prepare the solutions. A 3-dimensional porous nickel foam (Shenzhen Rolinsia Power Materials Ltd.) used was 1.0 mm thick with pore density of 110 ppi(pore per inch). Before use, it was washed by acetone, and then with double-distilled water. After that, a mixed aqueous solution of 1M $Co(NO_3)_2$ and 1M $Mn(NO_3)_2$ was dropped onto the surface of the 3-dimensional porous nickel foam by a micro-syringe. After dried at room temperature, the electrode was heated in air at 250°C for 2 h to form cobalt-manganese oxide by thermal decomposition of cobalt and manganese nitrate precursors. In case of preparation of cobalt-manganese oxide/VGCF composite electrode, a weighed quantity of VGCF was added to the cobalt-manganese nitrate solution, sonicated for 1 h and then dropped onto the nickel foam and annealed at 250°C for 2 h. The mass of cobalt-manganese oxide contained in the nickel foam was measured by the weight difference of the substrate with and without cobalt-manganese oxide using a micro-balance (Mettler Toledo) that had a sensitivity of 1.0 μg. The used cobalt-manganese oxide/VGCF composite electrode contained 5 wt% VGCF. The morphology of the cobalt-manganese oxide/VGCF composite electrodes was investigated by scanning electron microscopy (SEM, Jeol JSM-6390). The structure of the electrode was examined by XRD (X-ray diffraction, Rigaku). Electrochemical characterizations on cobalt-manganese oxide/VGCF composite electrode were carried out by using cyclic voltammetry (Autolab, P/G-Stat 100). A standard three-electrode cell was employed. The cobalt-manganese oxide/VGCF composite electrodes with a geometric area of 1.0 cm^2 were used as a working electrode. A platinum foil was served as a counter electrode (2x2 cm^2) and an Ag/AgCl (3M KCl, 0.196 V vs. SCE, Metrohm) was used as a reference electrode. All electrochemical experiments were carried out in 1M KOH electrolyte solution at room temperature and in the potential window of 0~0.5 V in the different scan rates of 5, 10, 20, 50, 100 mVs^{-1}, respectively. The electrolyte solution was purged with nitrogen gas to eliminate oxygen before use.

3. RESULTS AND DISCUSSION

Fig. 1 shows the SEM images of cobalt-manganese oxide/VGCF composite and cobalt-manganese oxide without VGCF, which is formed in the pore of the nickel foam. It can be seen from Fig. 1(a) that the surface and pore of the porous nickel foam are filled with the cobalt-manganese oxide/VGCF, and VGCFs are well-dispersed in the bulk of the metal oxide as fibers, which are clear from the comparison between cobalt-manganese oxide with and without VGCF, as shown in Fig. 1(b). The rough morphology of the cobalt-manganese oxide/VGCF electrode and the improved electrical conductivity offered by the VGCF are believed to play a favorable role in improving higher specific capacitance of cobalt-manganese oxide/VGCF electrode.

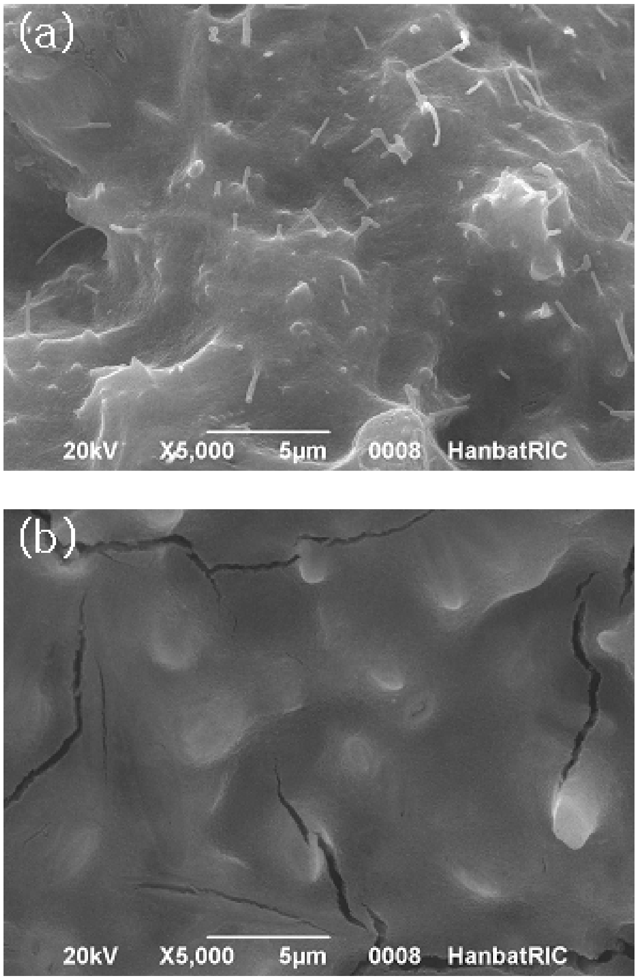

Figure 1. Scanning electron microscope images of (a) $CoMnO_2$/VGCF(x5000), (b)$CoMnO_2$(x5000)

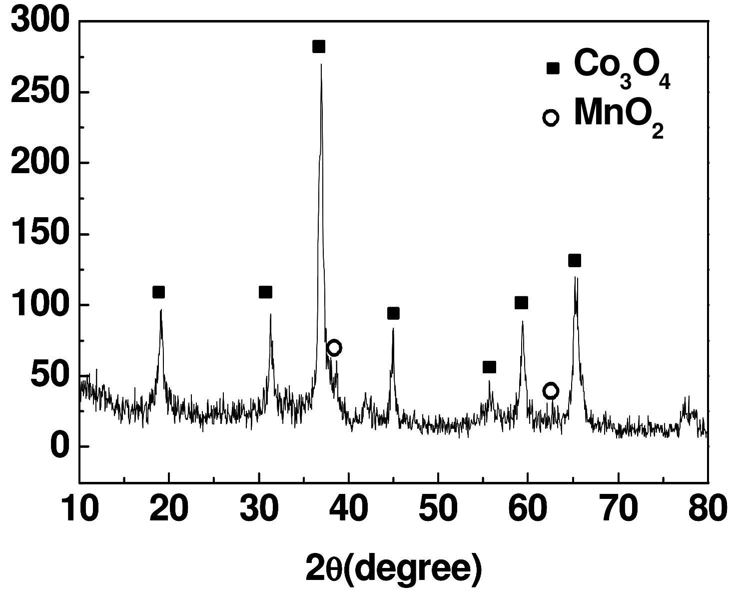

Figure 2. X-ray diffraction pattern of $CoMnO_2$

Fig. 2 shows the XRD pattern of cobalt-manganese oxide formed in surface of the pore in the nickel foam. The corresponding result demonstrates that the cobalt and manganese oxide exist as Co_3O_4 and MnO_2, respectively. This result is consistent with those of the references [12-14].

Electrochemical characteristics of the two kinds of electrodes were investigated with CV at various scan rates ranging from 5 to 100 mVs^{-1}. The obtained CVs are presented in Fig. 3. The current values in the figures are normalized to the weight of active material (VGCF is not considered as active material) in the electrode. It can be noted from the figure that the current values and voltammetric shape of the cobalt-manganese oxide/VGCF composite electrode are much better than those of the cobalt-manganese oxide electrode without VGCF. Even at the high scan rate of 100 mVs^{-1}, the cobalt-manganese oxide/VGCF composite electrode shows well-defined shape of CVs and better electrochemical reversibility. For the Co_3O_4-MnO_2, the corresponding peak potentials are observed at ca. 0.4 V and 0.22 V, respectively, at the scan rate of 100 mVs^{-1}, which come from Co_3O_4/CoOOH, $Mn(OH)_2$/MnOOH redox pair in 1 M KOH aqueous solution, as following redox reactions[12,15,16],

$$Co_3O_4 + H_2O + OH^- \rightleftarrows 3CoOOH + e^- \qquad (1)$$

$$MnOOH + OH- \rightleftarrows MnO2 + H_2O + e^- \qquad (2)$$

CoOOH and MnOOH undergo transformation between +3 and +4, and the transformati- n between these two oxidation states is highly reversible. The good electrochemical performance of the cobalt-manganese oxide/VGCF composite electrode can be attributed to its higher electrical conductivity and facile ionic transportation that are offered by the VGCF additive.

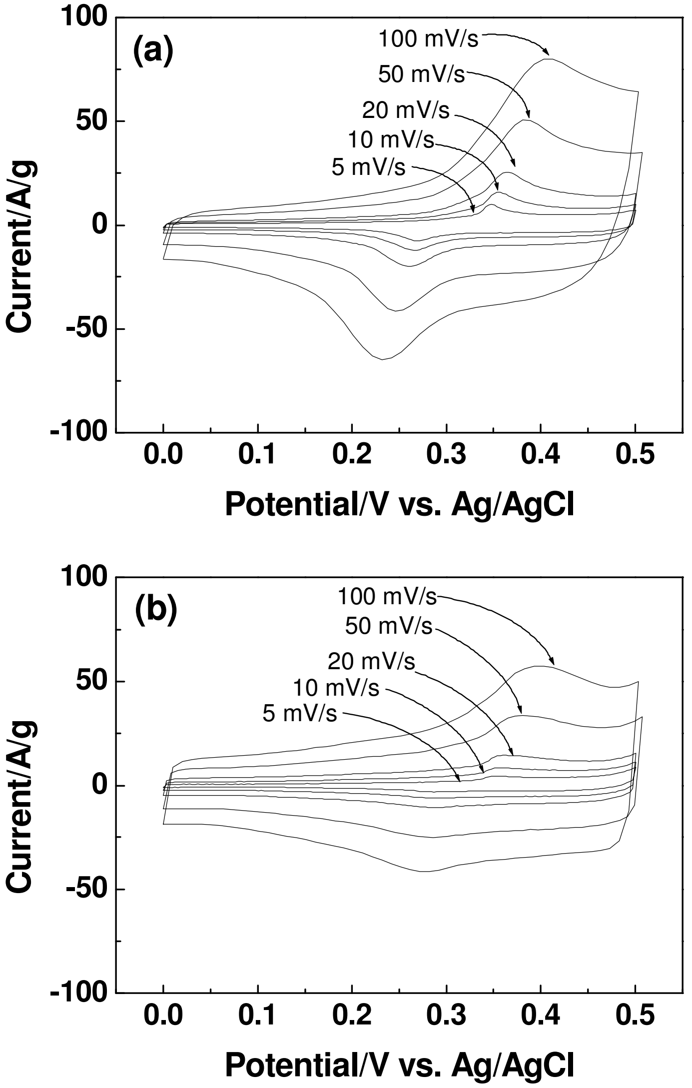

Figure 3. Cyclic voltammograms of (a) $CoMnO_2$/VGCF and (b) $CoMnO_2$ at the different scan rates in 1.0 M KOH aqueous solution

From the CV recorded at various scan rates, specific capacitance values are calculated by using the formula of $Q/(\Delta E \cdot m)$, where Q refers to the charge integrated from the cathodic curves, ΔE and m refers to the difference in the voltage window (here, 0.5 V) and weight of the cobalt-manganese oxide (1.31 $mgcm^{-2}$(1.38 $mgcm^{-2}$ based on composite)) in the composite. Specific capacitance values calculated from these CV curves are plotted in Fig. 4. From these plot, it can be observed that at the lowest scan rate of 5 mVs^{-1}, the specific capacitance of cobalt-manganese oxide/VGCF composite and cobalt-manganese oxide are 630 and 419 Fg^{-1} based on the weight of cobalt-manganese oxide and at a scan rate of 100 mVs^{-1}, the capacitance values are 342 and 283 Fg^{-1}, respectively. This result clearly demonstrates the advantage of VGCF as a conducting additive in cobalt-manganese oxide electrode. Even based on the total weight of the cobalt-manganese oxide/VGCF composite, its specific capacitance is higher than only cobalt-manganese oxide. This difference is believed mainly due to the support of VGCF by means of offering good electronically conducting pathways to the bulk and surface of cobalt-manganese oxide. It is interesting to note that capacitance values are not rapidly decreased even at high scan rate of 100 mVs^{-1}. It means that the redox kinetics of the cobalt-manganese oxide/VGCF composite (and cobalt-manganese oxide) electrodes are very fast, indicating that the electric interfacial resistance between nickel foam and cobalt-manganese oxide is relatively small, and the diffusion of charge carriers can easily satisfy the fast redox reaction. This is resulted from the close contact of cobalt-manganese oxide with nickel foam current collector due to without binders used in the electrode preparation.

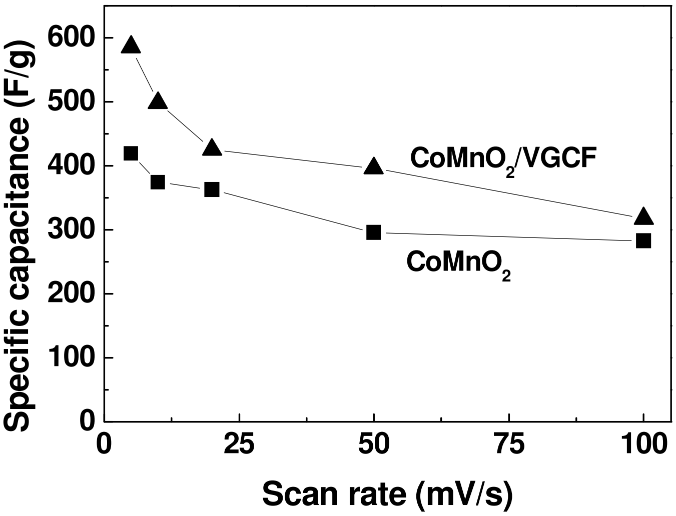

Figure 4. Specific capacitance values as a function of scan rate for $CoMnO_2$/VGCF and $CoMnO_2$ electrodes

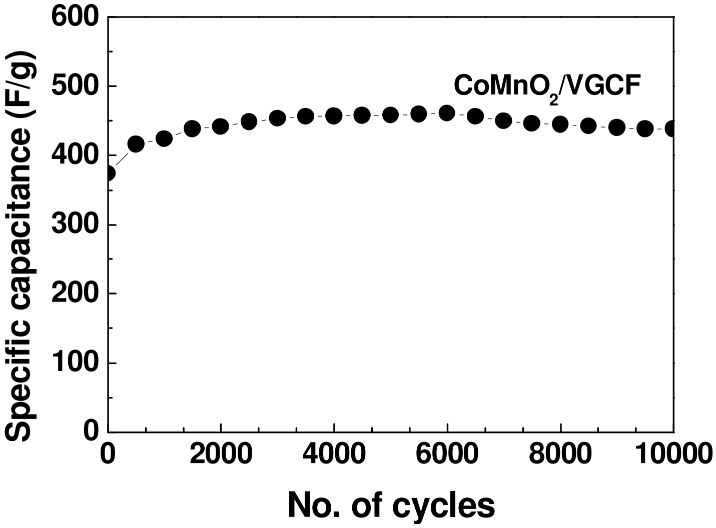

Figure 5. Specific capacitance values as a function of cycle number for $CoMnO_2$/VGCF electrode.

Fig. 5 shows the cyclic stability of the cobalt-manganese oxide/VGCF composite electrode at a scan rate of 200mV/s between 0 and 0.5 V in 1molL^{-1} KOH solution. As indicated in Fig. 5, there is a increase in the specific capacitance value for the 6000 cycles, and the specific capacitance remains almost constant during the following 4000 cycles. It can be seen that the cobalt-manganese oxide/VGCF composite electrode retain 95% of 6000th capacitance value after the 10^4 cycling at 200 mV/s, indicating that the cobalt-manganese oxide/VGCF composite electrode has excellent cycle life. This result means that the redox process of the cobalt-manganese oxide/VGCF composite electrode are chemically and electrochemically reversible due to the better electrical contact between electrode materials and between 3-dimensional nickel foam current collector substrate and cobalt-manganese oxide/VGCF composite electrode materials.

4. CONCLUSIONS

The cobalt-manganese oxide/VGCF composite electrodes were prepared on the surface of pore in the 3-dimensional nickel foam substrate. Cyclic voltammetry for the cobalt-manganese oxide/VGCF composite electrode exhibited specific capacitance values of 630 Fg^{-1} at 5 mVs^{-1} and 342 Fg^{-1} at 100 mVs^{-1} and excellent capacitance retention(95% after 10^4 cycles). Hence, the cobalt-manganese oxide/VGCF material is considered as a promising material for supercapacitors.

References

1. B.J. Lee, S.R. Sivakkumar, J.M. Ko, J.H. Kim, S.M. Jo, and D.Y. Kim, *J. Power Sources* 168 (2007) 546.
2. J.P. Zheng, T.R. Jow, *J. Electrochem. Soc*. 142 (1995) L6.
3. J.H. Park, J.M. Ko, O.O. Park, *J. Electrochem. Soc.,* 150, (2003)864.
4. T.R. Jow, J.P. Zheng, *J. Electrochem. Soc*. 145 (1998) 49.
5. I-H. Kim, K-B. Kim*, J. Electrochem. Soc*. 153 (2006) A383.
6. C. Lin, J.A. Ritter, and B.N. Popov, *J. Electrochem. Soc*. 160 (1998) 4097.
7. T.-C. Liu, W.G. Pell, and B.E. Conway, *Electochim Acta* 44 (1999) 2829.
8. V. Srinivasan and J.W. Weidner, *J. Power Sources* 108 (2002) 15.
9. J.W. Long, A.L. Young, D.R. Rolison, *J. Electrochem. Soc*. 150 (2003) A1161.
10. C.-C. Hu, C.-C. Wang, *J. Electrochem. Soc*. 150 (2003) A1079.
11. J.-K. Chang, W.-T. Tsai, *J. Electrochem. Soc*. 150 (2003) A1333.
12. F. Švegl, B. Orel, M. G. Hutchins, and K. Kalcher, *J. Electrochem. Soc*. 143 (1996) 1532.
13. Z. Fan, J. Chen, K. Cui, F. Sun, Y. Xu, Y. Kuang, *Electrochim. Acta* 52 (2007) 2959.
14. S.R. Sivakkumar, J.M. Ko, D.Y. Kim, B.C. Kim, G.G. Wallace, *Electrochim. Acta* 52 (2007) 7377.
15. V. Srinivasan and J. W. Weidner, *J. Power Sources* 108 (2002) 15.
16. J-K. Chang, M.-T. Lee, W.-T. Tsai, *J. Power Sources* 166 (2007) 590.
17. S.R. Sivakkumar, J.M. Ko, D.Y. Kim, B.C. Kim and G.G. Wallace, *Electrochimica Acta*, 52(2007) 7377
18. Y.l. Yoon and J.M. Ko, *Int. J. Electrochem. Sci*., 3 (2008) 1340
19. J.M. Ko, K.M. Kim, *Materials Chemistry and Physics* 114 (2009) 837

20. J. Chang, M. Lee, C. Huang, W. Tsai, *Materials Chemistry and Physics* 108 (2008) 124
21. Z. Fan, J. Chen, K. Cui, F. Sun, Y. Xu, Y. Kuang, *Electrochimica Acta* 52 (2007) 2959