

CoNi Oxide/Carbon-Nanofiber Composite Electrodes for Supercapacitors

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Cobalt-nickel oxide/VGCF(vapor grown carbon fiber) composites were prepared by thermally decomposing cobalt and nickel nitrates directly onto the pore of nickel foam as a current collector and their electrochemical properties were investigated by means of cyclic voltammetry. Cyclic voltammetry for the cobalt-nickel oxide/VGCF composite electrode exhibited specific capacitance values of 1271 Fg^{-1} at a scan rate of 5 mVs^{-1} based on cobalt-nickel oxide. SEM images showed that the VGCFs were well-dispersed in the bulk matrix of the cobalt-nickel oxide to give electrical conductivity. It is concluded that the VGCF played the roles in reducing the interfacial resistance in the cobalt-nickel oxide to improve capacitance performance.

Keywords: Supercapacitor, Cobalt-nickel 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].

There are two types of supercapacitor, electrical double-layer and redox supercapacitors[1-3]. 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[1].

Various metal oxides such as RuO_2 , IrO_2 and NiOx , have been studied as electrode materials in redox supercapacitors. Among them, hydrous RuO_2 has been recognized as one of the most promising electrodes due to its high specific capacitance, highly reversible redox reaction, and good cycleability

[2-4]. However, for the practical commercialization, the RuO₂ has some disadvantages including its high cost and poor abundance. Further, it has been reported that only a very thin layer of RuO₂ participates in the charge-storage process and the rest of material under this thin layer remains inactive and cause low gravimetric capacitance[1].

In order to overcome the disadvantages of RuOx, other metals oxides have been studied for the substitute of RuO₂. Recently, cobalt-nickel oxide have been developed as alternative electrode materials for supercapacitors[5-11].

On the other hand, the capacitance values for supercapacitor electrodes depend on current collector substrate and physical conditions including sample thickness and weight, and morphology[1]. To our knowledge, among them, there have been poor studies on the effect of current collector substrate on capacitance value. It is considered that there are two kinds of substrates, 2-dimensional metallic foil and 3-dimensional metallic foam. There are some advantages for the 3-dimensional metallic foam substrate as a current collector substrate including a dimensional stability of electrode material and low contact resistance between electrode active materials and current collector substrate. Despite of these good advantages, it has not been mainly used for the fabrication of supercapacitor electrodes.

On the other hand, the supercapacitive properties can be improved when metal oxides are composited with various carbons including carbon nanotube, fiber, and activated carbon powder. Among them, it is believed that vapor grown carbon fiber(VGCF) is a good candidate for making a composite electrode with metal oxides to enhance supercapacitive properties because it has higher electrical conductivity of 83.3 Scm⁻¹ and fibrous nature of aspect ratio of 67.

In the present work, the cobalt-nickel oxide/VGCF composite electrodes were prepared simply by thermally decomposing cobalt and nickel nitrates onto the pore in the 3-dimensional porous nickel foam current collector and their supercapacitive properties were investigated by using cyclic voltammetry. In addition, the influence of loading mass of cobalt-nickel oxide on capacitive properties for the composites was reported.

2. EXPERIMENTAL PART

VGCF (Showa Denko K.K, Japan) used in this study has the specific surface area of 13 m²g⁻¹, specific resistance of 0.012 Ωcm, and aspect ratio of 67. All other chemicals were purchased from Aldrich and used as received. 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), as seen in Fig.1. Before use, it was washed by acetone, and then with double-distilled water. After that, a mixed aqueous solution of 1M Co(NO₃)₂ and 1M Ni(NO₃)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□ for 2 h to form cobalt-nickel oxide by thermal decomposition of cobalt and nickel nitrate precursors. For the preparation of cobalt-nickel oxide/VGCF composite electrode, a weighed quantity of VGCF was added to the cobalt-nickel 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-nickel oxide embedding in the nickel foam was

measured by the weight difference of the substrate with and without cobalt-nickel oxide using a micro-balance (Mettler Toledo) that had a sensitivity of 1.0 μg . The used cobalt-nickel oxide/VGCF composite electrode contained 5 wt% VGCF. The morphology of the cobalt-nickel oxide/VGCF composite electrodes was investigated by scanning electron microscopy (SEM, Jeol JSM-6390). The structure of the Co_3O_4 , NiO was examined by XRD (X-ray diffraction, Rigaku). Electrochemical characterizations for the cobalt-nickel oxide/VGCF composite electrode were carried out using cyclic voltammetry (Autolab, P/G-Stat 100). The cobalt-nickel oxide/VGCF composite electrodes to be 1.0 cm^2 were used as a working electrode in a three-electrode cell. A platinum foil was served as a counter electrode ($2 \times 2 \text{ cm}^2$) 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 the potential window of 0~0.5 V with different scan rates of 5, 10, 50, 100 mVs^{-1} in 1 M KOH aqueous electrolyte solution at room temperature.

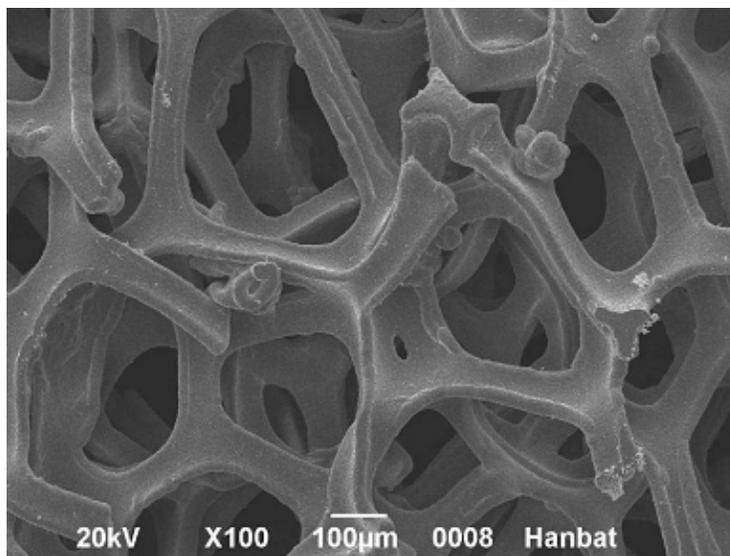


Figure 1. SEM image of the used Ni foam

3. RESULTS AND DISCUSSION

Fig. 1 shows the SEM image for the 3-dimensional porous nickel foam used. It is expected that the nickel foam can give the dimensional stability to electrode materials and may play a role in improving the supercapacitive properties of cobalt-nickel oxide/VGCF composite because of its low interface resistance between the active metal oxide and current collector, and possibility of high loading of metal oxide in the porous foam. In our case, the binders such as polymeric materials, which are usually used in electrode preparation, are not needed because the cobalt-nickel oxide/VGCF composite can be directly formed onto the pore of the nickel foam.

Fig. 2 shows the SEM images for the cobalt-nickel oxide/VGCF composite and for a cobalt-nickel oxide without VGCF, which is formed in the pore of the nickel foam. It can be seen from Fig. 2(a) and (b) that the surface and pore of the porous nickel foam are covered and filled with the cobalt-nickel oxide/VGCF composite and the VGCFs are well-dispersed in the surface and bulk of the metal oxide as fibers, which are clear from the comparison with Fig. 2(c). The morphology of the cobalt-nickel oxide/VGCF composite with the improved electrical conductivity offered by the VGCF are believed to play a favorable role in improving higher specific capacitance.

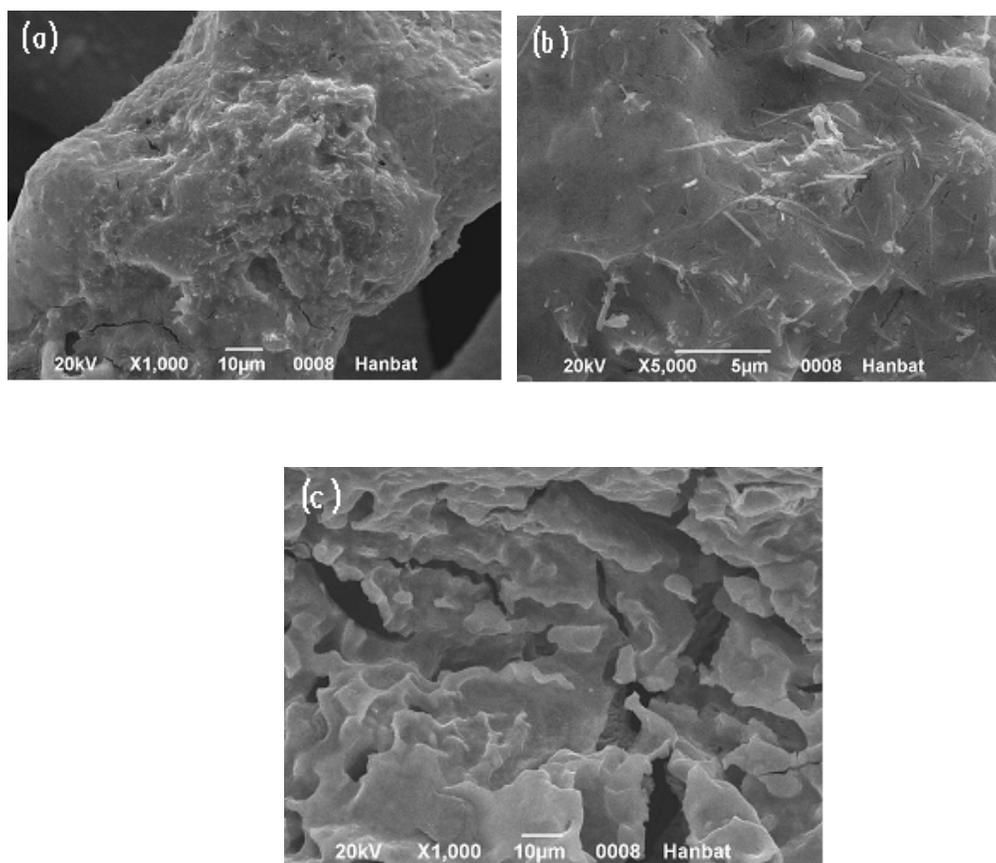


Figure 2. SEM images of the cobalt-nickel oxide/VGCF composite electrodes (x1000(a), x5000(b)), and cobalt-nickel oxide without VGCF (x1000(c))

Fig. 3 shows the XRD pattern for the cobalt-nickel oxide formed in surface of the pore in the nickel foam. The corresponding result demonstrates that the cobalt and nickel oxide exist as Co_3O_4 and NiO , respectively. This result is consistent with those of the references [12,13].

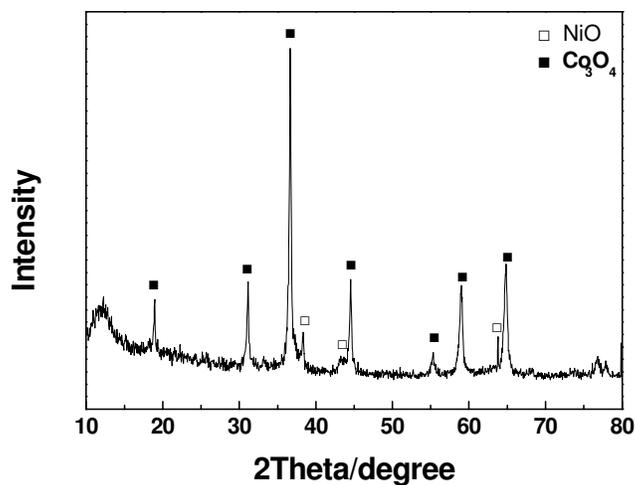


Figure 3. X-ray diffraction pattern of the cobalt-nickel oxide

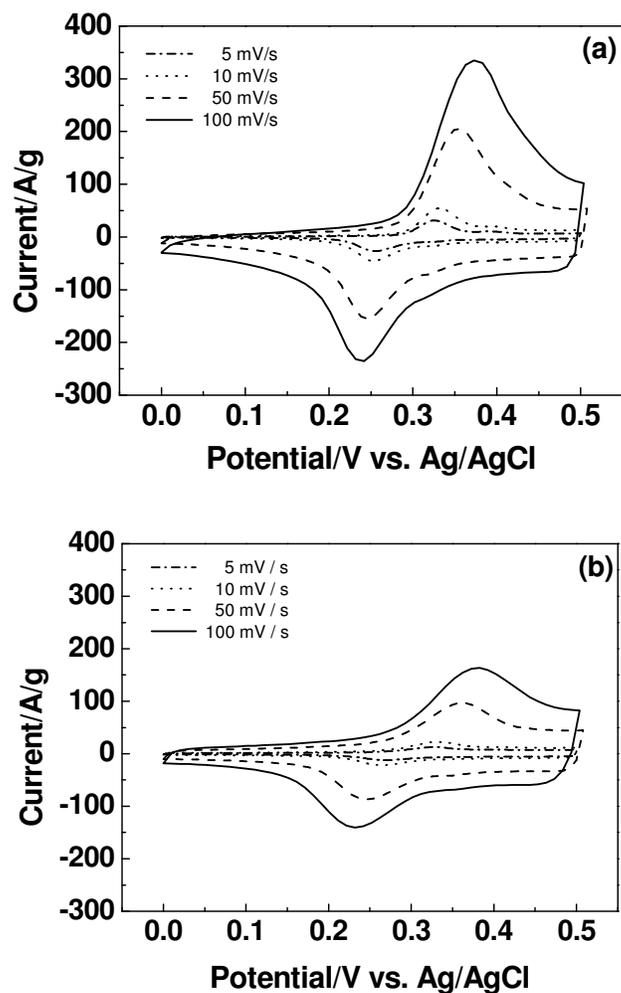


Figure 4. Cyclic voltammograms of (a) cobalt-nickel oxide/VGCF composite electrodes, (b) cobalt-nickel oxide at the different scan rates in 1.0 M KOH aqueous solution.

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. 4. 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-nickel oxide/VGCF composite electrode are much higher and better than those of the cobalt-nickel oxide electrode without VGCF. Even at the high scan rate of 100 mVs^{-1} , the cobalt-nickel oxide/VGCF composite electrode shows well-defined shape of CVs and better electrochemical reversibility. For the $\text{Co}_3\text{O}_4\text{-NiO}$, the corresponding peak potentials are observed at 0.38 V and 0.24 V at the scan rate of 100 mVs^{-1} , which come from $\text{Co}_3\text{O}_4/\text{CoOOH}$, $\text{Ni(OH)}_2/\text{NiOOH}$ redox pair in 1 M KOH aqueous solution, as following redox reactions[12,14],

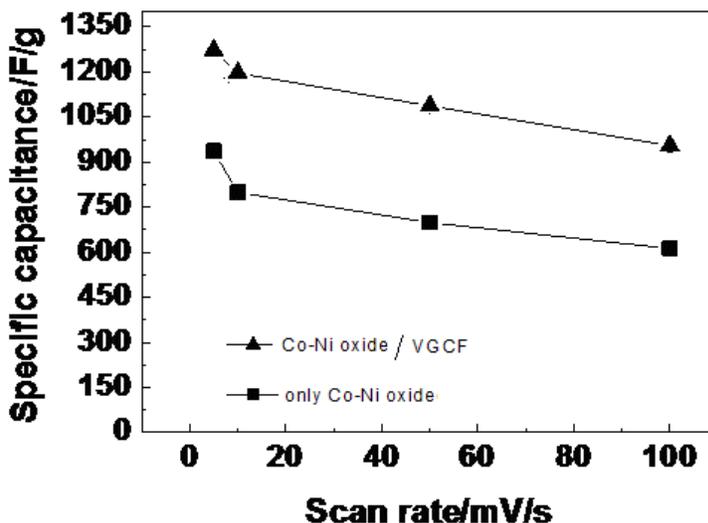
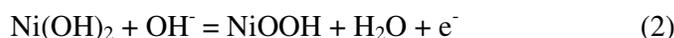


Figure 5. Specific capacitances for the cobalt-nickel oxide/VGCF composite electrode as a function of scan rate.

The good electrochemical performance of the cobalt-nickel oxide/VGCF composite electrode can be attributed to its improved electrical conductivity and facile ionic transportation that are offered by the VGCF additive. 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-nickel oxide (0.77 mgcm^{-2} (0.81 mgcm^{-2} based on composite)) in the composite. Specific capacitance values calculated from these CV curves are plotted in Fig. 5. From these plot, it can be observed that at the lowest scan rate of 5 mVs^{-1} , the specific capacitance of cobalt-nickel oxide/VGCF composite and cobalt-nickel oxide are 1271 and 936 Fg^{-1} based on the weight of cobalt-nickel oxide and at a scan rate of 100 mVs^{-1} , the capacitance values are 955 and 612 Fg^{-1} , respectively. This result clearly

demonstrates the advantage of VGCF in the cobalt-nickel electrode. Even based on the total weight of the cobalt-nickel oxide/VGCF composite, its specific capacitance is higher than only cobalt-nickel 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-nickel oxide. To our knowledge, this value is highest among the capacitance values for the cobalt-nickel oxide electrodes published until now. Also, 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-nickel oxide/VGCF composite electrodes are very fast, indicating that the electric interfacial resistance between nickel foam and cobalt-nickel 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-nickel oxide with nickel foam current collector due to without binders used in the electrode preparation.

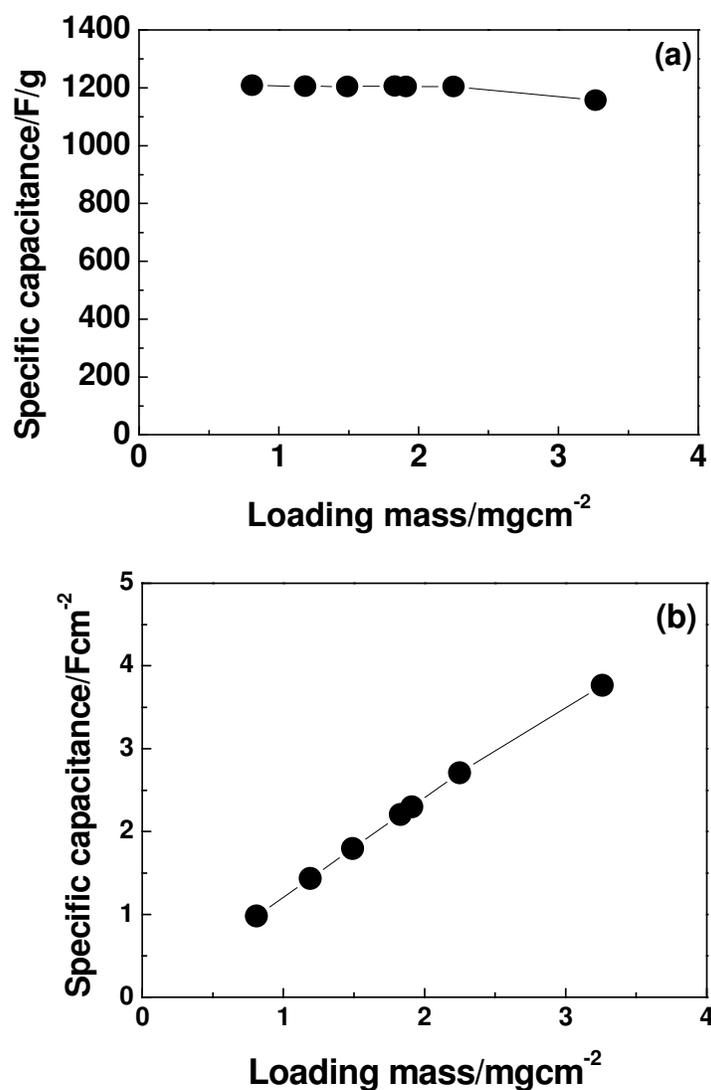


Figure 6. The effect of loading mass of the cobalt-nickel oxide on specific capacitance values per the sample weight (a) and per the surface area of the electrode (b) for the cobalt-nickel oxide/VGCF composite electrode.

The effect of loading mass of the cobalt-nickel oxide/VGCF composite material inside the nickel foam on the specific capacitance was investigated by means of cyclic voltammetry and the corresponding results are shown in Fig. 6. It is observed from Fig. 6 that the specific capacitances are proportional to the loading mass of cobalt-nickel oxide in the range from 0.81 to 3.26 mgcm⁻². This is because the nickel foam as a porous current collector played the roles in reducing the interfacial resistance with cobalt-nickel oxide/VGCF composite and in improving the electrode density by embedding greater amount of cobalt-nickel oxide/VGCF within it.

4. CONCLUSIONS

The cobalt-nickel oxide/VGCF composite electrodes were prepared onto the pore in the 3-dimensional nickel foam substrate. Cyclic voltammetry for the cobalt-nickel oxide/VGCF composite electrode exhibited specific capacitance values of 1271 Fg⁻¹ at 5 mVs⁻¹ and 955 Fg⁻¹ at 100 mVs⁻¹. It is concluded that the VGCF and the 3-dimensional porous nickel foam substrate played the roles in reducing the interfacial resistance with the cobalt-nickel oxide/VGCF composite and in improving the electrode density by embedding greater amount of the cobalt-nickel oxide/VGCF composite.

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