



The electrochemical enhancement due to the aligned structural effect of carbon nanofibers in a supercapacitor electrode



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ABSTRACT

Aligned carbon nanofibers (ACNFs) were fabricated by electrospinning using a high speed of rotary collector (2000 rpm). To achieve a synergy effect of the electron double layer and redox faradaic reaction, NiCo_2O_4 was deposited on the surface of the ACNFs using an electrodeposition method. The improved electrochemical performance of the electrodes was investigated by cyclic voltammetry, galvanostatic charge-discharge testing, and electrochemical impedance analysis. Among the prepared electrodes, which were deposited for different times (5, 10, 20, and 30 s), the sample deposited by NiCo_2O_4 for 10 s had the highest specific capacitance (90.1 F g^{-1} at 5 mV s^{-1}), good rate capability (64.7%), and cycle stability (85.2% after 1000 cycles). In addition, to examine the effects of the alignment and redox faradaic reaction of NiCo_2O_4 , the ACNFs covered with NiCo_2O_4 for 10 s (NC-ACNFs) were compared with the ACNFs deposited by Co_3O_4 (C-ACNFs) and randomly oriented carbon nanofibers covered with NiCo_2O_4 (NC-RCNFs). The NC-ACNFs had a 15.8% and 11.3% higher specific capacitance than that of the C-ACNFs and NC-RCNFs, respectively. These results suggested that the electrochemical properties of carbon nanofibers could be improved through the structural effects of aligned nanofibers and a redox faradaic reaction of NiCo_2O_4 .

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1. Introduction

With the advances in science as well as population and economic growth in the last century, the dependence on energy has increased steadily. As the demand for energy increases, modern society is faced with problems of environmental pollution caused by the use fossil fuels to produce energy. To overcome these problems, developments of alternative energy technologies are required, such as solar and wind energy systems. On the other hand, this energy is intermittent requiring efficient and economical storage systems. In this regard, electrochemical energy storage devices, involving a high energy and power density as well as high cycle capacity, play an important role in the efficient storage of energy. Among energy-storage devices, batteries and supercapacitors have taken center stage. In particular, supercapacitors have a higher specific power density than batteries and a higher specific energy density than dielectric capacitors [1–4].

Supercapacitors are based on an electrical charging and discharging mechanism at the electrode-electrolyte interface of high surface area materials. According to the mechanism, supercapacitors can be divided into two types: i) electric double layer capacitors (EDLCs) and ii) pseudo-capacitors (PCs) [5–7]. EDLCs use an energy storage mechanism that prepares an electric double layer at the electrode/electrolyte interface by physical charge accumulation. PCs accumulate energy by a redox faradaic reaction process of electrochemically active electrode materials, e.g., metal oxides, conducting polymers [8]. On the other hand, some disadvantages of each supercapacitor have been exposed, such as low average specific capacitance value, energy density (in case of EDLCs), and poor cycle stability (in case of PCs) [9–12]. To overcome these demerits, hybrid supercapacitors, the systems containing combinations of double layer, and pseudo capacitance, have used for industry applications [10,13].

In the hybrid capacitor system, the low electrical conductivity of metal oxides, which act as a PC is a hurdle that should be solved to improve the properties of a hybrid capacitor. To clear the obstacle, a range of carbon materials with diverse morphologies have been used for applications in hybrid systems, because it has high electrical conductivity and large surface area for power applications and enhanced capacitance [14]. Among them, carbon

Abbreviations: CNFs, carbon nanofibers; NC, ACNFs aligned carbon nanofibers coated with NiCo_2O_4 ; C-ACNFs, aligned carbon nanofibers coated with Co_3O_4 ; NC-RCNFs, randomly oriented carbon nanofibers coated with NiCo_2O_4 .

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nanofibers (CNFs), which have a one dimensional structure, have a range of advantages, such as high electrical conductivity caused by the high aspect ratio and chemically stability [15–17]. To fabricate CNFs, an electrospinning method is used widely because of its high product yield, easy and inexpensive way for fabrication. In addition, one of the merits of the technique is that it can fabricate a range of CNFs, such as yarn, paper, and aligned fibrous arrays [18–20]. In particular, aligned carbon nanofibers (ACNFs) prepared by controlling the speed of disk type collector can maximize the merits of CNFs as a supercapacitor electrode, because it has a higher surface area caused by a small diameter of nanofibers, and better electrical conductivity due to the unique 1-dimensional oriented structure than other range of CNFs and randomly oriented carbon nanofibers (RCNFs) [10,21,22].

Not only carbon materials, but also metal oxides play a crucial role in the system because it can have the role of offsetting the demerits of carbon materials, such as low energy density [23]. RuO₂ has higher electrical conductivity and relatively high specific capacitance than other metal oxides. However, its practical application has been impeded by its high cost, rareness, and toxicity [24]. Recently, mixed transition metal oxides with the formula, A_xB_{3-x}O₄, have attracted huge attention, because it can offer richer redox faradaic reactions and enhanced electronic conductivity compared to unity transition metal oxides [25]. In particular, spinel NiCo₂O₄ is beneficial to electrochemical electrode materials because of its higher electronic conductivity and electrochemical activity than NiO and Co₃O₄. In addition, it is naturally abundant, low cost, and has low toxicity [26,27]. Using this material, a synergy effect with advanced carbon materials has been expected.

In the present study, to improve the electrochemical performance of the hybrid capacitor, the one-directional aligned structure of CNFs for improvement of surface properties and electrical conductivity, and the deposition of a small quantity of NiCo₂O₄ on the surface of CNFs for synergy effect of pseudo capacitance were used. The ACNFs deposited NiCo₂O₄ for 10 s using electrochemical deposition showed the 28% higher specific capacitance than it of raw-CNFs because of contribution of pseudo reaction caused by deposition of NiCo₂O₄. Also, the specific capacitance of ACNFs deposited NiCo₂O₄ was 11.3% enhanced than RCNFs deposited of it because of their unique aligned structure. Therefore, we suggest that the electrical performance of supercapacitor was enhanced by the aligned structure of CNFs and pseudo effect using deposition of a small quantity of NiCo₂O₄.

2. Experimental

2.1. Materials

Polyacrylonitrile (PAN, M_w = 150,000 g mol⁻¹), cobalt(II) nitrate hexahydrate (Co(NO₃)₂·6H₂O, ACS reagent), and nickel(II) nitrate hexahydrate (Ni(NO₃)₂·6H₂O, crystalline) were purchased from Sigma-Aldrich. Potassium hydroxide (KOH, assay 93.0% min.) was received by Samchun (South Korea) and *N,N*-dimethylformamide (DMF, assay 99.5% min.) were supplied by Daejung (South Korea).

2.2. Synthesis of electrode materials

Polyacrylonitrile (PAN) nanofibers were fabricated by electrospinning apparatus (Nano NC, South Korea) using electrospun solution of 12 wt.% PAN/DMF. A syringe containing the solution for electrospinning was connected to a syringe pump that was pushed at 1 mL h⁻¹. The disk type collector was used for collecting PAN nanofibers. The diameter of collector was 25 cm and the width for collecting the nanofibers was 1.7 cm. The parameters for the electrospinning are as follows: an internal diameter of syringe of

0.25 mm, distance between the spinneret and the collector of 18 cm, applied voltage of 18 kV for 2 h, and a collector speed of 250 and 2000 rpm to prepare randomly arranged and aligned PAN nanofibers, respectively.

The prepared PAN nanofibers were dried in an oven at 60 °C for 24 h and carbonized under a nitrogen atmosphere in a tube furnace (Korea Furnace Development Co., Ltd., South Korea). The first process to fabricate the ACNFs was stabilization in that the temperature increased to 300 °C at a heating rate of 1.5 °C min⁻¹, and retained at that temperature for 1 h in air. The next step was carbonization in a nitrogen atmosphere. The temperature was increased from 300 °C to 900 °C at a heating rate of 5 °C min⁻¹ and maintained at that temperature for 1 h by blowing nitrogen gas at a flow rate of 100 mL min⁻¹, followed by cooling to room temperature in a nitrogen atmosphere. The yield after carbonization of PAN fibers was from 58.8 to 61.1%.

Subsequently, the RCNFs and ACNFs were coated with NiCo₂O₄ using an electrodeposition method at room temperature. The two CNFs, which were attached to gas diffusion layer (SGL group, SIGRACET[®] BC grades), were used as the working electrode; Ag/AgCl was used as the reference electrode; Pt wire was used as counter electrode. A 0.1 M Co(NO₃)₂·6H₂O and 0.05 M Ni(NO₃)₂·6H₂O solution, mixed with stirring to use as precursor of NiCo₂O₄, was employed as the electrolyte and potentiostatic mode of electrodeposition was used (−0.95 V vs. Ag/AgCl reference electrode) at different deposition times (5, 10, 20, and 30 s). After electrodeposition, the samples were rinsed several times with distilled water and ethanol then dried at 60 °C for 24 h. The dried samples were annealed at 300 °C, for 2 h under an air atmosphere to obtain the final NiCo₂O₄ phase with a spinel structure [28]. At the same method and conditions, the ACNFs were coated with Co₃O₄ in the 0.1 M Co(NO₃)₂·6H₂O solution to prepare the ACNFs deposited by Co₃O₄.

2.3. Characterizations

The morphologies and microstructures were characterized by scanning electron microscopy (SEM, S-4300 SE, Hitachi, Japan), which was conducted at 15 kV and the samples were coated with platinum prior to analysis and the content of the sample was measured by energy dispersive X-ray spectroscopy (EDX). The chemical composition of the electrode samples was analyzed by X-ray photoelectron spectroscopy (XPS, K-Alpha, Thermo-scientific, USA) using monochromated Al K α radiation (h ν = 1486.6 eV) and inductively coupled plasma optical emission spectrometry (ICP-OES, OPTIMA 7300 DV, PerkinElmer, USA). The electrical conductivity of sample was measured using a resistivity meter (Loresta-GP, Mitsubishi Chemical Co., Japan). High resolution X-Ray diffraction (XRD, X'Pert-PROMRD, Phillips, Netherlands) using Cu K α radiation over the range, 10° to 80° 2 θ at the scanning speed of 2° min⁻¹, was used to examine the crystalline structure of the samples. The specific surface areas and pore size distributions of samples were examined using a full automatic physisorption analyzer (BELSORP-max, BEL Japan, Japan) according to the Brunauer-Emmett-Teller (BET) equation. The total pore volumes mean the amount adsorbed at a P/P₀ of 0.99.

The prepared samples were attached to a current collector (Ni foam) by giving pressure of 20 MPa and used directly as the electrodes for electrochemical analysis without a binder. The electrochemical tests of the samples were carried out on a potentiostat (Bio-Logic Science Instruments, France) using a three-electrode system: 1 M KOH as an electrolyte solution, and platinum wire and Ag/AgCl as the counter and reference electrodes, respectively. Cyclic voltammetry (CV) of the electrodes was measured at scan rate of 5, 10, 20, 40, and 60 mV s⁻¹ at potential windows between −0.4–0.2 V. Galvanostatic charge-discharge

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