Fabrication and Electrochemical Property of Hybrid Carbon Nanofibers Based on Polyimide Precursor and Manganese Dioxide

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ABSTRACT

We herein reports the preparation and characterization of hybrid carbon nanofibers (CNFs) based on polyimide (PI) and manganese dioxide (MnO_2) as self-standing and binder-free superacapacitor electrodes, which are prepared via electrospinning, imidization, and carbonization of mixed solutions of PI precursor, poly(vinyl pyrrolidone) (PVP), and manganese acetate. The microstructures and morphological features of the hybrid CNFs are characterized as a function of carbonization temperature. The electrochemical performance of the hybrid CNFs as self-standing supercapacitor electrodes is investigated with aids of cyclic voltammetry and galvanostatic charge/discharge test.

Keywords: carbon nanofibers, electrospinning, polyimide, manganese dioxide, supercapacitor electrode

1 INTRODUCTION

Electrochemical supercapacitors have recently received great interest from industry and academia as one of energy storage devices owing to their high power density, fast charge/discharge time, and long cycle life. However, supercapacitors have relatively low energy density, compared to lithium ion batteries. Among the electrically conductive materials for supercapacitor electrodes, carbon materials are extensively used due to their high performance, low cost, and versatile existing forms such as particles, fibers, and felts. Particularly, carbon nanofibers (CNFs) is known to have hig specific surface area, electrical conductivity, electrolyte wettability and mechanical stability. To increase the energy density of supercapacitors, transitional metal oxides have been utilized for the electrode materials of pseudocapacitors. Among the transition metal oxide materials, manganese oxides (MnO_2) are considered as the most promising electrode materials for supercapacitors owing to their high specific capacitance, natural abundance, low environmental toxicity, and cost effectiveness.

In this study, we have fabricated a new kind of hybrid CNFs based on polyimide (PI) precursor and MnO_2, as a free-standing and binder-free supercapcitor electode material, via electrospinning, imidization, and carbonization processes. The microstructures of PI/MnO_2-based hybrid CNFs were characterized by using SEM, XRD, and Raman spectroscopy. The electrochemical property of the hybrid CNFs was investigated with aids of cyclic voltammetry and galvanostatic charge/discharge test.

2 EXPERIMENT

3,3',4,4'-Biphenyltetracarboxylic dianhydride (BPDA, 97%, Sigma Aldrich Com.) and *p*-phenylenediamine (PPD, ≥99%, Sigma Aldrich Com.) were chosen as the monomers for the synthesis of poly(amic acid) (PAA) as the PI precursor. N,N-dimethylformamide (DMF, ≥99.5%, Sigma Aldrich. Com.) was used for the polymerization solvent. Manganese(II) acetate tetrahydrate (MnAc) was chosen as MnO_2 precursor. The methyl alcohol (MeOH) was used for the solvent. Poly(vinyl pyrrolidone) (PVP) was adopted as a polymeric matrix for the electrospinning of MnAc.

Poly(amic acid) (PAA) was synthesized as follows. Firstly, PPD was dissolved in DMF solvent with magnetic stirring at room temperature for 2 hr under nitrogen atmosphere. BPDA was then added into the solution and stirred for 24 hr for the polymerization.

To obtain a precursor solution for fabricating MnO_2 nanofiber, MnAc and PVP were dissolved in MeOh volvent until a homogeneous mixture was obtained.

The PAA solution and MnAc/PVP solution were electrospun simultaneously on a rotaing collector at the flow rate of 0.5 ml/h, 13-15 kV, and 25 cm distance between a syring tip and a collector.

The electrospun PAA/MnAc-PVP nanofibers were imidized by heating at 250 ºC for 30 min and 370 ºC for 30 min under air atmosphere. After then, carbonization was carried out at different temperatures of 800-1000 ºC.

3 RESULTS AND DISCUSSION

The morphologies of the electrospun precursor nanofiber and its CNFs were characterized by using SEM images, as shown in Figure 1. Although the morphological feature of the electrospun precursor nanofibers remained unchanged during the imidization process, the surfaces and diameters of CNFs became rougher and smaller, respectively, with increasing the carbonization temperatures.

Figure 2 shows the TGA and DTG curves of electrospun precursor nanofibers under nitrogen conditon. The residue at 800 ºC for the PAA/MnAc-PVP nanofibers was characteried to be ~35%.

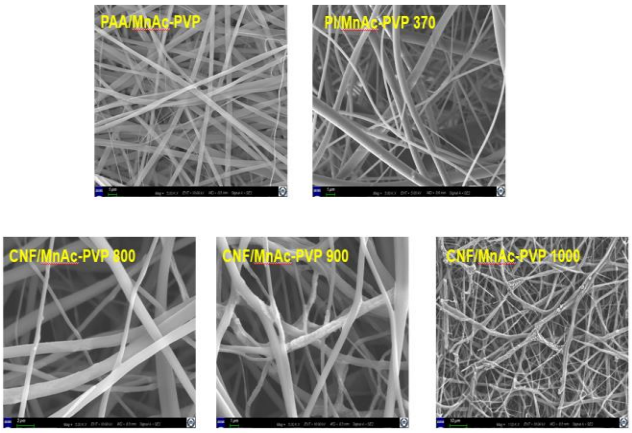

Figure 1. SEM images of as spun, imized and carbonized nanofibers.

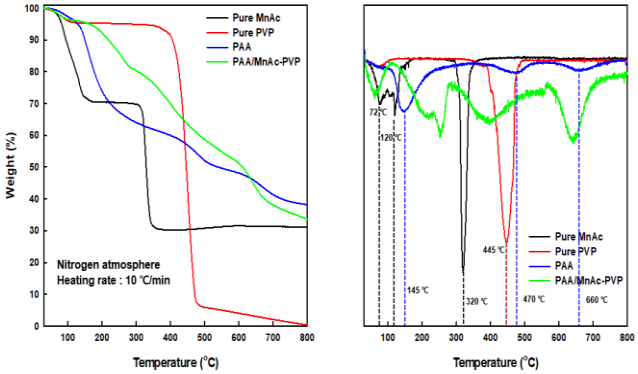

Figure 2. TGA and DTGA curves of pure MnAc, pure PVP, PAA and PAA/MnAc-PVP nanofiber.

In order to characterize the graphitic structural development during the carbonization, Raman spectra of CNFs was obtained, as shown in Figure 3. The peaks at 1350 and 1580 cm^{-1} correspond to D band and G band respectively. It is well known that the G band indicates ordered graphite carbon structure (sp^2), whereas the D band is typical of defects in carbon material. With increasing the carbonization temperature, the graphitic structure was found to be devleped gradually in the hybrid CNFs.

The cyclic voltammetric and charge-discharge curves of the CNFs fabricated at the carbonization temperature of 900 ºC are shown in Figure 4. The cyclic voltammograms showed rectangular form which corresponds to an ideal capacitor behavior, although they distort slightly at higher scan rates of 10-100 mV/s. The specific capacitance of the hybrid CNFs carbonized at 900 ºC was evaluated to be ~201 F/g at the scan rate of 10 mV/s. The galvanostatic charge-discharge test was carried out in a potential range from 0 to 0.8 V at differnt current densities of 0.4-1.0 A/g The galvanostatic charge-discharge curves showed a symmetrical triangles shape. The discharge time of the hybid CNFs carbonized at 900 ºC was ~500 sec at the current density of 0.4 A/g.

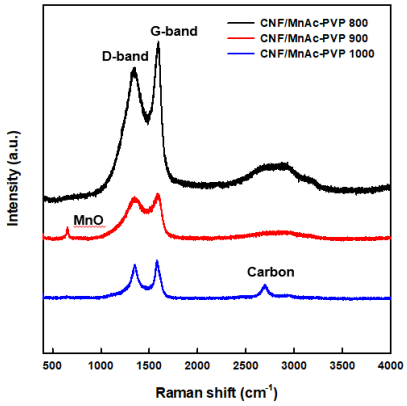

Figure 3. Raman spectrum of the hybrid CNFs carbonized at different temperatures of 800-1000 ºC.

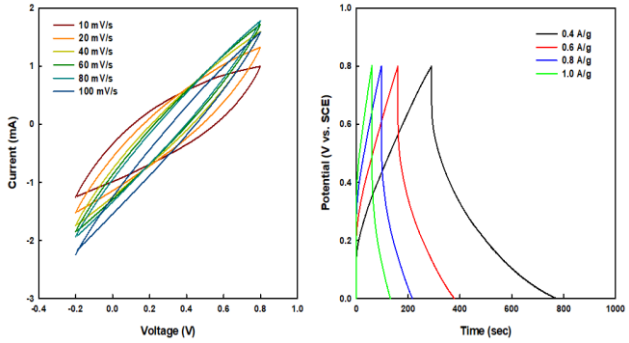

Figure 4. The cyclic voltammetry curves of the hybrid CNFs carbon nanofibers carbonized at 900 ºC and the galvanostatic charge-discharge curves

4 CONCLUSION

In this study, the hybrid CNFs based on PI precursor and MnO_2 were fabricated by electrospinning, imidization, and carbonization process. After carbonization, the surface of the hybrid CNFs became rougher because of the decomposition of PVP as well as the crystalline structure formation of MnO_2. The hybrid CNFs carboniated at 900 ºC showed good electrochemical performance such as a specific capacitance of ~201 F/g at the scan rate of 10 mV/s and a discharge time of ~500 sec at the crrent densit of 0.4 A/g. Overall, it is valid to contend that PI/MnAc-derived hybrid CNFs have great potential to be utilized as self-standing and binder-free supercapacitor electrode materials.

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