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Core-Shell Tubular Nanostructured Electrode of Hollow Carbon Nanofiber/Manganese Oxide for Electrochemical Capacitors

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ABSTRACT

Here we propose a core-shell tubular nanostructure consisted of hollow carbon nanofiber and manganese oxide (MnO_2) for the application of high capacitance electrochemical capacitors. Hollow nanostructured carbon nanofibers are prepared using an electrospinning technique with a dual nozzle. The hollow channel of carbon nanofibers enables the uptake of MnO_2 precursor solution inside the hollow carbon nanofiber, leading to the formation of MnO_2 layer on both the inner and outer surfaces of hollow carbon nanofiber. The utilization of both surfaces of hollow carbon nanofiber increases the effective reaction sites of electrode materials contacted with an electrolyte as well as maximizes the loading mass of MnO_2 on the surface of hollow carbon nanofiber (94% compared to carbon contents), consequently enabling the fabrication of electrochemical capacitors with the increased specific capacitance of 237 F/g.

1. Introduction

Electrochemical capacitors have been attracting attention as a promising energy device that exhibits high power density and long life cycle stability, and also bridges the gap in the energy density of conventional capacitors and rechargeable lithium ion batteries [1–3]. They can be categorized into electrical double layered capacitor (EDLC) and pseudocapacitor according to the charging mechanism [2]. In the case of EDLC, charges accumulate on the surface of electrode and simultaneously ions gather at the interface of electrode-electrolyte during the charging process. This reaction occurs at the interface between electrode and electrolyte, thus the increase in the surface area of electrode is prerequisite for obtaining high performance EDLC [1–3]. For this purpose, carbonaceous materials having large surface area have been utilized [1–3]. Although many attempts have been made to optimize their surface area and pore structure for achieving high capacitance EDLC, the specific capacitance of EDLC electrode materials still remains as low as 100-400 F/g [3].

To overcome such low specific capacitance of EDLC, pseudocapacitor has been proposed. In the case of pseudocapacitor, charging and discharging are based on the fast and reversible Faradaic reaction of electrode materials with electrolyte ions [2,4]. Metal oxides such as MnO_2, NiO, Co_3O_4, and their hydroxide forms or compounds have been widely investigated as electrode materials for pseudocapacitor application [2,4]. Some of these materials exhibit the specific capacitance as high as 2,000 F/g [5,6]. However, they suffer from their low electronic conductivity. Thus, active materials have been mixed together with conducting additives, providing efficient electron pathways to pseudocapacitor electrodes. In addition, polymeric binders that glue all the electrode constituents onto the current collector have been included. General binders are inactive and electrically insulating materials; therefore their presence in the electrode deteriorates the electrochemical performance of electrochemical capacitors.

Recently, binder-free processes that utilize a freestanding conducting mat have been suggested to avoid this issue [7–11]. Such conducting mat can be fabricated with 1D or 2D carbonaceous materials such as carbon nanotube, graphene, carbon nanofiber or their mixture. Among them, carbon nanofiber is considered as a promising conducting material for constructing efficient conducting pathways because electrons can be freely transported through the intimate contact points between carbon nanofibers as well as through the body of carbon nanofiber. Poly(acrylonitrile)(PAN) has been widely utilized as a starting material for producing carbon nanofibers [12,13]. PAN nanofibers can be prepared via a facile electrospinning, which is converted into carbon nanofibers through a successive process of structure stabilization and carbonization. The resulting carbon nanofibers can be decorated with redox-based

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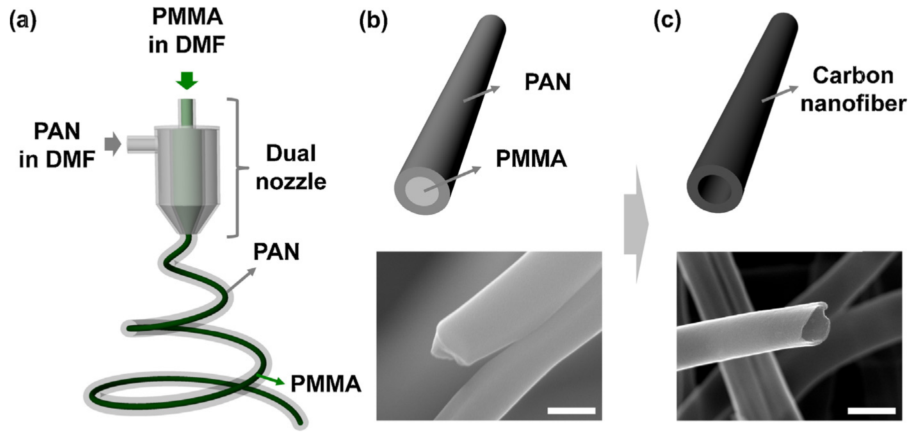

Fig. 1. Preparation steps for hollow carbon nanofiber. (a) Electrospinning with a dual nozzle system, (b) PMMA-PAN core-shell nanofibers, and (c) hollow carbon nanofibers. All scale bars are 500 nm.

metal oxides [14] or conducting polymers [15], which has been utilized to fabricate the high performance pseudocapacitor. Meanwhile, conventional carbon nanofiber is an imporous material. Since the electrochemical reaction in the electrochemical capacitors only occurs at the interface between electrode materials and electrolyte, the core part of the carbon nanofibers does not participate in the reaction. Finally, it leads to the decrease in the specific capacitance of electrochemical capacitors.

In this study, we demonstrate a unique nanostructured electrode to achieve high performance electrochemical capacitors by constructing a hollow open channel along the axis of carbon nanofiber. The hollow structured carbon nanofibers that are proposed here minimize the unreacted part of the carbon nanofiber. In addition, ions can be transported through the inner hollow channel, increasing ion-accessible surface area. Such dual contribution of hollow carbon nanofibers expects the increase in the specific capacitance of electrochemical capacitors fabricated with hollow carbon nanofibers. An electrospinning system equipped with a dual nozzle is utilized to produce core-shell nanofibers consisted of sacrificial poly(methyl methacrylate) (PMMA) core and PAN shell (Fig. 1). One-step annealing process generates hollow carbon nanofibers. To further increase the specific capacitance of carbon nanofibers, we decorate their surface with MnO_2 that is a typical electrochemically active material exhibiting high theoretical specific capacitance of 1,370 F/g [16]. Also, the precursor solution for MnO_2 formation can be freely penetrated into the hollow channel of hollow carbon nanofiber, enabling the formation of MnO_2 layer on both inner and outer surfaces of hollow carbon nanofibers. This approach is expected to contribute to utilize both inner and outer surfaces as reactive sites for the electrochemical reaction as well as obtain the high mass loading of MnO_2, eventually achieving high capacitance electrochemical capacitors.

2. Experimental

2.1. Preparation of starting materials

1 g of PAN (Mw 150,000, Sigma-Aldrich) and 3 g of PMMA (Mw 120,000, Alfa Aesar) were dissolved in 9 g of N,N-dimethylformamide (DMF, CHROMASOLV Plus, HPLC, 99.9%,

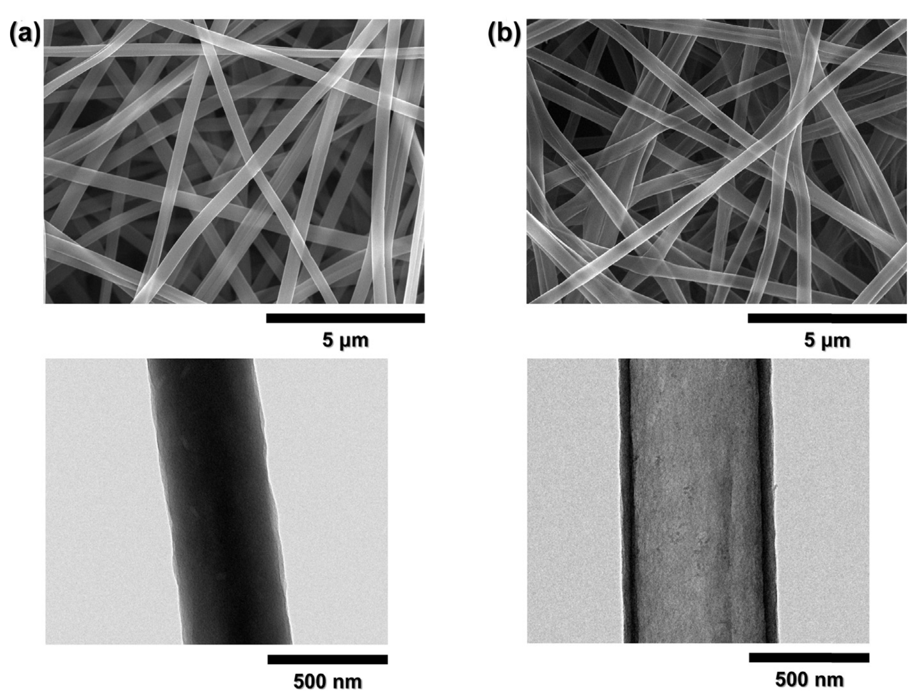

Fig. 2. (a) SEM (upper) and TEM (lower) images of carbon nanofibers and (b) hollow carbon nanofibers.