

SYNTHESIS AND SUPERCAPACITIVE PERFORMANCES OF ELECTROSPUN CARBON NANOFIBERS DECORATED WITH SPINEL $\text{Co}_{1.5}\text{Mn}_{1.5}\text{O}_4$ NANOCRYSTALS

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Summary: Herein, a novel composite material of coupled carbon fibers and $\text{Co}_{1.5}\text{Mn}_{1.5}\text{O}_4$ spinel oxide crystals has been fabricated by a facile two-stage process. In the first stage, fibers were produced by single-spinneret electrospinning of polymer solutions with the cobalt and manganese acetate precursors. In the second stage, fibers were heat-treated to convert them into composite structure. Scanning electron microscopy (SEM) analysis confirmed the formation of composite fibers with spinel crystals deposited on the surface. Scanning transmission electron microscopy (STEM) and energy dispersive X-ray spectroscopy (EDS) analysis of composite fibers cross-section revealed that carbon occupies space inside spinel rings. The composite electrode delivers a specific capacity of about 740 mAh g^{-1} , at a current density of 5 A g^{-1} in alkaline solution, which is more than 37 times superior to neat carbon fibers. Furthermore, the electrode retained 135% of its initial capacity, after 1000 cycles of galvanostatic charge/discharge at 5 A g^{-1} .

Keywords: electrospinning, carbon fibers, spinel, composite, supercapacitor.

INTRODUCTION

There has been an urgent need for exploring renewable and sustainable energy systems and technologies related to the energy conversion and storage due to global crisis caused by the over-consumption of fossil fuels [1]. Various electrical energy storage (EES) technologies have been developed so far and some of them are used in everyday life. Among EES devices, lithium-ion batteries and supercapacitors are the most important ones. Supercapacitors currently bridge the wide gap between batteries and traditional electrolytic capacitors. They can offer very long cycle life, outstanding power performances, and simple working principles, which can be integrated in high-performance electronic devices, memory back-up systems, industrial power and energy management *etc.* [2,3].

Electric double-layer (EDL) capacitors store charge electrostatically through reversible adsorption/desorption of electrolyte ions onto high-specific area carbon materials (activated carbons, graphene, carbon nanotubes *etc.*) [4,5]. Pseudocapacitors (PCs) store charge from reversible surface redox reactions. The spinel transition metal oxides with advanced architectures are considered as high-performance pseudocapacitive materials, but, poor conductivity and limited electrochemical cycling stability restrict their wide use as electrodes for supercapacitors [6]. To overcome this problem, carbon materials and spinel oxides can be assembled together in composite structures by using various fabrication methods. The promising route is electrospinning of phase-separated polymers with metal precursors and subsequent thermal treatment [7,8].

In this study, we have fabricated composite fibers of nonprecious spinel oxide $\text{Co}_{1.5}\text{Mn}_{1.5}\text{O}_4$ nanocrystals decorated on the carbon fibers (CFs) matrix. CFs are chosen as cost-effective, highly conductive materials allowing simultaneous contribution of EDL capacity and pseudocapacity. The synergistic effect of such spinel structure and CFs showed excellent specific capacity of 740 mAh g^{-1} with increased stability of 135% after 1000 cycles, at a current density of 5 A g^{-1} in potassium hydroxide (KOH) solution.

RESULTS AND DISCUSSION

The first stage involved single-spinneret electrospinning of polyacrylonitrile (PAN) and polyvinylpyrrolidone (PVP) polymer solutions with the cobalt and manganese acetate precursors in 1:1 molar ratio. In the second stage, the metallic salt-incorporated fibers were air-stabilized at $280 \text{ }^\circ\text{C}$ and heated at $600 \text{ }^\circ\text{C}$ in high-purity argon atmosphere thereby converting them into composites structure. The field-emission scanning electron microscopy (FE-SEM) images of fibers in various fabrication stages are given in *Figure 1*.

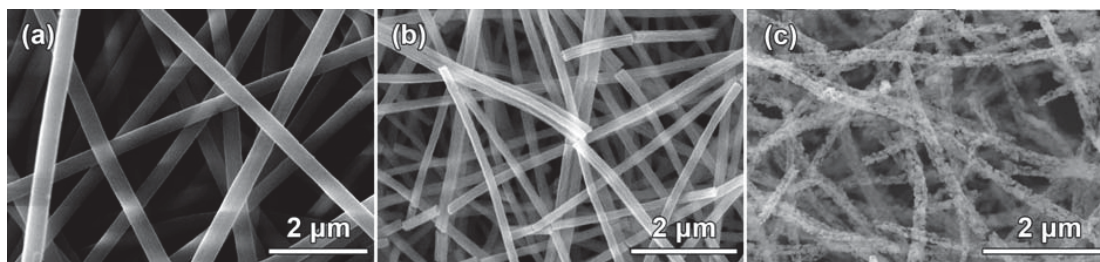


Figure 1: FE-SEM images of (a) as-spun, (b) air-stabilized and (c) composite fibers

In the intermediate step, the smooth as-spun fibers (Figure 1a) were air-stabilized into fibers with the rough surface morphology (Figure 1b). As expected, the average fiber diameter of these fibers was reduced. In this step, PAN polymer absorbed oxygen in the air leading to complex chemical changes, thus, resulting in the formation of a ladder-like structure that does not melt [9]. Accordingly, fibrous structure was preserved at high temperature of 600 °C under inert atmosphere (Figure 1c). PVP polymer acted as a sacrificial template and the preferential site for nucleation and growth of metal oxide structures. It can be observed that crystals are covering the surface of composite fibers. The crystalline nature of these surface crystals was verified by X-ray diffraction (XRD) analysis (not shown) indicating $Co_{1.5}Mn_{1.5}O_4$ tetragonal spinel phase. High-angle annular dark field - scanning transmission electron microscopy (HAADF-STEM) image (Figure 2a) exhibits cross-sections of composite fibers.

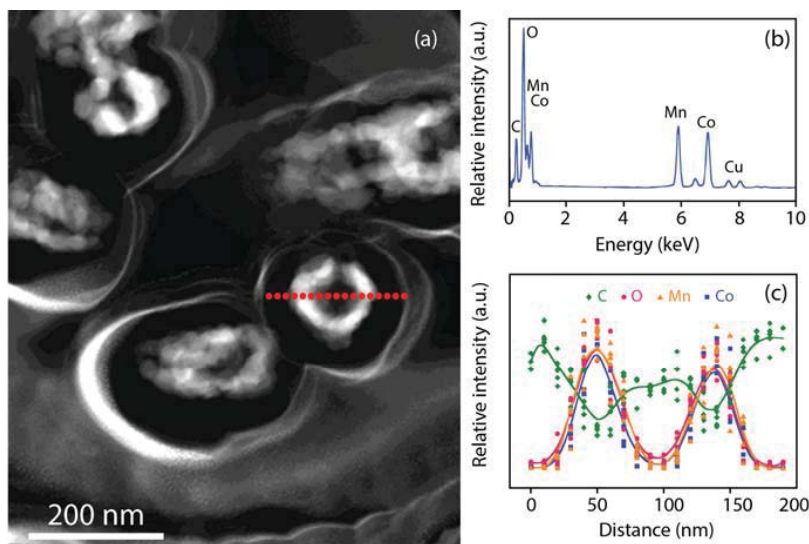


Figure 2. (a): HAADF-STEM image with (b) corresponding EDS spectrum and (c) line scan profile of cross-sectional lift-out composite fibers (denoted with red dotted line)

The chemical analysis by the energy dispersive X-ray spectroscopy (EDS) shows signals of C, Co, Mn and O (Figure 2b). The line profile scan (Figure 2c) was used to analyze the distribution of elements through the fiber cross section (noted by red line in Figure 2a). It can be seen that carbon occupies inner space inside spinel rings. In detail, the area of high carbon intensity (*i.e.* concentration) in the range 75-125 nm corresponds to the carbon fiber in composite material, while areas in the ranges 0-30 nm and 160-200 nm present space outside of the composite fiber cross-section. Here, carbon has been added by electron beam deposition in the focused ion beam (FIB) - SEM for sample protection purposes. These areas are in good agreement with low intensity (*i.e.* concentration) of Co, Mn and O.

The capacitive properties were investigated by cyclic voltammetry (CV) and galvanostatic charge/discharge (GCD) experiments. Electrodes were prepared in the form of thin-layers deposited on the surface of glassy carbon (GC) current collector. The measurements were performed in three-electrode (3E) configuration with a Pt-mesh and a saturated calomel electrode (SCE) as the counter and reference electrode, respectively. The specific capacity values (Q_s , mAh g⁻¹) were calculated from discharge curves by using the following equation:

$$Q_s = \frac{l_{dis} t_{dis}}{3.6m}$$

where I_{dis} (A) is the discharge current, t_{dis} (s) is the discharge time and m is the active mass of electrode materials. In order to compare electrochemical performances, neat carbon fibers are prepared following the experimental procedure.

The nearly rectangular shape of CVs and linear voltage profile during charging/discharging (Figure 3a,b) indicate typical response for EDL capacitors. The decrease of the sweep rates caused the specific capacity increase, since at high sweep rates, the accessibility of internal surface is limited to the electrolyte ions. On the other hand, the specific capacity increase at low rate was more pronounced for composite electrode due to the distinct capacitive behaviour. The presence of redox peaks (Figure 3c) indicates simultaneous contribution of pseudocapacitance and EDL capacity. Impressively, it delivers a specific capacity of about 740 mAh g^{-1} (Figure 3d), at a current density of 5 A g^{-1} in 3 M KOH, which is more than 37 times superior to neat carbon fibers. Moreover, after 1000 consecutive cycles, the composite retained 135% of its initial capacity (Figure 4).

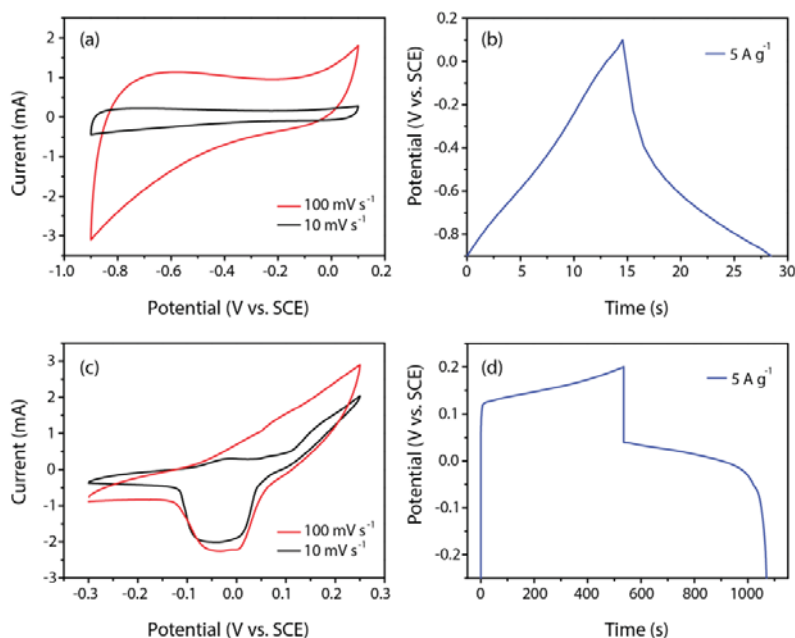


Figure 3: CV curves at different sweep rates and GCD profiles (current density: 5 A g^{-1}) for (a,b) neat carbon and (c,d) composite fibers, respectively

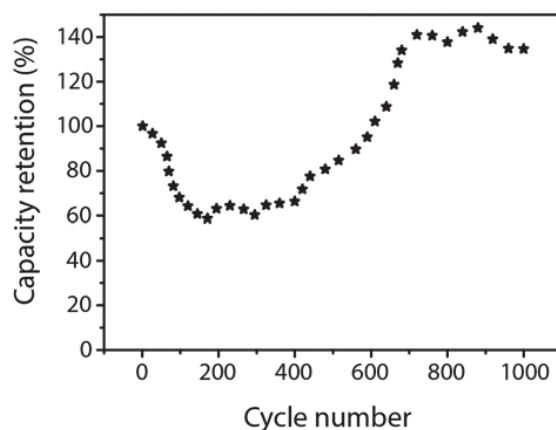


Figure 4: Cyclic performances of composite material (current density: 5 A g^{-1})

CONCLUSIONS

Carbon fibers decorated with spinel oxide $\text{Co}_{1.5}\text{Mn}_{1.5}\text{O}_4$ crystals have been fabricated by using electrospinning method and properly designed thermal treatment. Benefiting from the unique structure this composite electrode exhibit

ultrahigh specific capacity of 740 mAh g⁻¹ and excellent cycling stability of 135% at a current density of 5 A g⁻¹ in alkaline solution. The synergistic effect of conductive carbon fibers and redox active spinel oxide makes these composites attractive for high-performance electrodes for supercapacitors.

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