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Short communication

Flexible all-fiber electrospun supercapacitor

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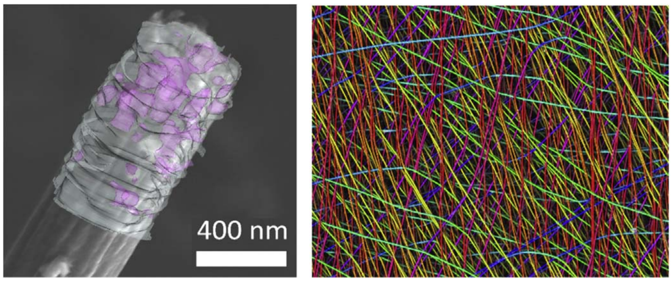
HIGHLIGHTS

- Electrospun all-fiber flexible supercapacitor with nanofiber electrodes/separator.
- Increased graphitic degree with the addition of MnACAC and thermal decomposition.
- Enhanced capacitive performance with the addition of MnO.
- Quantified nanofiber alignment and increased bias with MnO over undoped fibers.
- FIBSEM tomography of nanofibers showing MnO disitribution in carbon nanofibers.

GRAPHICAL ABSTRACT



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ABSTRACT

We present an all-fiber flexible supercapacitor with composite nanofiber electrodes made via electrospinning and an electrospun separator. With the addition of manganese acetylacetonate (MnACAC) to polyacrylonitrile (PAN) as a precursor for the electrospinning process and subsequent heat treatment, the performance of pure PAN supercapacitors was improved from 90 $F\,g^{-1}$ to 200 $F\,g^{-1}$ (2.5 $mV\,s^{-1}$) with possible mass loadings of MnACAC demonstrated as high as 40 wt%. X-ray diffraction measurements showed that after thermal treatment, the MnACAC was converted to MnO, meanwile, the thermal decomposition of MnACAC increased the graphitic degree of the carbonised PAN. Scanning electron microscopy and image processing showed that static electrospinning of pure PAN and PAN-Mn resulted in fiber diameters of 460 nm and 480 nm respectively after carbonisation. Further analysis showed that the fiber orientation exhibited a slight bias which was amplified with the addition of MnACAC. Use of focused ion beam scanning electron microscopy tomography also showed that MnO particles were evenly distributed through the fiber at low MnACAC concentrations, while at a 40 wt% loading the MnO particles were also visible on the surface. Comparison of the electrospun separators showed improved performance relative to a commercial Celgard separator (200 $F\,g^{-1}$ vs 141 $F\,g^{-1}$).

1. Introduction

Electrochemical capacitors, or supercapacitors, are energy storage devices which possess high power densities and lifetimes, relative to lithium-ion batteries, due to the low resistance associated with their non-faradaic charge storage mechanism [1,2]. They are currently used in a range of applications requiring high power, for instance as a complimentary energy storage device to reduce detrimental load

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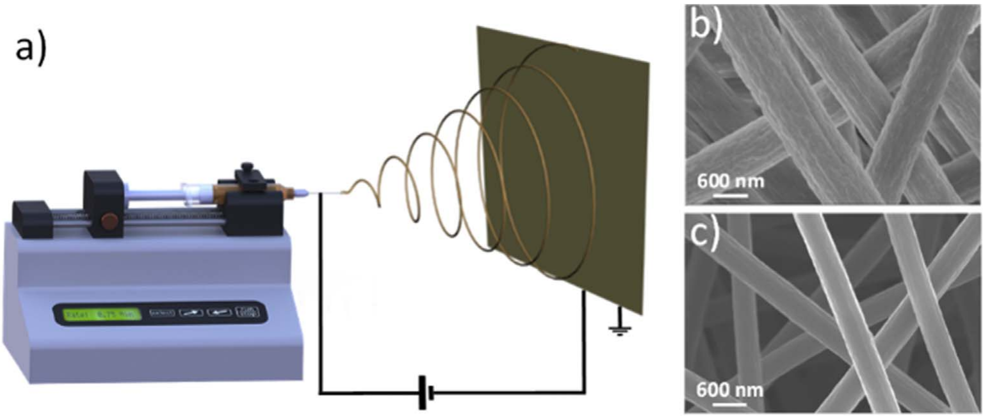

Fig. 1. a) Schematic illustration of the preparation of carbon nanofiber films by electrospinning, b) SEM image of PAN-20 wt% MnACAC before carbonisation, c) SEM image of PAN-20 wt % MnACAC after carbonisation.

cycling in automotive fuel cell systems which can cause catastrophic failure [3,4]. Furthermore, the mechanical properties of these devices are increasingly important when considering their application as structural components in vehicle applications or as flexible energy storage devices for wearable electronics [5–7].

Commercially available electrochemical double layer capacitors (EDLCs) generally use activated carbons as electrode materials with specific surface areas in the range 500–3000 m^2g^{-1} [8]. These store electrical energy through the formation of a charge double layer, which forms at the electrode-electrolyte interface. In EDLCs specific capacitance is generally limited by active electrode surface area and activity of the material, while rate capability is controlled by the electrical conductivity and the mass transport properties of the electrodes [9].

Alongside conventional activated carbons, many other carbonaceous materials have been extensively studied for use in EDLCs, such as carbon nanotubes, carbon nanofibers (CNFs), graphene, carbon aerogels and carbon spheres [6,10–15]. CNFs have been extensively studied for use in EDLCs due to their high specific surface area, low cost precursors, simple synthesis and flexible nature [16–18].

Electrospinning has been widely studied in recent years as a low cost, scalable and simple manufacturing technique for creating CNFs, and by changing the spinneret design, collection method, spinning conditions and precursor, the nanofiber structure can be controlled [19,20]. Multiple strategies for enhancing the performance of electrospun CNF electrodes have been studied, for example using hollow or highly porous nanofibers to gain to improved electrochemical performance [18,21,22].

Polyacrylonitrile (PAN) is commonly used as a precursor polymer for electrospinning CNFs as it is easily electrospun and carbonised with reported performance for PAN based supercapacitors ranging from 100 to 250 $F\,g^{-1}$ [8,23]. Improved specific capacitance can be achieved by using modified precursors [24,25], activation with steam [26], CO_2 [27] or via acidic surface treatments [28]. Specific capacitances as high as 432 $F\,g^{-1}$ (2 $mV\,s^{-1}$ scan rate) are reported using surface modification of oxygen plasma to improve electrolyte wetting [29].

The separator has also been identified as a key component which dictates the performance of a supercapacitor, as high ionic resistance will limit performance [30]. However, relatively little work on separators for supercapacitors is available. In order to develop high power density supercapacitors, it is important to have a separator with high porosity, low through-plane tortuosity factor and reduced thickness so as to minimise ionic diffusion resistance [31,32]. Electrospun PAN fibers have been shown in lithium-ion batteries to exhibit higher porosities compared to conventional separator membranes, increased wettability, improved rate capabilities and lower diffusion resistances [33–35]. These properties may lead to improved supercapacitor performance, however electrospun PAN fiber membranes have not been extensively explored as supercapacitor separator membranes [36]. The importance of microstructure is also frequently highlighted, yet detailed analysis and quantification of the relationship between structure and process parameters is seldom reported. Further research efforts are currently focusing on methods of increasing the specific capacitance of electrospun CNF electrodes through the addition of electro-active materials. Thus, there is an emergent need to understand how different dopant materials can improve the electrochemical properties of electrospun electrodes and link processing parameters with electrode microstructure and performance.

In this work we present a novel all-fiber supercapacitor using carbonised PAN-derived electrospun films for electrodes and PAN-nanofiber as the separator. A high mass loading of up to 40 wt% Manganese acetylacetonate (MnACAC) was incorporated into the electrospinning precursor solution which enhanced the electroactive properties of the PAN though a pseudocapacitive mechanism; dramatically increasing the electrochemical performance over undoped CNF electrodes. To date, there have been no reports of the use of MnACAC as a precursor for electrospun supercapacitor electrodes. The resultant symmetric, all-fiber devices can be produced as thin and free standing films which are flexible and retain good performance over a wide bending range.

2. Experimental section

2.1. Preparation of fiber electrodes

The electrospinning precursor was prepared by dissolving 0.3 g of PAN powder (Goodfellow Cambridge Limited Huntingdon, mean particle size 50 μm, mean molecular weight 230,000 $g\,mol^{-1}$) in 3 ml dimethylformamide (DMF, VWR chemicals, 99.90%). To prepare the electrodes, MnACAC powder (Merck Schuchardt OHG, ≥98%) was added in ratios ranging from 5 to 40 wt% relative to PAN and mixed for 12 h at 50 °C. For electrospinning, the as-prepared precursor solution was filled into a syringe and driven into the electrospinning needle (13 mm length, flat-tipped, 0.41 mm inside diameter, 0.71 mm outside diameter) by a syringe pump (Graesby 3300). The needle was held at 10 kV using a high voltage power supply (GenVolt 73,030) a distance of 17.5 cm from the grounded collector plate, which was a 20 × 20 cm polished aluminium plate. The set-up is shown in Fig. 1a. Fibers were collected after 1 h of spinning (25 °C, 50% of humidity).

The collected nanofiber films were then removed from the collector plate, cut and pre-carbonised at 290 °C in air (initial ramp rate 10 $°C.min^{-1}$, dwell time of 8 h at 80 °C, ramp rate of 5 $°C\ min^{-1}$ to 290 °C, dwell time 2 h). The films were then fully carbonised at 850 °C in N_2 (initial ramp rate 5 $°C\ min^{-1}$, dwell time of 2 h at 550 °C, ramp rate of 2 $°C\ min^{-1}$ to 850 °C, dwell time 2 h).

After carbonisation, electrodes with a diameter of 16 mm were cut