Short communication

Flexible all-fiber electrospun supercapacitor

Xinhua Liu, Max Naylor Marlow, Samuel J. Cooper, Bowen Song, Xiaolong Chen, Nigel P. Brandon, Billy Wu

Dyson School of Design Engineering, Imperial College London, United Kingdom
Earth Science and Engineering, Imperial College London, United Kingdom

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 distribution in carbon nanofibers.

GRAPHICAL ABSTRACT

ARTICLE INFO

Keywords:
Electrospinning
Supercapacitor
Nanofiber
Manganese oxide
Separator

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, meanwhile, 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 carbo-nisation. 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
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$^2$g$^{-1}$ [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 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 Fg$^{-1}$ [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 Fg$^{-1}$ (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 Huntington, 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.

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.
from the resultant fiber mat using a hole punch and weighed. Separator membranes with a diameter of 22 mm were directly cut from the PAN mat. The mass of the single fiber electrode film was 1.0 ± 0.1 mg, while the mass of the separator is 0.3 mg.

2.2. Imaging and materials analysis

Scanning electron microscopy (SEM) was carried out using a LEO Gemini 1525 (Zeiss) operated at 5 kV. All the imaged samples were coated with a 10 nm layer of Chromium. Focussed ion beam SEM (FIB-SEM) tomography (Auriga Cross Beam, Zeiss) was carried out to examine fiber subsurface microstructure. The fibers were impregnated with a low viscosity epoxy resin under vacuum and milled with 1 nA milling current. Avizo 9.0.0 (Visualization 13 Science Group) was used for images segmentation and 3D microstructural reconstruction. Energy-dispersive X-ray spectroscopy (EDS) was carried out on a Phenom ProX (Phenom) at 15 kV. X-ray diffraction (XRD) analysis was carried out using a PANalytical X’Pert (PANalytical) instrument, and the data analysis was carried out with Jade 6.5.

2.3. Preparation of all-fiber supercapacitors

The all-fiber supercapacitors were tested in a split flat cell (MTI Corporation) and were assembled by stacking pre-cut fiber mats in the cell. Carbonised nanofiber electrodes were used with a PAN nanofiber separator and 16 mm diameter grafoil current collector. The electrolyte was 0.25 M aqueous bis(trifluoromethane)sulfonimide lithium (LiTFSI, Sigma Aldrich, purity ≥ 99.0%).

To test the electrochemical performance of the all-fiber supercapacitor while flexing, pouch cells were produced using 20 × 20 mm electrodes and an aluminum foil current collector. The separator and electrolyte were as above. The conductivities were measured using a Solartron 1260 frequency response analyser over the frequency range 10 Hz to 2 MHz [34–36]. The cyclic voltammetry, impedance measurements and chronopotentiometry were carried out using a Metrohm Autolab PGSTA302 N potentiostat-galvanostat (Metrohm).

3. Results and discussion

The electrospinning synthesis strategy for Mn@CNF composites coupled with post annealing is schematically depicted in Fig. 1. In a typical procedure, the polymeric nanofibers containing MnACAC and PAN were first electrospun from the precursor and then pre-carbonised at 290 °C in air. As seen in Fig. 1b, the PAN with 20 wt% MnACAC precursor forms continuous nanofibers. The PAN nanofiber film with 20 wt% MnACAC is then oxidized in air to form MnO nanoparticles embedded in the nanofibers. Meanwhile, the manganese salt is decomposed and further reduced to MnO nanoparticles during carbonisation in an inert N2 atmosphere at a high temperature of 850 °C. Fig. 1c shows the SEM images of the PAN nanofiber film with 20 wt% MnACAC after carbonisation (20 Mn@CNF) with reduced diameter due to shrinkage during the heat treatment. Since static electrospinning was used, where the ground collector plate is stationary, fibers with a random orientation were expected.

Fig. 2a shows an SEM image of pure PAN fibers, colourised to highlight orientation using the Orientation plugin for ImageJ [37] and Fig. 2b shows a normalised comparison between the distribution of fiber orientations between the two fiber compositions. It can be seen that pure PAN fibers have a slight bias in fiber orientation, which is amplified when MnACAC is added and is potentially due to the influence of gravity. Fig. 2c shows a bar chart of fiber diameters for each of the production stages. These diameters were measured based on SEM data using ImageJ. The error bars represent the standard deviation of each sample of 20 measurements. Approximately 30% shrinkage is seen during the annealing for both fiber compositions. Fig. 2d is an SEM image of 40 Mn@CNF to highlight the presents of MnO nanoparticles on the surface of the fibers after carbonisation. The precursors can form nanofiber films with a wide concentration range of MnACAC from 0 wt% to a high value of 40 wt%. At a lower concentration, the final MnO nanoparticles are contained within the fibers, however when the addition of MnACAC reaches high values of 40 wt%, the MnO nanoparticles can be found both inside and outside of the nanofibers (Fig. 2d).

Free standing films can also be produced from these samples. As shown in Fig. 2e, the PAN-20 wt% MnACAC film retains its mechanical integrity after pre-carbonisation. Moreover, as can be seen from Fig. 2f, the post-carbonised 20 Mn@CNF film has good mechanical integrity and can be easily wound around a glass rod, indicating the possible application for flexible energy devices.

XRD was used for the characterisation of polycrystalline materials and the average crystal parameters can be obtained from the diffraction patterns. Fig. 3a shows the XRD patterns of the pure PAN based carbon nanofiber (PAN-CNF) and PAN based carbon nanofiber with 40 wt% MnACAC (40 Mn@CNF). All the strong diffraction peaks in the XRD pattern could be readily indexed as a pure cubic phase {space group: Fm3m (225)} of MnO (PDF-# 78-0424). As shown in Fig. 3b and c, the XRD patterns of PAN-CNF and 40 Mn@CNF show a broadened diffraction peak at 20 ∼ 25°, which correspond to the (002) diffraction peak of a low graphitization degree carbon. According to the diffraction peaks of both samples, they have a mixed polycrystalline structure of graphitic and disordered domains. Therefore, the approximate structural information of both samples can be estimated by analysis of diffraction patterns. The XRD patterns can be analysed by data fitting to distinguish different regions in the broadened (002) diffraction peak, indicating the different crystal regions in PAN-CNF and 40 Mn@CNF. The interlayer distances (D002) are calculated from the (002) main peaks and their individual fitted graphitic region and disordered region.

For the XRD data of disordered carbons, the use of the Scherrer equation is the classical way to estimate the size of the crystallites. The Scherrer Equation is $D_{\text{Scherrer}} = \frac{0.9 \lambda}{β \cos θ}$, where $D_{\text{Scherrer}}$ is the crystallite size in angstroms, $λ$ is the wavelength of the X-rays, $β$ is the width (full-width at half-maximum) of the X-ray diffraction peak in radians and $θ$ is the Bragg angle [38,39].

Structural information according to the main and fitted peaks is listed in Table 1. Although unknown peaks at 20 ∼ 28.51° are attributed to the PAN carbon source, which cannot be fitted to the data profile, the graphitic region and disordered region give the necessary structural information. The d002 peak of 40 Mn@CNF is higher than that of PAN-CNF. 40 Mn@CNF shows a graphitic proportion of 52.87%. It is worth noting that a clear trend of increasing graphitic degree was seen with higher concentration Mn@CNF samples, with a more graphitic and less disordered structure found, leading to higher electrical conductivity of the carbon phase. Although MnO is less conductive, the Mn@CNF samples maintain a relatively good conductivity.

Fig. 3d shows a reconstruction of a FIB-SEM serial sectioning image sequence of a single fiber. The internal MnO particles are highlighted in purple and show some degree of agglomeration within the fiber. However, at this weight percent of MnO, the carbon phase was observed to be well percolated, suggesting the electrical conductivity would not to be significantly affected, which is critical for maintaining performance.

The all-fiber supercapacitor was assembled using two fiber Mn@CNF electrodes and one fiber separator. The layered structure of the all-fiber supercapacitor is shown in Fig. 3e with further EDX elemental mapping and the elements of C, Mn and O were clearly detected in the electrode layers.

Fig. 4a shows the cyclic voltammetry (CV) curves of the 10 Mn@CNF based all-fiber supercapacitor at different scan rates, indicating good capacitive performance. Comparison of specific capacitance (Csp) at various scan rates with various MnO loadings is shown in

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Fig. 4b. Fig. 4c presents their Csp values at the scan rate of 2.5 mV s\(^{-1}\). As can be seen in Fig. 4c, the composite Mn@CNF based all-fiber devices can achieve a higher capacitive value than pure PAN-CNF, which reaches 90 F g\(^{-1}\) at a scan rate of 2.5 mV s\(^{-1}\). The 10 Mn@CNF shows the highest Csp value of 200 F g\(^{-1}\), and the 5 Mn@CNF also achieves a high value of 182 F g\(^{-1}\). A similar trend of capacitive performance at various current densities can be found in Fig. S1. The highest Csp value of 196 F g\(^{-1}\) is achieved at a current density of 0.1 A g\(^{-1}\) for 10 Mn@CNF device while the 5 Mn@CNF based device also achieves a high value of 185 F g\(^{-1}\) at 0.1 A g\(^{-1}\). 10 Mn@CNF achieves a value of 163 F g\(^{-1}\) and 5 Mn@CNF has 144 F g\(^{-1}\) at 0.25 A g\(^{-1}\). The pure PAN-CNF based all-fiber supercapacitor shows a limited capacitive value of 60 F g\(^{-1}\) at 0.25 A g\(^{-1}\). The similar enhancements with the addition of MnO can also be found in their areal and volumetric capacitances which were shown in Fig. S2.

The cycling performance of 10Mn@CNF based all-fiber supercapacitor and commercial Celgard (3501) based device are shown in Fig. S3 which exhibits good performance after 10,000 cycles. Compared to the PAN based electrodes, the enhanced capacitive performances of Mn@CNF electrodes can be attributed to the additional manganese...
oxides present. The increased capacitances of Mn@CNF electrodes with various concentrations further supports this assumption. However, as shown in Fig. 4d, the impedance Nyquist plots of the PAN-CNF, 10 Mn@CNF and 30 Mn@CNF based supercapacitors show increased resistance. The observed increased charge transfer resistance is attributed to the increasing pseudocapacitive behaviour of the MnO. The XRD measurements also suggest the Mn salts can improve the graphitic degree of the heat-treated CNFs, however the conductivities of the Mn@CNF (Fig. 4e) decreases with the increase of added Mn salts due to the poor electrical conductivity of MnO [40–42].

Comparison of the all-fiber cell with a commercial Celgard separator (Celgard 3501) based supercapacitor with the same symmetric 10 Mn@CNF fiber electrodes is presented in Fig. 5a. Here, a lower $C_{sp}$ value of 141 F g$^{-1}$ at 2.5 mV s$^{-1}$ and 193 F g$^{-1}$ at 0.1 A g$^{-1}$ can be obtained according to both CV and charge-discharge cycling, highlighting the potential of electrospun separators for supercapacitor applications. Most interestingly, the flexible free standing electrode film can be used to assemble a flexible pouch cell. The dynamic CV curves of the pouch cell with bending angle from 0° to 180° is shown in Fig. 4f. The dynamic CV curves are relatively stable during the bending process and indicate the potential of the CNF electrodes as flexible devices.

4. Conclusions

It has been shown that through the addition of MnACAC, the electrochemical performance of PAN-based supercapacitors fabricated using electrospinning can be improved from 90 F g$^{-1}$ to 200 F g$^{-1}$ (2.5 mV s$^{-1}$) via additional pseudocapacitive charge storage. XRD measurements have shown that through the heat treatment of the electrodes, the MnACAC decomposes into MnO and that the Mn salt increases the graphitic degree of the carbon. It was also shown that mass loadings as high as 40 wt% could be achieved. SEM imaging and image analysis showed that static electrospinning of pure PAN fibers resulted in a slight alignment bias which was amplified by the addition of the MnACAC. This may be due to the effect of gravity acting on the denser manganese salt in the fibers. Fiber analysis showed an average diameter of 500 nm for pure PAN which decreased to 460 nm after carbonisation. A similar shrinkage was observed in the PAN-Mn samples which showed a reduction in diameter from 720 nm to 480 nm. FIB-SEM tomography showed that lower mass loading resulted in unpercelated MnO particles being embedded into the fiber, whilst at high loadings MnO particles were also found on the surface of the fibers. Whilst the addition of MnACAC allowed for an increase in pseudocapacitive behaviour and therefore an increase in the capacitance relative to pure PAN, 4-point conductivity measurements showed a decrease in electrical conductivity due to the lower conductivity of MnO and EIS showed an increase in charge transfer resistance due to the increased pseudocapacitive behaviour. Thus, the best performing mass loading in this study was found to be 10 wt% MnACAC.

Comparison of the as spun PAN separators and a commercial Celgard 3501 showed that the PAN separator provided superior performance (200 F g$^{-1}$ vs 141 F g$^{-1}$). Furthermore, the concept of the all-fiber supercapacitor was also successfully demonstrated. The all-fiber nature of the supercapacitors allows for flexible operation opening up new possibilities for the design of free standing electrodes and separators for all-fiber flexible energy storage devices.

Fig. 4. a) The CV curves of the 10 Mn@CNF based all-fiber supercapacitor at different scan rates, b) Specific capacitance of the all-fiber supercapacitors as a function of scan rate for CNF with different MnACAC concentrations, c) Specific capacitances of the all-fiber supercapacitors with different MnACAC concentrations at 2.5 mV s$^{-1}$, d) Impedance Nyquist plots of the PAN-CNF, 10 Mn@CNF and 30 Mn@CNF based supercapacitors, e) the conductivity of the electrode films with different MnACAC concentrations, f) the dynamic CV curves and the maintained capacitances of the pouch cell with bending angle from 0°, 45°, 90°, 135° and 180°.
