Activated carbon fibers with manganese dioxide coating for flexible fiber supercapacitors with high capacitive performance

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A B S T R A C T
Fiber supercapacitor (FSC) is a promising power source for wearable/stretchable electronics and high capacitive performance of FSCs is highly desirable for practice flexible applications. Here, we report a composite of manganese dioxide (MnO₂) and activated carbon fibers (ACFs) with high MnO₂ mass loading and microporous structure (abbreviated as MnO₂@ACF), which is used as a fiber electrode to produce a FSC with a high capacitive performance and a good flexibility. The MnO₂@ACF composite electrode in FSC delivers an ultrahigh specific capacitance of 410 mF/cm² at 0.1 mA/cm², corresponding to a high energy density of 36 μWh/cm² and high power density of 726 μW/cm². Such high capacitive performance and simple fabrication method indicates that the MnO₂@ACF composite is a very promising electrode material for flexible fiber supercapacitors.

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1. Introduction
Wearable smart clothes and miniaturized electronics are among the key topics for rapidly developing flexible energy storage devices [1–6], especially for high-energy density flexible energy storage devices [7]. Recent years have seen many smart supercapacitor configurations, such as shape-memory supercapacitors [8,9], ring-type supercapacitors [10], highly stretchable fiber-shaped supercapacitors [11,12], meters-long wire-supercapacitors [13]. Among them, fiber supercapacitors (FSCs) are regarded as the most promising power sources for the manufacture of next-generation intelligent fabrics [14–21]. For this purpose, fiber-structured electrodes are usually constructed with electrochemically active materials and fibrous supports [22–27]. One common approach is to coat redox-active materials onto carbonaceous materials that combine pseudocapacitance and electric double layer capacitance to achieve a high specific capacitance and energy density. Typical examples are polyaniline (PANI) coated carbon nanotube (CNT) fibers [28], MnO₂ coated CNT fibers [29], and PEDOT:PSS combined with graphene fibers [30]. However, these FSCs suffer from complicated fabrication methods, complex structures, rigidity or relatively poor flexibility, and low capacitance, which restrict their scalability for practical applications. The need to construct a FSC with high energy density and good flexibility is therefore quite important.

MnO₂ has been extensively studied and is regarded as one of the most promising pseudocapacitive materials for supercapacitors due to its high theoretical capacitance (1370 F g⁻¹), environmental friendliness and low cost [31–34]. Depositing MnO₂ onto carbonaceous materials by KMnO₄ partial etching is a simple and effective method of preparing composite electrode materials [35,36]. Our group has extended this approach to prepare a high performance nanoporous MnO₂ pseudocapacitive material for supercapacitors by replicating a 3D network of graphene oxide hydrogel, which is used as a reactive template to entirely react with KMnO₄ for a thin-layered graphene structure [37]. Compared with other flexible carbonaceous substrates, fibrous porous carbons, namely activated carbon fibers (ACFs), hold great promise with respect to loading active materials because of their large specific surface area, abundant pore structure and highly reactive surface. Recently, ACF has been chosen as the body material for the production of ACFs/MnO₂/CNTs composite textile and fiber electrodes for aqueous supercapacitors [38]. However, no further attempts have been made to demonstrate their possibility in solid-state FSCs.

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Here, the capability and potential of ACFs in FSC with gel electrolyte have been investigated, and the results show that ACFs have great advantage as fibrous substrates to fabricate composite electrodes with a high MnO$_2$ mass loading for high capacitive FSCs. As a multifunctional carbon substrate, the ACFs serve as fibrous substrate, active material and sacrificial reductant reactive carbon to load MnO$_2$ nanoparticles at the same time. The resultant MnO$_2$@ACF composite electrode in FSCS exhibits an ultrahigh specific capacitance of 410 mF/cm$^2$ at 0.1 mA/cm$^2$, which is greatly higher than previously reported results of solid-state fiber supercapacitor [39–47]. Using the ACFs is therefore a promising way to construct high performance fiber electrode for flexible energy storage in a large scale.

2. Experimental

2.1. Fabrication of MnO$_2$@ACF electrodes

A bunch of ACFs were respectively rinsed with acetone and ethanol in an ultrasonic bath for 30 min and then washed in a large quantity of deionized (DI) water. For the deposition of MnO$_2$, they were immersed in the reaction solution of 0.1 M KMnO$_4$ and 1 M Na$_2$SO$_4$ with equal volumes for several hours at room temperature. Finally, the obtained MnO$_2$@ACF composites were rinsed several times in DI water and dried at 70 °C. The as-prepared composites with different reaction times were designated MnO$_2$@ACF-x (where x stands for the reaction time in hours). For reference, CFs were used as substrates to composite with MnO$_2$ using the same approach.

2.2. Fabrication of solid-state FSCs

The solid-state FSCs were fabricated by the assembly of two same fiber electrodes in parallel with a carboxymethyl cellulose sodium (CMC)/Na$_2$SO$_4$ gel electrolyte coated homogeneously on the fibers. The CMC/Na$_2$SO$_4$ gel electrolyte was prepared by using the similar method reported in the literature [48]. Briefly, 3 g CMC and 6 g Na$_2$SO$_4$ were added to 100 mL DI water at 80 °C with 3 h of vigorous stirring until the solution became clear. The fiber electrodes were dipped into the CMC/Na$_2$SO$_4$ electrolyte first for at least one hour to ensure that the electrodes were fully infiltrated. The CMC/Na$_2$SO$_4$ gel was then coated onto the pre-soaked fibers and was solidified by evaporation of the extra solvent in ambient condition for several hours. Finally, two parallel fiber electrodes were mounted onto a flexible polyester (PET) substrate without any binder, current collector, separator or packaging material to obtain a solid-state FSC for measurement.

2.3. Materials charaterizations

The surface morphologies of samples were examined by scanning electron microscopy (SEM) (Hitachi S4800, Japan) with an accelerating voltage of 5.0 kV. TEM observations were performed on a JEM 3100F (JEOL, Japan) operated at 200 kV. X-ray diffraction (XRD) measurements were conducted on a Bruker D-8 (Cu Kα radiation, λ = 0.154056 nm) at room temperature and the data was collected from 10° to 80° with a scan rate of 10°/min. Thermogravimetric analysis (TGA) was performed on a TG 8120 (Rigaku, Japan) by heating the samples to 800 °C at 10 °C min$^{-1}$ in the atmosphere of air. X-ray photoelectron spectroscopy (XPS) analysis was conducted with an ESCALAB 250 XI System (Thermo Fisher Scientific, USA) to characterize the chemical state of the samples. Raman spectra were recorded using a multi-wavelength micro-Raman spectroscope (JY HR800) with 532.05 nm incident radiation and a 50× aperture. Nitrogen adsorption–desorption isotherms (77 K) were measured by a BelSorp-Mini instrument (BEL Inc., Japan). The samples were heated at 200 °C under vacuum to remove all the adsorbed species before the nitrogen adsorption measurement. Specific surface area and pore size distributions were obtained from the adsorption isotherm by the Brunauer–Emmett–Teller (BET) and density functional theory (DFT) methods, respectively.

2.4. Electrochemical measurements

The electrochemical performance of fiber electrodes was first investigated in a three-electrode aqueous system (1 M Na$_2$SO$_4$) where a saturated calomel electrode (SCE) and a Pt electrode (1 cm × 1 cm) were used as reference and counter electrodes, respectively. All the electrochemical tests of fiber electrodes and as-prepared fiber supercapacitor were performed on the Eco Chemie Autolab 128N (Metrohm, Switzerland) electrochemical workstation at room temperature. Electrochemical impedance spectroscopy (EIS) was measured in a frequency range between 10$^2$ and 10$^{-2}$ Hz with a voltage amplitude of 5 mV at open-circuit potential.

The specific capacitance of a single electrode in the three-electrode configuration was calculated from the charge–discharge curves using the following formula:

$$C_s = I × \Delta t/(S × ΔV) \tag{1}$$

Where, I (A), Δt (s) and ΔV (V) are the discharge current, discharge time and the potential window, respectively. S could represent surface area (A) or effective length (L) of fiber electrode for the determination of areal specific capacitance (C_A) and length specific capacitance (C_L), respectively.

The specific capacitance of a single electrode of a symmetric fiber supercapacitor was calculated from the charge–discharge curves by the following equation:

$$C = 2I × \Delta t/(S × ΔV) \tag{2}$$

Where, I (A), Δt (s) and ΔV (V) are the discharge current, discharge time and potential window of the solid-state fiber supercapacitor, respectively. S could be area (A) or effective length (L) of fiber electrode for the calculation of areal specific capacitance (C_A) and length specific capacitance (C_L), respectively. The area (A) of fiber electrode was calculated by:

$$A = L × \pi × d \tag{3}$$

Where, d (cm) is the diameter of fiber electrode, and L (cm) is the length of the fiber immersed into the electrolyte, respectively.

The specific energy density (E) and power density (P) of a single fiber electrode were calculated by:

$$E = C_s × ΔV^2/(2 × 3600) \tag{4}$$

$$P = E × 3600/Δt \tag{5}$$

Where, ΔV (V) is the potential window; Δt (s) is the discharge time; C_s (mF/cm$^2$) is the specific capacitance of the device; E (Wh/m$^2$) is the specific energy density and P (mW/cm$^2$) is the specific power density of a single fiber electrode.

3. Results and discussion

A bunch of ACFs were used as a fibrous substrate for loading with MnO$_2$ by immersing them in a KMnO$_4$ aqueous solution for several hours at room temperature, and the resulting composite fibers are denoted MnO$_2$@ACF-x (where x is the reaction time in hours). The following key redox reaction between KMnO$_4$ and carbon is responsible for the in-situ growth of MnO$_2$ on the carbon [30,32]:

$$4\text{MnO}_4^- + 3\text{C} + \text{H}_2\text{O} \rightarrow 4\text{MnO}_2 + \text{CO}_3^{2-} + 2\text{HCO}_3^- \tag{1}$$
SEM images show that ACFs are composed of thousands of microfibers with a diameter ~7 μm and that the ACF surface is smoothed after the reaction of six hours (Figs. 1(a), (b) and S1). The elemental distributions of C, Mn, O on the surface and inside the ACF, have been characterized by X-ray energy-dispersive spectroscopy (EDS). As shown in Fig. 1(c), the elemental maps of MnO₂@ACF-6 show a uniform distribution of MnO₂ on the surface of the ACF and its concentration decreases significantly towards the center of the fiber as shown in Fig. S2, demonstrating that the reaction between MnO₂ and carbon becomes more difficult inside the fiber. From the cross-sectional SEM observation of MnO₂@ACF-6 shown in Fig. 1(d) and (e), a smooth MnO₂ coating layer less than 100 nm thick is uniformly deposited on the surface of the ACF to form a core–shell structure with outer MnO₂ and inner ACF, while the fiber still shows great flexibility after compositing it with MnO₂ as shown in the bend test (Fig. 1(f)).

The nanostructure of the incorporated MnO₂ in the composite fibers was characterized by TEM. Fig. 2(a) shows MnO₂ with a clear lattice fringe spacing of about 0.35 nm, a typical value for (002) planes of δ-MnO₂. XRD results (Fig. 2(b)) also suggest the existence of δ-MnO₂ (JCPDS 80-1098), while the broader and weaker diffraction peaks indicate the nano-crystalline MnO₂. The chemical composition of MnO₂@ACF-6 was further probed by X-ray photo-electron spectroscopy (XPS). In the O 1s spectrum (Fig. 2(c)), peaks centered at 529.2 eV and 531.4 eV are attributed to the Mn–O–Mn bond for the tetravalent oxide and the Mn–OH bond for a hydrated trivalent oxide, while the peak centered at 532.5 eV is attributed to an H–O–H bond for residual adsorbed water [49]. Notably, the C=O bond at 531.6 eV and the C–O bond at 533.2 eV are from oxygen functional groups in the ACF (Fig. S3) [50]. The average oxidation state of manganese in MnO₂ in the composites is calculated to be 3.72 from the O 1s spectrum, which is in excellent agreement with the above results [51]. According to the Mn 2p XPS spectrum (Fig. 2(c) inset), Mn 2p₃/₂ and Mn 2p₁/₂ peaks are respectively located at 641.6 and 653.4 eV, with a spin-energy separation of 11.8 eV, further revealing the dominance of Mn⁴⁺ in the composite [52]. Nitrogen adsorption–desorption isotherms of ACF and MnO₂@ACF-x are presented in Figs. 2(f) and S4a and show a type I isotherm characteristic, indicating their microporous properties. It should be noted that the composite fibers have the similar pore size distribution as the parent fibers even after 24 h reaction, while the specific surface area of the composite fibers decreases with a longer reaction time (Fig. S4b and Table S1), indicating that the microporous structure of the parent fibers is preserved after the oxidation process with some micropores blocked by MnO₂ deposition.

For reference, we also deposited MnO₂ onto carbon fibers (CFs) and the composite materials obtained are abbreviated MnO₂@CF-x where x is the reaction time in hours. Similar MnO₂ nanoparticles were observed on the fiber surface after the same KMnO₄ reducing process when the CF used as the etched substrate (Figs. S5 and S6). The thermal behavior and the mass loading of MnO₂ in the composites were analyzed by the thermogravimetric analysis (TGA). Both the composite fibers have a lower thermal stability in air compared to the parent fibers as shown in TG curves (Figs. 3(a) and S7), which may result from the more active properties of carbon after the etching reaction and the catalytic effect of Mn species. The MnO₂ loading in the ACF is much higher than that in the CF under the same synthesis conditions, indicating the higher reactivity of ACF (Fig. 3(b)). Interestingly, the deposition rate of MnO₂ in ACF almost reaches a plateau after 9 h reaction, which is consistent with the changes in the MnO₂ layer thickness with reaction time (Fig. S8). These results demonstrate a self-limiting reaction between KMnO₄ aqueous solution and ACF carbon substrate, which means that the further etching reaction will terminate once no more KMnO₄ enter and MnO₂ mass loading and the thickness of MnO₂ layer will no longer be able to increase. This mainly because the structure of MnO₂ layer becomes relatively compact with an extension of reaction time to 9h or longer, and the compact MnO₂ layer will restrict the access of KMnO₄ to the inside of the ACF, which is apparently detrimental to the ion transport in the charge–discharge process as well. Thus the reaction time is important for the composite fiber preparation to control the structure of MnO₂ layer and get a better electrochemical performance. The Raman analyses in Fig. 3(c) show that the defect density in ACF is higher than CF indicated by the higher intensity ratio between the D and G peak, which may lead to a higher reactivity of ACF in KMnO₄ solution.

The electrochemical performance of the composite fiber electrodes was first investigated in a three-electrode aqueous system. The galvanostatic charge–discharge curves of CF, ACF and their composites at 0.25 mA/cm² and the calculated specific capacitances
Fig. 2. Structural characterizations of MnO$_2$-loaded ACF. (a) TEM image of MnO$_2$ in MnO$_2$@ACF-6. (b) XRD patterns of ACF and MnO$_2$@ACF-6. (c) O 1s XPS spectrum of MnO$_2$@ACF-6 (the inset is the corresponding Mn 2p spectrum). (d) Nitrogen adsorption–desorption isotherms of ACF and MnO$_2$@ACF-6.

Fig. 3. Structural characterizations and their MnO$_2$ mass loading of ACF and CF. (a) TGA curves of CF, ACF, MnO$_2$@ACF-6 and MnO$_2$@CF-6. (b) The relationship between the MnO$_2$ content in MnO$_2$@ACF and MnO$_2$@CF with reaction time. (c) Raman spectra of CF and ACF.

at various current densities are shown in Fig. S9. The MnO$_2$@ACF electrodes have a ~4 times higher specific capacitance than that of MnO$_2$@CF, which can be attributed to their characteristic porous structure and high MnO$_2$ mass loading. Notably, MnO$_2$@ACF prepared by 6h etching shows better electrochemical performance than other electrodes even with a higher MnO$_2$ mass loading.

Furthermore, flexible solid-state FSC was assembled by placing two symmetric composite electrodes parallel to each other and coating them with a CMC/Na$_2$SO$_4$ gel as both electrolyte and separator (Fig. 4(a)). Among all MnO$_2$@ACF composites, the MnO$_2$@ACF-6 electrode with a high MnO$_2$ mass loading of 31.2 wt% demonstrates a maximum specific areal capacitance up to 410 mF/cm$^2$ (converting to a length specific capacitance of 77 mF/cm) at 0.1 mA/cm$^2$ (Fig. 4(b)), corresponding to a high energy density of 36 μWh/cm$^2$ (or 7 μWh/cm) and a power density of 726 μW/cm$^2$ (or 136 μW/cm), which is among the highest value in previously reported work to the best of our knowledge (Table S2). The results further indicate that the reaction time has an important effect on the electrochemical performance of the composite fibers. In other words, there is a trade-off between the mass loading of MnO$_2$ and electrolyte ion transport channel in composite fibers to get an enhanced electrochemical performance. As shown in Figs. 4(c),
S10(a) and (b), the MnO$_2$@ACF electrode exhibits a much better capacitive performance than ACF and MnO$_2$@CF. The greatly enhanced capacitive performance is mainly attributed to a porous structure, a high specific surface area and a much higher MnO$_2$ mass loading of ACFs than that of CFs. In addition, an excellent cycling stability of MnO$_2$@ACF-6 (80.3% capacitance retention after 5000 cycles) was observed (Fig. S10c). The electrochemical performance under different mechanical deformations is also evaluated by a bend test. As shown in Fig. 4(d), the charge–discharge curves are almost coincident for a wide range of bending angles (0°–180°), illustrating the high flexibility of such devices. Moreover, the FSCs could be readily connected in parallel or in series to provide a higher current or voltage output. The voltage window of three FSCs connected in parallel was unchanged, but the discharge time was tripled (Fig. 4(e)). As shown in Fig. 4(f), three FSCs connected in series with voltage window of 2.4 V exhibit almost the same discharge time, which could be used to light a commercial red light-emitting diode (LED).

4. Conclusions

As a porous fibrous substrate, ACF was used to produce MnO$_2$ composite fiber with a high MnO$_2$ mass loading and a microporous structure for solid-state FSC. The composite fiber electrode has an excellent areal specific capacitance of up to 410 mF/cm$^2$ simultaneously with a good flexibility and stable cyclic performance, which is among the highest value reported to date for solid state FSCs. In addition, the integrated devices constructed by multiple FSC connected together in parallel and in series could power a LED, demonstrating their potential to meet the energy and power needs on various occasions. We believe that using ACF to construct composite fiber electrodes can be easily scaled up for low-cost flexible energy storage devices.

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Supplementary materials

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