

CARBON FIBRE MODIFICATIONS FOR COMPOSITE STRUCTURAL POWER DEVICES

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Abstract

This research project focuses on the development of new multifunctional composite materials, which allow energy storage functionality to be imbued upon low weight structural components. A crucial requirement for efficient structural energy storage composites is the development of structural carbon fibre electrode materials that possess high electrochemical surface area and stability whilst supporting high mechanical loads. In the present work, a variety of carbon fibre modifications were investigated, including chemical activation, carbon nanotube (CNT) sizing and CNT-grafting. The effects of these different modification methods on the fibre surface microstructure, electrochemical, and mechanical performance were studied and compared. In the most promising cases, up to a hundred-fold improvement in electrical storage capacity was achieved. Furthermore, single fibre tensile tests demonstrated that the intrinsically excellent mechanical properties of the carbon fibre were retained after the modifications.

1 Introduction

Since the 1960s, carbon fibre-reinforced polymer composite materials have made a huge impact, particularly in the aerospace and oil/gas industries, due to their light weight and excellent mechanical performance [1]. Recently, the interest in multifunctional composite materials is rapidly increased [2]. This research project is based on multifunctional development of new composite materials, which allows for full integration of the energy storage systems into the structural low weight components. Such composites could significantly reduce the weight and volume of traditional energy storage devices and simultaneously serve as the load-carrying structural body [3].

A crucial requirement for efficient structural energy storage devices is the development of structural carbon fibre electrode materials that possess high energy storage and stable electrochemical performance whilst under mechanical load. In the present work, a variety of carbon fibre modifications were investigated, such as chemical activation, carbon nanotube

(CNT) sizing, and CNT grafting onto carbon fibres. Effects of different modifications on the fibre surface microstructure, electrochemical, and mechanical properties were studied.

2 Materials and testing methods

2.1 Chemical activation of carbon fibres

HTA 3k plain weave (TISSA Glasweberei AG; 200 g/m²) and T300 3k 5-satin harness weave carbon fabrics (Advanced Composites Group; 283 g/m²) were soaked in KOH (VWR) solution for 3 h; the typical KOH loading was approximately 6.5 wt%, after drying. The KOH-loaded carbon fabrics were then transferred to the furnace (Lenton ECF 12/30), and activated at 800°C for 30 min under N₂, with a flow rate of 0.5 L/min. The reacted carbon fabrics were washed with purified water until neutral and dried in a vacuum oven. The typical burn-off was around 6%.

2.2 CNT modification of carbon fibres

Two routes of CNT modification of T300 carbon fabrics; CNT sizing and CNT grafting, were studied. CNT sizing was achieved by applying CNT aqueous dispersion (Aquacyl™ 3%, CNT diameter ~9 nm, Nanocyl) onto carbon fabrics, followed by a pyrolysis step under N₂ at 450°C. Around 45 wt% of CNT-sizing was obtained. To obtain CNT-grafting, direct growth of CNTs on catalyst-loaded carbon fabrics was carried out using chemical vapour deposition (CVD) method under a mixture of N₂/H₂/C₂H₄. The loading of grafted CNTs on fibres was in a range of 10-35 wt% by using different growth times.

2.3 Characterisation

SEM characterisation was carried out using a field emission gun SEM (Gemini LEO 1525 FEG-SEM, Carl Zeiss NTS GmbH), operating at 5 kV. Specific surface area and pore size of the activated carbon fabrics were further studied using a Micromeritics TriStar 3000 analyser (Micromeritics UK Ltd.) with pure N₂, based on the Brunauer, Emmet, Teller (BET) method. Electrochemical tests were performed on the carbon fabrics before and after the activation process at ambient temperature, using a three-electrode cell (platinum wire counter electrode, silver-silver chloride (Ag/AgCl) reference electrode and 3M KCl electrolyte solution (Sigma-Aldrich)). Cyclic voltammetry (CV) experiments were conducted between -0.1 and 0.1 V, at a scan rate of 5 mV/s, using a SI 1287 electrochemical interface (Solartron Instruments). Single fibre tensile tests were carried out at room temperature, according to the standard BS ISO 11566:1996 (1996) using a TST 350 tensile stress testing system (Linkam Scientific Instrument Ltd.), equipped with a 20 N load cell. The gauge length was 25 mm. A crosshead speed of 15 µm/s was used for the tests and a minimum of 20 measurements were conducted for each fibre configuration.

3 Results and Discussion

3.1 Chemical activation of carbon fibres

Chemical activation is an effective way for preparing non-structural activated carbon materials, offering advantages of higher carbon yield (i.e. less burn-off), reduced surface damage and a controlled pore size distribution [4]. During high temperature reactions, the activating agent, KOH, reacts with carbon, developing porosity. As shown in Figure 1, the as-received fibres showed clear crenulations on the surface, which were formed during the production process. After chemical activation, most of the crenulations were etched away and

the fibre diameter had decreased from 7 to 6.9 μm . Moreover, the fibre surface became noticeably rougher, as a result of the porosity development during the activation process. A significant increase (around 100-fold) in the BET surface area was observed for the activated carbon fabrics, from 0.21 to 21.39 m^2/g . This increase can be attributed to the change of surface roughness and the formation of pore structure, with an average pore size around 2.5 nm. As expected, the specific capacitance of carbon fabric significantly improved after the activation, from 0.06 to 2.63 F/g, which was consistent with the increase of surface area and porosity.

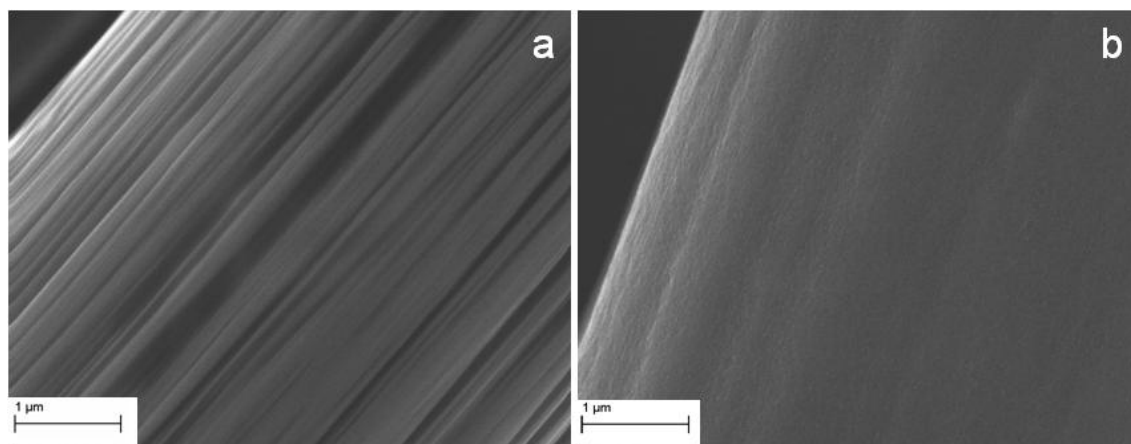


Figure 1. SEM images of (a) as-received and (b) activated carbon fibres.

It is known that the tensile strength of carbon fibres can be increased by modifying or removing the surface flaws by oxidative etching treatments, but extensive oxidation can cause significant reductions in the strength [5]. In the present case, the fibre tensile strength was observed to increase by around 20%, after the activation process (Table 1); the result can be attributed to the removal of surface defects by using a relatively small loading of activating agent. The tensile modulus of the activated carbon fibres was maintained.

	As-received	Activated
Diameter (μm)	7.0	6.9
BET surface area (m^2/g)	0.21	21.39
Capacitance (F/g)	0.06 (0.01)	2.63 (0.09)
Tensile strength (MPa)	3290 (90)	3960 (130)
Tensile modulus (GPa)	204 (4)	207 (4)

Table 1. Comparison of Properties of HTA Carbon Fibres before and after the Chemical Activation. The Standard Errors are Shown in the Brackets where Significant.

3.2 CNT modification

CNTs are considered as an ideal candidate for nanoscale reinforcement of composites due to their excellent properties and interest has rapidly expanded in introducing CNTs into conventional carbon fibre-reinforced polymer composites to form hierarchical composites [6]. The advantages of this approach include improved primary fibre surface area and interfacial properties of composites [7]. In addition, the applications of CNTs in structural energy storage devices could also benefit from their excellent electrical conductivity.

SEM characterisation demonstrated uniform coating of CNTs on both CNT-sized and grafted carbon fabrics. The CVD-grown CNT diameter was in a range of 20-50 nm. Similar increases, compared with chemical activation, in specific surface area were observed, up to 33.4 and

45.8 m²/g for CNT sizing and grafting, respectively (Figure 2). As a result, considerable improvement in the specific capacitance of carbon fabrics was achieved. Further improvement could be expected by reducing the CNT diameter, increasing the loading, and optimising the surface chemistry of CNTs.

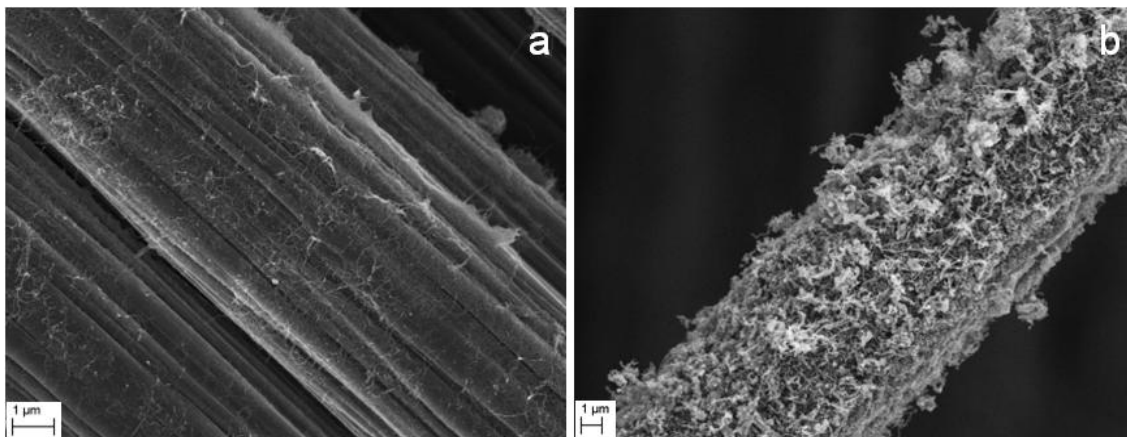


Figure 2. SEM images of (a) CNT-sized and (b) CNT-grafted carbon fibres.

4 Conclusions

High surface area structural carbon fabrics were prepared using different methods, including chemical activation, CNT-sizing and CNT-grafting. Significant increases in electrochemical activity were obtained (Figure 3) without any degradation in the mechanical properties, suggesting the potential application of these modified carbon fabrics as electrodes in multifunctional structural energy devices.

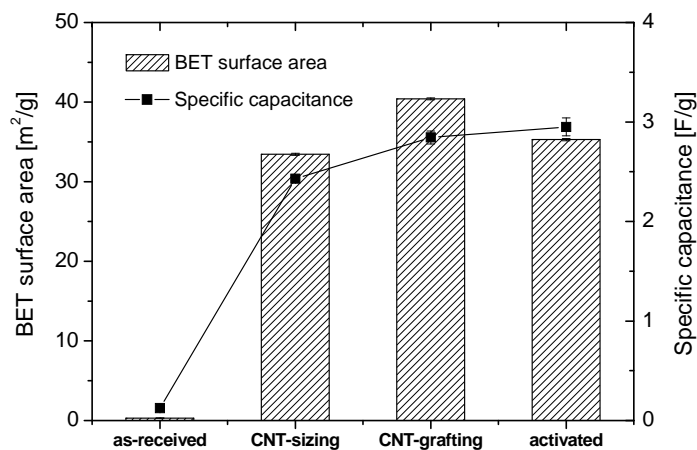


Figure 3. Comparison of specific surface area and capacitance of T300 carbon fabrics after different modifications.

Acknowledgements

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