FISEVIER

Contents lists available at ScienceDirect

Composites Science and Technology





Towards separator-free structural composite supercapacitors



Olivier Hubert^a, Nikola Todorovic^a, Alexander Bismarck^{a,b,*}

^a Polymer & Composite Engineering (PaCE) Group, Institute of Materials Chemistry and Research, Faculty of Chemistry, University of Vienna, Währinger Str. 42, 1090 Vienna, Austria

^b Department of Chemical Engineering, Imperial College London, South Kensington Campus, London, SW7 2AZ, UK

ARTICLE INFO

Keywords: A Carbon fibres Multifunctional composites B Electro-chemical behaviour Multifunctional properties Surface treatments

ABSTRACT

Structural supercapacitors can both carry load and store electrical energy. An approach to build such devices is to modify carbon fibre surfaces to increase their specific surface area and to embed them into a structural electrolyte. We present a way to coat carbon fibres with graphene nanoplatelets by electrophoretic deposition in water. The effect of time and voltage on the mechanical properties of the carbon fibres, the structure of the coating and the specific surface area of the coated carbon fibres are discussed. A specific capacity of 1.44 F/g was reached, which is 130% higher than state-of-the-art structural electrodes. We demonstrate the scalability of the deposition process to continuous production of coated carbon fibres. These carbon fibre electrodes were used to realise large (21 cm long) structural supercapacitor demonstrators without the need for a separator, having a specific capacity of 623 mF/g.

1. Introduction

An increasing interest in electric vehicles has driven researchers to develop new solutions for electrochemical energy storage devices. Between regular capacitors with a high power but low energy density and lithium-ion batteries with high energy but limited power density and consequently long charging time, electrostatic double-layer capacitors (supercapacitors) offer a solution for fast charging and decent energy density [1]. The energy storage mechanism in supercapacitors only involves electrostatic interactions. Compared to batteries, the absence of chemical reactions not only allows higher power densities but also higher reversibility; up to 10000 cycles without capacity loss have been reported [2]. Electrochemical energy storage systems remain nonetheless much heavier than petrol for the same amount of stored energy. Therefore, new solutions to reduce the total weight of electric vehicles are investigated. Structural energy storage systems are among them. By using a multifunctional material that can simultaneously bear loads and store electrical energy, substantial weight savings can be achieved [3]. Luo et al. [4] presented the first electrochemical structural energy storage device in 2001; a capacitor using carbon fibres acting simultaneously as electrodes, current collectors and reinforcement. Carbon fibres are strong, stiff [5] and electron conductors [6] and thus are used both as reinforcement and current collector in structural energy storage

devices [7]. However, the potential drop induced by the higher resistance of carbon fibres $(1.3 \cdot 10^{-3} \Omega \text{ cm} \text{ for T800S carbon fibres [8]})$ when compared to common metallic current collectors $(2.65 \cdot 10^{-6} \Omega \text{ cm} \text{ for}$ aluminium [9]) prevent to use them for very large applications without risking an energy loss by Joule heating [10]. Several other approaches were investigated and devices such as structural batteries [11], fuel cells [12] and supercapacitors [13] were reported. Structural energy storage would allow to increase range and/or reduce the overall weight of (hybrid) electric vehicles. In weight critical applications such as aircrafts [14], structural energy storage allows for more design opportunities and potential energy savings [15].

Supercapacitors are composed of two electrodes, a separator and an electrolyte [16]. In the case of symmetric devices, the positive and negative electrodes are similar. The device capacity is proportional to the specific surface area of the electrodes [17]. Therefore, the electrode material should be chosen carefully. Typically supercapacitor electrodes are carbon materials [6,18,19]. Activated carbon is the oldest and still most commonly used electrode material for supercapacitors as it is cheap and widely available. More recently, carbon nanotubes [20] and graphene [21] have been investigated as potential electrode materials. Graphene is a two-dimensional hexagonal lattice of carbon. Individual graphene sheets have a specific surface area of 2600 m^2/g . Graphene networks produced from graphene oxide can reach specific surface areas

https://doi.org/10.1016/j.compscitech.2021.109126

Received 3 June 2021; Received in revised form 17 September 2021; Accepted 31 October 2021 Available online 2 November 2021

0266-3538/© 2021 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).

^{*} Corresponding author. Polymer & Composite Engineering (PaCE) Group, Institute of Materials Chemistry and Research, Faculty of Chemistry, University of Vienna, Währinger Str. 42, 1090, Vienna, Austria.

E-mail address: alexander.bismarck@univie.ac.at (A. Bismarck).

above 550 m^2/g before treatment and 3500 m^2/g after chemical activation [22]. Graphene has already been used in supercapacitor applications [23,24], including structural energy storage devices [25].

Several routes to produce structural electrodes have already been investigated; Activated carbon fibres and carbon papers made from carbon nanotubes or nanofoams were also investigated but have poor mechanical properties and hence are not suitable for structural applications [26]. Chemical and physical activation of structural carbon fibres can increase the specific surface area without degrading the mechanical properties. Activation of carbon fibres with KOH increased the specific surface area from $0.33 \text{ m}^2/\text{g}$ to $32.8 \text{ m}^2/\text{g}$ [27]. The specific capacity, measured in aqueous KCl (3 M), increased for such activated carbon fibres from 0.06 F/g to 2.63 F/g [28]. Similar results were obtained when grafting or sizing carbon fibres with carbon nanotubes [29]. Coating carbon fibres with carbon aerogel resulted in the highest specific capacity reported so far for structural electrodes with 14.3 F/g in 3M KCl in water [30]. Nevertheless, these techniques are work and energy intensive and most materials lose much of their capacity when combined with a structural polymer electrolyte, such as poly(ethylene glycol)-based electrolytes. The authors [30] attributed the capacity drop between liquid electrolyte and structural electrolyte to the lower ionic conductivity in the latter. The highest specific capacity of a structural supercapacitor reported thus far was 603 mF/g [30].

Electrophoretic deposition (EPD) is a cheap, easily scalable and adjustable technique to deposit materials on a conductive substrate. It has been used for various materials such as ceramics, porous materials, biomaterials and nanoparticles [31]. The particles to be deposited are suspended in a liquid medium and a voltage is applied between the substrate and a counter electrode. Charged particles consequently move towards the oppositely charged electrode and coat its surface. The amount of deposited material is proportional to the deposition time, the surface of the electrodes, the applied electric field, the particle concentration and their electrophoretic mobility [32]. Time, electrode surface and applied electric field can be directly controlled and adjusted before or during the coating process. Electrophoretic mobility in a given medium can be modified by changing the chemical environment of the suspended particles, e.g. by changing the ionic strength of the solution. In an aqueous suspension, the electrophoretic mobility of particles depends strongly on the pH. EPD of electrode material was used for the production of structural lithium-ion battery cathodes [33] but no information was found for structural supercapacitor applications. A continuous process for the EPD of graphene oxide on carbon fibres was already studied but only with the aim to improve the mechanical properties of composites [34].

We describe a simple method to produce carbon material coated structural carbon fibres by electrophoretic deposition. We optimised the EPD process parameters and outcome of graphene coated carbon fibres in a batch process. The coating quality and the capacity of the electrodes in both liquid and structural electrolyte was analysed. Furthermore, we developed a continuous EPD process to produce graphene coated carbon fibres. Separator-free structural supercapacitor demonstrators were prepared using these coated fibres. The impact of the coating process on the tensile properties of the carbon fibres is also presented.

2. Experimental

2.1. Materials

Unsized, untreated polyacrylonitrile (PAN) based carbon fibres (12k AS4D) were kindly provided by Hexcel (Duxford, UK). The suspended carbon materials included high specific surface area (1800 m²/g) carbon black (YP50F), multi-walled carbon nanotubes kindly provided by Kuraray Co. Ltd. (Tokyo, Japan) and Arkema (Lacq, France), respectively, and graphene nanoplatelets (XGnP C-750, XGSciences) with a surface area of 750 m²/g purchased from SigmaAldrich. As binder we used styrene butadiene rubber (BM400B) kindly provided by Zeon corp.

(Düsseldorf, Germany). NaOH was supplied by Sigma Aldrich. Sigraflex F01513TH graphite paper (SGL Carbon, Germany) was used as counter electrode. For the electrolytes, tetraethyl ammonium tetrafluoroborate (TEABF₄), propylene carbonate (PC), poly(ethylene glycol) diglycidyl ether (PEGDGE) and triethylenetetramine (TETA) were all purchased from Sigma Aldrich and 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIBF₄) from Iolitec (Heilbronn, Germany). The separators used were cellulose-based TF40-30 kindly provided by NKK Nippon Kodoshi Corp. (Koshi, Japan). All chemicals were used as received.

2.2. Spreading of carbon fibres

The carbon fibres were spread using an air-assisted fibre tow spreading unit (Izumi International Inc., USA) following the method described by Diao et al. [35] In brief, this device sucks air through the fibre tow at low fibre tension resulting in the fibres in the roving being separated from each other. The tow width increased from 20 mm to 50 mm reducing the average tow thickness from \sim 120 µm to \sim 50 µm.

2.3. EPD of carbon materials on carbon fibres

To increase the specific surface area of the carbon fibres (geometric surface area $\approx 0.3 \text{ m}^2/\text{g}$), we coated them with three different high specific surface area carbon materials: carbon black, carbon nanotubes and graphene nanoplatelets. We also investigated a mixture of carbon black with graphene nanoplatelets or carbon nanotubes. The carbon black had a particle size over 5 µm on average, too close to the diameter of the carbon fibres (6.7 μ m) to produce a good coating quality at the fibre level. The original carbon nanotubes investigated could not be suspended in water due to their hydrophobic nature. After plasma treating (Pico, Diener electronic, Ebhausen, Germany) them for 2 min in air, the nanotubes were more hydrophilic but unfortunately aggregated after less than 5 min. Therefore, we chose to investigate further only graphene suspensions. Preliminary results of other carbons can be found in the supplementary information (ESI Figs. S1-4). The graphene suspension used for EPD contained 90 wt% of graphene nanoplatelets and 10 wt% of styrene butadiene rubber with a total concentration of 2 mg/ mL in water. The pH was adjusted to 10 using NaOH. After mixing all components, the suspension was stirred for 10 min, and then sonicated for 15 min. The suspension was again stirred 1 min and sonicated 3 min between subsequent depositions. Spread carbon fibres were immersed into the suspension using a purpose-built sample holder (Fig. 1); The working electrode was 12 cm long spread 12k tow carbon fibres. To avoid any metal oxide in the suspension, we used graphite paper taped to PVC plates as counter electrode consisting of four interconnected graphite paper sheets of $4 \times 5 \text{ cm}^2$ arranged around and in-between the working electrode. Voltage ranging from 10 to 30 V were applied for a duration of 30-180 s using a laboratory power generator (EA-PS 3065-05 B, Elektro-Automatik, Germany). After EPD, the carbon fibres were pre-dried on the sample holder using a heat gun (air around 40 °C). Finally, the samples were dried to constant weight in an oven at 110 °C for 1 h to remove any residual water.

2.4. Development of a continuous EPD coating process

The main interest in using EPD is the ability to scale up the process to be run in a continuous fashion. For the continuous process we adapted our laboratory composite production line [36]; the fibres were spread inline, EPD coated and dried resulting in ready-to-assemble spread tow electrodes. After passing the spreading unit, the fibres passed 20 cm through a suspension bath in which EPD was performed. We adjusted the line speed to 0.15 m/min resulting in a residence time of the fibres between the electrodes of 80 s. The voltage was set to 30 V or 40 V because the distance between the carbon fibres acting as working electrode and the counter electrodes was larger as compared to the batch process. The counter electrodes were two 20 \times 5 cm² graphite paper



Fig. 1. Scheme of the electrophoretic deposition setup.

sheets taped to PVC plates. The carbon fibres were connected to the electrical circuit by passing over two graphite sleeves, one at the beginning and one at the end of the EPD bath. After EPD, the fibres went through two 80 cm long infrared heated ovens, the first operated at 120 °C and the second at 110 °C. The fibres were pulled by a winding unit at a speed adjusted to match the speed of the spreading process. Fig. 2 shows a schematic of the fibre coating line.

2.5. Characterisation of graphene and binder suspensions

To assess the ability of the particles to move in an applied electrical field and, therefore, to coat the carbon fibres, the electrophoretic mobility μ of the suspended materials was measured. Suspensions of 2 mg/mL of graphene nanoplatelets, binder and a 9:1 (graphene:binder) mixture were characterised by electrophoresis (Zetasizer Nano ZS, Malvern Panalytical, UK). μ was measured from pH 3 to 11 in a 1 mM solution of KCl in water. For each point, three samples were measured three times each. The sedimentation of the particles in suspension was

also evaluated qualitatively. Zeta (ζ) potential is proportional to the electrophoretic mobility μ as given by Henry's equation [37,38]:

$$\zeta = \frac{3\%\eta\%\mu}{2\%\varepsilon\%f(\kappa a)} \tag{1}$$

where $\varepsilon (= \varepsilon_r \Re \varepsilon_0)$ is the dielectric constant, η the viscosity of water and f (κ a) Henry's function, which typically takes values from 1 to 1.5.

2.6. Characterisation of graphene coated carbon fibres

The graphene coating on the carbon fibres was inspected by scanning electron microscopy (Zeiss Supra 55 VP SEM) to characterize the thickness and morphology of the coating. To ensure a good conductivity of the surface and consequently a good quality of the micrographs, the carbon fibres were first coated with a thin layer of gold. The specific surface area of the graphene coated carbon fibres was determined by nitrogen adsorption using the Brunauer–Emmett–Teller (BET) method (Tristar II Plus, Micromeritics). The graphene loading on the carbon fibres was determined by measuring the length and weighing the samples. The linear mass of the carbon fibres (m_l) is 0.765 g/m. The following equation gives the graphene loading G%:

$$G_{\%} = \frac{m_t - l_t \% m_l}{m_t - l_{nc} \% m_l} \% 100$$
(2)

where m_t is the total mass of the sample {coating + coated carbon fibres + uncoated carbon fibres}, l_t the total length and l_{nc} the uncoated length of fibres (see ESI Fig. S5 for illustration).

The surface of the fibres prior and after coating was analysed using Xray photoelectron spectroscopy (XPS). 5 samples were analysed: graphene nanoplatelets, pristine carbon fibres, two samples of coated carbon fibres after having removed the coating and graphene coated carbon fibres. To remove the coating, the coated carbon fibres were sonicated in deionized water for 30 min, rinsed with ultrapure water and dried. The data were acquired using an X-ray photoelectron spectrometer (Nexsa, Thermo Scientific, UK) using Al-K_{α}X-rays and a spot size of 400 µm. First a survey spectrum was recorded and then element specific highresolution spectra with an energy step size of 0.1 eV were taken. We



Fig. 2. Scheme of the fibre treatment line for continuous deposition on carbon fibres.



Fig. 3. (a) A schematic of the assembly of a supercapacitor with liquid electrolyte, (b) a photograph of a structural supercapacitor pouch cell.



Fig. 4. Scheme of the vacuum bag. 1: Metal plate, 2: vacuum bag, 3: carbon fibres, 4: peel-ply, 5: release film, 6: vacuum valve, 7: breathing cloth, 8: sealing tape.

monitored specifically carbon (279–298 eV), oxygen (525–545 eV), and nitrogen (392–410 eV).

2.7. Assembly of supercapacitors

To assemble supercapacitors coated carbon fibre samples were cut in the middle and both sides served as a square $5 \times 5 \text{ cm}^2$ electrode. 5 cm of uncoated fibres were left to allow for electrical connection and the rest was cut off on each side. The supercapacitors consisted of one layer of aluminium foil, one layer of coated carbon fibres, the separator, then again coated carbon fibres and aluminium. Fig. 3a shows a schematic of this layup. The layup was performed in a 3D-printed PLA holder that allowed pushing all layers together to ensure good contact between them. The electrolyte used was PC containing 1M TEABF₄.

2.8. Assembly of structural supercapacitors

Structural supercapacitors were assembled in a glovebox (MBraun, Germany). The electrodes and separator layup was placed between two sheets of release film (Upilex-25S, UBE, Osaka, Japan) and impregnated with 0.8 mL of structural electrolyte. The electrolyte used was described before [30], and consisted of 82.6 wt% PEGDGE, 7.4 wt% TETA and 10 wt% EMIBF₄. The samples were cured 24 h at 80 °C in the oven compartment of the glovebox. During curing, this layup was sandwiched between two metallic plates using a spring clamp to apply pressure. The uncoated part of the carbon fibre electrodes was not impregnated with electrolyte to be able to connect them to the potentiostat. When the samples were fully cured, they were sealed in a plastic pouch before being taken out of the glovebox for testing. The plastic pouch included two aluminium connectors in contact with the uncoated fibre section (Fig. 3b).

2.9. Assembly of structural separator-free supercapacitor demonstrators

Continuously coated fibres were cut into 23 cm long strips to prepare 21 cm electrodes with extra 2 cm for electrical connections. Copper tape was attached to one side of the electrode to allow for electrical contact to the potentiostat (Fig. 11). A vacuum bag was prepared on an aluminium plate and the prepared fibre electrodes were placed into the bag. The layup consisted of a layer of polyimide release film on the Al plate, a layer of PTFE coated glass fibre peel-ply (FF03PM, Cytec Engineered Materials Ltd., UK), two coated carbon fibre electrodes side-by-side, another layer of peel-ply followed by release film and finally the vacuum bag (see Fig. 4). 0.8 mL of structural electrolyte was drop casted on each carbon fibre electrode. The vacuum bag was then sealed with thermal resistant tape (Airdam 1, Airtech, Luxembourg) and a 21×21 cm² metal plate was placed on top. The vacuum bag was then pressclaved. Vacuum was applied and the temperature of the hot press raised to 80 °C. A pressure of 1.2 MPa was applied. After 10 min, the vacuum pump was turned off. After 4 h, the pressure was released, the plate removed from the hot press and allowed to cool down for 30 min. Then, the individual coated carbon fibre electrodes were superimposed over the active 21 cm, with the copper connections on opposite sides. 0.3 mL of electrolyte was coated over the interface for bonding the two layers.

This layup was then placed between two Al plates covered with release film and placed in an oven with a 5 kg weight on top. The oven was operated at 80 $^{\circ}$ C and the assembled supercapacitors were left to cure for 20 h. Three supercapacitor demonstrators were manufactured.

2.10. Electrochemical characterisation of the supercapacitors

The assembled supercapacitors were tested using a potentiostat (Reference 600, Gamry). Cyclic voltammograms were recorded between 1 V and -1 V at a charging rate of 5 mV/s. The capacity C was calculated:

$$I = C\% \left(\frac{dV}{dt}\right)_{V=0} \tag{3}$$

where I is the current and V the voltage. C was calculated at zero voltage to limit the impact of resistance and pseudo-capacitance on the results. Three cycles were recorded. The reported capacity is the average value of the 2nd and the 3rd cycles. A minimum of five supercapacitors was tested for each condition.

2.11. Characterisation of separator-free supercapacitor demonstrators

The composites were weighed to evaluate the fibre weight fraction and their thickness was measured using a micrometre screw gauge. The separator-free supercapacitors were electrochemically tested using cyclic voltammetry at a rate of 5 mV/s between -1 V and 1 V for 1500 cycles to assess their performance. We calculated the capacity for each cycle using Eq. (3). The energy density of the separator-free structural supercapacitor demonstrators was calculated using a galvanostatic charge-discharge measurement. A voltage step of 1 V was applied for 60 s and then the specimen was allowed to discharge for another 60 s. The fitting and calculation were performed as described by Qian et al. [30].

2.12. Characterisation of single fibre tensile properties

To quantify the impact of EPD on the mechanical properties of the carbon fibres we measured the breaking stress of pristine and coated fibres (Favimat + single-fibre tester, Textechno). For both pristine and coated carbon fibres, a minimum of 80 single fibres was characterized at 4 different gauge lengths (18, 25, 35 and 50 mm). The fibres to be characterised were extracted from continuously EPD (U = 40 V, t = 80 s) coated fibre tows. The measurements were performed following the standard ASTM C1557 with a test speed of 0.5 mm/min. To determine the fibre diameter, the linear density was measured using the frequency of resonance of the fibres and then divided by the density of carbon fibres (1.79 g/cm³). All data were then processed using unimodal Weibull analysis [39,40] following the standard ASTM C1239 to report the characteristic strength, Weibull modulus as well as the 90% confidence interval for each tested condition.

2.13. Characterisation of tensile properties of composite supercapacitors

The ultimate tensile strength as well as the Young modulus of the separator-free structural supercapacitors were measured with a method



Fig. 5. (a) Zeta potential of graphene nanoplatelets and binder as a function of pH and (b) electrophoretic mobility of graphene and binder as a function of pH both measured at supporting electrolyte concentration of [KCl] = 1 mM.

adapted from ASTM D3039. First the sample were cut to a width of 25 mm. Then, glass fibre epoxy composite end tabs of 40 \times 25 mm² were attached on each side of the specimens using Araldite® glue. The remaining gauge length was 130 mm and the thickness, varying for each sample, from 260 μm to 190 μm . The prepared specimen were loaded in tension using a universal test frame (Instron 5969) equipped with a 50 kN load cell at a 1 mm/min rate. 5 samples were measured.

3. Results and discussion

3.1. Zeta potential and electrophoretic mobility of graphene and binder

The graphene used was easily suspended in water without the need for any surfactant. Graphene suspensions with a pH between 7 and 11

appeared stable (clear black suspensions) over more than 3h (ESI Fig. S6). Fig. 5a shows the ζ -potential as a function of pH of graphene and binder. $\zeta = f(pH)$ of graphene confirmed the presence of Brønsted acid surface oxides with a $\zeta_{plateau}$ of -35 mV and an i.e.p., where $\zeta = 0$, of 4.2. Similar results for graphene were reported in the literature before [41]. A suspension is usually considered stable when $|\zeta| > 25$ mV [42]. All graphene suspensions with pH > 8 were, according to this criterion, stable. However, at pH < 8 the graphene suspensions became unstable, and most particles settled to the bottom of the vial. When emptied, some sediment remained at the bottom of every vial, confirming that sedimentation did occur. The ζ -potential of the binder remained virtually constant over the whole pH range with an average $\zeta = -48$ mV, which was likely caused by the presence of an anionic surfactant used for its synthesis.



Fig. 6. Characteristic micrographs of carbon fibres EPD coated with graphene nanoplatelets using the batch process using the following process parameters (a) 10V 1min (b) 20V 1min (c) 30V 1min (d) 10V 3min and (e) 20V 3min.



Fig. 7. Characteristic micrographs of graphene nanoplatelet coated carbon fibres produced using the continuous EPD process at the following conditions (a) 30V 1min and (b) 40V 1min.



Fig. 8. Specific surface area of graphene nanoplatelets coated carbon fibres calculated using BET theory (a) as a function of time and (b) as a function of graphene loading.

The measured electrophoretic mobility, from which ζ was calculated, gives the ability of a suspended particle to move in an applied electrical field. During EPD the higher the electrophoretic mobility the faster the coating will form. Fig. 5b shows $\mu = f(pH)$ for graphene, binder and a 9:1 (graphene:binder weight ratio) mixture. The addition of binder to the graphene suspension increased its electrophoretic mobility for pH < 8 but had very little effect on suspensions at higher pH. The electrophoretic mobility of a suspension that had been used for deposition was analysed and an electrophoretic mobility of $\mu = -2.52 \pm 0.09 \ \mu m \ cm/Vs$ was measured, showing that there was no significant variation of this value after deposition.

3.2. Morphology, graphene loading and surface properties of coated carbon fibres

Micrographs of carbon fibres coated with graphene at different voltage and duration are shown Fig. 6. We can see from these micrographs that the coating consists of aggregates of graphene nanoplatelets attached to the carbon fibres. When the voltage and/or time was increased a continuous layer of graphene formed on top of the fibre tow; not encasing individual fibres. During handling, some of the coating detached and many cracks can be seen on the surface of the fibre electrode (Fig. 6e). A higher graphene loading will inevitably result in a lower fibre volume fraction in the prepared structural supercapacitor electrodes and hence lower mechanical properties of the final composite. The graphene aggregates stacking between the fibres were not affected by handling, graphene not only adhered to the carbon fibres but also stuck between the fibres occupying the volume between them.

The graphene loading of fibres continuously EPD coated at low voltage was much lower as compared to the batch process because of the larger gap between counter electrodes and carbon fibres used as working electrode. When using a voltage of 30 V (Fig. 7a), the carbon fibres started to be coated with graphene aggregates, but the amount was still very low compared to the batch process. However, when using 40 V (Fig. 7b), the morphology was very similar to the one observed for carbon fibres EPD coated at 10 V for 1 min in the batch process (Fig. 6a).

The specific surface area A_s of the graphene coated carbon fibres were consistent with the amount of coating deposited as observed in the SEM (Fig. 6); A_s increased with increasing applied voltage and EPD time (Fig. 8a) indicating an increased graphene loading on the low A_s (0.49 m²/g) carbon fibres (Fig. 8b). The gravimetric method used to determine the graphene loading (G%) did not allow for very high precision, thus the large standard error. After 30 s of EPD, the voltage had a large impact on the resulting specific surface area: $33 \text{ m}^2/\text{g}$ at 10 V, 72 m²/g at 20 V and 153 m²/g at 30 V. However, after 60 s, the gap between the surface areas for different applied voltage decreased. After 180 s, EPD at

Table 1

Surface elemental composition of pristine carbon fibres (AS4D), EPD coated carbon fibres and after removal of the graphene coating as well as graphene; Atomic percentage of carbon, nitrogen and oxygen determined by XPS.

	С	0	Ν
Pristine CF	88.35	9.31	2.33
Coated CF 1	87.82	10.24	1.94
Coated CF 2	87.84	10.3	1.86
Coating	91.84	7.21	0.94
Graphene	95.35	4.26	0.39

20 V and 30 V produced coated fibres with identical A_s (191 m²/g and 193 m²/g, respectively). Previous work reported specific surface areas up to 163 m²/g for carbon aerogel coated carbon fibres [30]. The specific surface area of the coated fibres normalized to carbon aerogel was calculated to be 741 m²/g. When normalising our results of coated carbon fibres to graphene and binder content resulted in an average specific surface area of the coating material of 455 m²/g, confirming the formation of graphene aggregates. Much lower specific surface areas (A_s = 36.6 ± 1.5 m²/g) were achieved when using the continuous EPD process as compared to the batch process, which was likely due to the coating being removed from the fibre tows when pulled over sleeves after exiting the coating bath and during winding (see Fig. 2).

The current flowing in the circuit during EPD can cause anodic oxidation of the carbon fibre electrodes. Oxidation of the surface of the carbon fibres can affect both the mechanical properties of the fibres and the adhesion of the resin to the fibres, which will have an impact on the mechanical properties of the final composite [43]. Therefore, we characterized the surface composition of the carbon fibres (and graphene) by XPS. The atomic percentages of C. N and O for each sample are reported in Table 1. Coated CF 1 and 2 refer to the analysis of carbon fibres after removal of the coating. All the associated XP spectra can be found in the ESI Figs. S8–9. The XPS analysis of XGnP C-750 graphene nanoplatelets was discussed before [44]. Compared to their results we have a slightly higher carbon content but overall the results are similar. The XPS analysis of the graphene coating shows a higher oxygen content as compared to virgin graphene nanoplatelets. This difference can be explained by i) the graphene was oxidised during deposition and ii) the presence of the binder in the coating. The XPS spectra of the industrially oxidised AS4D carbon fibres and those after EPD process were not significantly different. A previous study reported a variation of the

oxygen content during anodic oxidation of more than 7% [45]. We observed less than 1% variation in oxygen content between the carbon fibres before and after EPD process. The influence of this small variation in chemical composition on the tensile strength of the carbon fibres is discussed below.

3.3. Electrochemical properties of small-scale supercapacitors with liquid and solid electrolyte

Supercapacitors assembled using graphene coated carbon fibres were first tested via cyclic voltammetry in a liquid TEABF₄ electrolyte. The specific capacities are summarised in Fig. 9a. The capacity was divided by the total mass of the electrodes, including the coated carbon fibres and the coating. The capacity and the specific surface area follow a linear correlation. An areal capacitance of 21 mF/m² with a good correlation ($R^2 = 0.989$) was determined by fitting. Supercapacitors made using carbon aerogel coated carbon fibres possessed a higher areal capacitance in aqueous 3M KCl with values up to 132 mF/m² [29]. Nevertheless, aqueous electrolytes typically result in higher capacitance, due to the pore size distribution, but limit the voltage window for electrochemical cycling [46]. Some pores in porous carbons can be accessed by K^+/Cl^- ions but not by the solvated ions dissolved in an organic electrolyte [47,48]. Furthermore, our measured values were acquired in a fully functional supercapacitor and not in a three electrode setup. Therefore, as presented later, it is closer to the capacity that will be obtained in a final structural supercapacitor.

Fig. 9b shows a characteristic cyclic voltammogram of graphene coated carbon fibres recorded in liquid electrolyte. The voltammogram is very close to the rectangular theoretical shape of a supercapacitor. Only a small oxidation peak can be seen for voltages approaching 1 V and -1 V. This peak could be caused by residual moisture still present in the supercapacitor layup, as the assembly was not performed in a controlled atmosphere. The charging and discharging curves are also slightly tilted, which is due to resistive effects in the supercapacitor. These effects should be cancelled at 0 V, from which the capacity was calculated.

Structural supercapacitors were assembled with a polyethylene glycol-based solid electrolyte. The specific capacity was again calculated accounting for the weight of the coated carbon fibres including the coating (Fig. 10). All our results exceed the highest reported specific capacity of a structural supercapacitor made using carbon aerogel



Fig. 9. (a) Specific capacity of supercapacitors made using pristine and graphene coated carbon fibres in 1M TEABF₄ in PC as function of specific surface area of the fibre electrodes and (b) characteristic cyclic voltammogram of a supercapacitor prepared using graphene coated carbon fibre electrodes in 1M TEABF₄ in PC recorded at a rate of 5 mV/s.



Fig. 10. Specific capacity of structural supercapacitors made using graphene coated carbon fibre electrodes and a PEG-based solid electrolyte as a function of the specific surface area of the electrodes. The green line indicates the highest reported value of similar devices [29]. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

coated carbon fibres and a very similar solid polymer electrolyte [29], indicating the potential of our electrode preparation method. The highest specific capacity of our small-scale structural supercapacitors was 1.44 F/g, an increase of more than 130% compared to similar devices previously reported.

3.4. Separator-free structural supercapacitor demonstrators

Previous studies investigated different separator materials, such as polypropylene (PP) separators [30] or glass fibres [29,49], in structural supercapacitors. PP separators (such as Celgard) are widely used in supercapacitors. However, PP does not provide any additional reinforcement to structural energy storage devices but can cause early delamination of multifunctional composites [30]. As an alternative, glass fibres are used in most structural energy storage composites because they are insulators and act as reinforcement, unfortunately with a weight penalty. The thinnest glass fibre separator reported for structural energy storage application was a 50 μm thick glass fibre fabric (with an areal density of 53 g/m^2) [50]. The volume occupied by the separator is inactive in the final assembly. Coated carbon fibres act as electrode and current collector and the matrix as electrolyte but the separator prevents short circuits. Being able to use the matrix as a separator would allow an increased energy density of structural supercapacitors. We will show proof-of-concept of such a system.

Fully cured supercapacitor composites assembled using two EPD



Fig. 12. Normalized capacity of separator-free structural supercapacitor demonstrators over 1500 cycles measured by cyclovoltammetry at a rate of 5 mV/s.

graphene coated carbon fibre electrodes had a thickness of $267 \pm 40 \,\mu m$ (Fig. 11). The fibre weight fraction was around 20% (around 14% fibre volume fraction), which is very low compared to standard structural composites, which typically have fibre weight fractions exceeding 40%. For demonstration purpose, we added excess electrolyte to ensure no electrical contact between the electrode layers. A picture of the cross-section of such a composite can be found in ESI Fig. S7.

The measured specific capacity for these supercapacitor demonstrators was 623 ± 52 mF/g. Qian et al. [30] reported a specific capacity of 71 mF/g for a structural supercapacitor containing two carbon aerogel coated carbon fibre electrodes and a glass fibre separator impregnated with a similar polymer electrolyte. A supercapacitor consisting of activated carbon fibre fabric electrodes and a glass fibre separator but with a slightly different polymer electrolyte system in which the ionic liquid was replaced by a standard electrolyte (1M LiTFSI in an EC:PC mixture), Reece et al. [51] reported a specific capacity of 102 mF/g. Our system without separator had a 6-fold higher specific capacity compared with their results, highlighting the benefit of removing the separator. The measured energy density and power density were 16.9 mWh/kg and 5.2 W/kg, respectively. Higher power densities have been reported before as it only depends on the internal resistance and applied voltage [52]. The limited power density is due to the higher resistance of carbon fibres as compared to metallic current collectors caused by the use of carbon fibres as current collectors. However, the energy density of these demonstrators exceed the ones reported before for structural supercapacitors [25,30]. Moreover, the use of ionic liquid could allow for



Fig. 11. Photograph of a separator-free structural supercapacitor demonstrator.



Fig. 13. (a) Characteristic breaking stress for pristine and EPD graphene coated carbon fibres. The error bars are the 90% confidence interval. (b) Unbiased estimate of Weibull moduli and associated 90% confidence interval for pristine and graphene coated carbon fibres determined using the unimodal Weibull analysis.

operating voltages up to 6 V if the device was protected from moisture thus allowing to increase the energy density even further. Further improvements will have to address the low carbon fibre volume fraction enabling a higher energy density but also better mechanical properties. Fig. 12 shows the evolution of the capacity of three separator-free structural supercapacitor demonstrators over 1500 cycles. The capacity was normalized to the average capacity of the 10 first cycles. The supercapacitors 1–3 retained 95%, 77% and 103% of their initial capacity. This cycling performance was in the range expected for supercapacitors containing carbon based electrodes [48]. The observed fluctuations are artefacts of the calculation method which only takes into account two points per cycle.

3.5. Single fibre tensile properties of carbon fibres used in structural supercapacitors

EPD in water can damage the surfaces of carbon fibres by anodic oxidation. No clear difference in the breaking stress was measured between coated and pristine carbon fibres (Fig. 13a). The values for the 18 mm gauge length seem to be deviating from the trend, probably due to device bias when measuring at small gauge length. The same deviation is also observed in the Weibull moduli. The Weibull moduli ranged between 4.1 and 6.4, which is typical for carbon fibres [53,54]. The unbiased Weibull moduli (m_{UF}) are summarised in Fig. 13b. The graphs containing all measured data can be found in the supplementary information (ESI Figs. S10–11).

We conclude from these results that the composite supercapacitors assembled with EPD graphene coated carbon fibres should retain their tensile properties compared to the composites made using pristine carbon fibres. Moreover, surface oxidation of the carbon fibres has been shown to improve the fibre-matrix interface [43]. EPD is a cheap and easy method to coat carbon fibres with active electrode materials without drastically affecting the mechanical properties of the fibre substrates.

3.6. Tensile properties of separator-free supercapacitor demonstrators

The stress – strain curves are shown ESI Fig. S12. The calculated breaking stress was 350 ± 100 MPa and the Young's modulus 26 ± 3 GPa. This places our material in the range of previously reported structural supercapacitors using a similar electrolyte [23]. It is

important to note that 4 out of 5 samples failed catastrophically, showing the ability of the electrolyte to distribute the load between the fibres (ESI Fig. S13). The early failure of the fifth specimen is assumed to be linked to fibre misalignment in the unidirectional laminate.

4. Conclusion

Structural supercapacitor electrodes were successfully manufactured by electrophoretic deposition of graphene nanoplatelets onto carbon fibres. Increasing time and voltage increased the graphene loading on the fibres, which consequently resulted in higher specific surface areas of the structural electrodes approaching 190 m^2/g . The highest specific capacity measured for small-scale structural composite supercapacitors was 1.44 F/g. The use of a structural polymer electrolyte allowed for the removal of the separator from the structural supercapacitor assembly, thus removing what is usually the parasitic material in composite supercapacitors. Our composite supercapacitor demonstrators had an average specific capacity of 623 mF/g and an energy density of 16.9 mWh/kg. Finally, we demonstrated that the EPD process does not significantly affect the tensile properties of the carbon fibres used as substrate for deposition of active electrode materials. With the possibility to coat material continuously, the process presented in this paper will allow for production of large-scale structural composite supercapacitors after optimisation of the process.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The research leading to these results has been performed in the framework of the HyFiSyn project, which was funded by the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 765881. We would also thank Dr. Andreas Mautner for his help and support in the project, Prof. Bo Madsen for his help with the analysis of the single fibre test data and the exchange student Maximilien Epeh Eyengue from University of Toulon, France for his help with the experimental work.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.compscitech.2021.109126.

Author statement

OH: experimental design, experiments, data collection and analysis, manuscript drafting and revision, NT: experiments, data collection and testing AB: conceptualisation, data analysis manuscript writing and revision, supervision and funding acquisition.

References

- M. Winter, R.J. Brodd, What are batteries, fuel cells, and supercapacitors? Chem. Rev. 104 (2004) 4245–4270, https://doi.org/10.1021/cr020730k.
- [2] O. Mashtalir, M.R. Lukatskaya, A.I. Kolesnikov, E. Raymundo-Piñero, M. Naguib, M.W. Barsoum, Y. Gogotsi, The effect of hydrazine intercalation on the structure and capacitance of 2D titanium carbide (MXene), Nanoscale 8 (2016) 9128–9133, https://doi.org/10.1039/C6NR01462C.
- [3] W. Johannisson, D. Zenkert, G. Lindbergh, Model of a structural battery and its potential for system level mass savings, Multifunct. Mater. 2 (2019), 035002, https://doi.org/10.1088/2399-7532/ab3bdd.
- [4] X. Luo, D.D.L. Chung, Carbon-fiber/polymer-matrix composites as capacitors, Compos. Sci. Technol. 61 (2001) 885–888, https://doi.org/10.1016/S0266-3538 (00)00166-4.
- [5] D.D. Edie, The effect of processing on the structure and properties of carbon fibers, Carbon 36 (1998) 345–362, https://doi.org/10.1016/S0008-6223(97)00185-1.
- [6] A.G. Pandolfo, A.F. Hollenkamp, Carbon properties and their role in supercapacitors, J. Power Sources 157 (2006) 11–27, https://doi.org/10.1016/j. ipowsour.2006.02.065.
- [7] E.D. Wetzel, Multifunctional composites intergrate power, communications and structure, AMPTAC Q 8 (2004) 91–95.
- [8] T800S technical data sheet, (n.d.). https://www.toraycma.com/wp-content/uploa ds/T800S-Technical-Data-Sheet-1.pdf.pdf. (Accessed 16 September 2021) accessed.
- [9] R.A. Serway, Principles of Physics, Saunders College Pub., Fort Worth, 1998. http: ://archive.org/details/principlesofphys00serw. (Accessed 16 September 2021). accessed.
- [10] W. Johannisson, D. Carlstedt, A. Nasiri, C. Buggisch, P. Linde, D. Zenkert, L.E. Asp, G. Lindbergh, B. Fiedler, A screen-printing method for manufacturing of current collectors for structural batteries, Multifunct. Mater. 4 (2021), 035002, https://doi. org/10.1088/2399-7532/ac2046.
- [11] L. Christodoulou, J.D. Venables, Multifunctional material systems: the first generation, JOM 55 (2003) 39–45, https://doi.org/10.1007/s11837-003-0008-z.
- [12] J.T. South, R.H. Carter, J.F. Snyder, C.D. Hilton, D.J. O'Brien, E.D. Wetzel, Multifunctional power-generating and energy-storing structural composites for U. S. Army applications, MRS Proc 851 (2004), https://doi.org/10.1557/PROC-851-NN4.6. NN4.6.
- [13] D.J. O'Brien, D.M. Baechle, E.D. Wetzel, Multifunctional structural composite capacitors for U.S. Army applications, in: SAMPE Fall Tech. Conf. Proc., Society for the Advancement of Material and Process Engineering, Dallas, TX, 2006, p. 11.
- [14] A. Bernasconi, Aircraft with electric batteries, in particular a hybrid aircraft, US 2019/0263498 A1. https://appft.uspto.gov/netacgi/nph-Parser?Sect1=PT01&Sect2=HITOFF&d=PG01&p=1&u=%2Fnetahtml%2FPT0%2Fsrchnum. html&r=1&f=G&1=50&s1=%220190263498%22.PGNR.&OS=DN/20190 263498&RS=DN/20190263498, 2019. (Accessed 17 May 2021) accessed.
- [15] S.N. Nguyen, A. Millereux, A. Pouyat, E.S. Greenhalgh, M.S.P. Shaffer, A.R.J. Kucernak, P. Linde, Conceptual multifunctional design, feasibility and requirements for structural power in aircraft cabins, J. Aircr. 0 (n.d.) 1–11. https://doi.org/10.2514/1.C036205.
- [16] H.I. Becker, Low Voltage Electrolytic Capacitor, US2800616A, 1957.
- [17] B.E. Conway, Transition from "supercapacitor" to "battery" behavior in electrochemical energy storage, J. Electrochem. Soc. 138 (1991) 1539, https://doi. org/10.1149/1.2085829.
- [18] Y. Zhang, H. Feng, X. Wu, L. Wang, A. Zhang, T. Xia, H. Dong, X. Li, L. Zhang, Progress of electrochemical capacitor electrode materials: a review, Int. J. Hydrog. Energy. 34 (2009) 4889–4899, https://doi.org/10.1016/j.ijhydene.2009.04.005.
- [19] G. Wang, L. Zhang, J. Zhang, A review of electrode materials for electrochemical supercapacitors, Chem. Soc. Rev. 41 (2012) 797–828, https://doi.org/10.1039/ C1CS15060J.
- [20] C. Du, N. Pan, Supercapacitors using carbon nanotubes films by electrophoretic deposition, J. Power Sources 160 (2006) 1487–1494, https://doi.org/10.1016/j. jpowsour.2006.02.092.
- [21] K. Sheng, Y. Sun, C. Li, W. Yuan, G. Shi, Ultrahigh-rate supercapacitors based on electrochemically reduced graphene oxide for ac line-filtering, Sci. Rep. 2 (2012) 1–5, https://doi.org/10.1038/srep00247.
- [22] Z. Li, B. Song, Z. Wu, Z. Lin, Y. Yao, K.-S. Moon, C.P. Wong, 3D porous graphene with ultrahigh surface area for microscale capacitive deionization, Nano Energy 11 (2015) 711–718, https://doi.org/10.1016/j.nanoen.2014.11.018.

- [23] S. Wang, B. Pei, X. Zhao, R.A.W. Dryfe, Highly porous graphene on carbon cloth as advanced electrodes for flexible all-solid-state supercapacitors, Nano Energy 2 (2013) 530–536, https://doi.org/10.1016/j.nanoen.2012.12.005.
- [24] M. Wang, L.D. Duong, N.T. Mai, S. Kim, Y. Kim, H. Seo, Y.C. Kim, W. Jang, Y. Lee, J. Suhr, J.-D. Nam, All-solid-state reduced graphene oxide supercapacitor with large volumetric capacitance and ultralong stability prepared by electrophoretic deposition method, ACS Appl. Mater. Interfaces 7 (2015) 1348–1354, https://doi. org/10.1021/am50765661.
- [25] X.F. Sánchez-Romate, A.D. Bosque, J. Artigas-Arnaudas, B.K. Muñoz, M. Sánchez, A. Ureña, A proof of concept of a structural supercapacitor made of graphene coated woven carbon fibers: EIS study and mechanical performance, Electrochimica Acta 370 (2021) 137746, https://doi.org/10.1016/j. electacta.2021.137746.
- [26] J.F. Snyder, E.L. Wong, C.W. Hubbard, Evaluation of commercially available carbon fibers, fabrics, and papers for potential use in multifunctional energy storage applications, J. Electrochem. Soc. 156 (2009) A215, https://doi.org/ 10.1149/1.3065070.
- [27] A. Javaid, K.K.C. Ho, A. Bismarck, M.S.P. Shaffer, J.H.G. Steinke, E.S. Greenhalgh, Multifunctional structural supercapacitors for electrical energy storage applications, J. Compos. Mater. 48 (12) (2013) 1409–1416, https://doi.org/ 10.1177/0021998313487239.
- [28] H. Qian, H. Diao, N. Shirshova, E.S. Greenhalgh, J.G.H. Steinke, M.S.P. Shaffer, A. Bismarck, Activation of structural carbon fibres for potential applications in multifunctional structural supercapacitors, J. Colloid Interface Sci. 395 (2013) 241–248, https://doi.org/10.1016/j.jcis.2012.12.015.
- [29] N. Shirshova, H. Qian, M. Houllé, J.H.G. Steinke, A.R.J. Kucernak, Q.P.V. Fontana, E.S. Greenhalgh, A. Bismarck, M.S.P. Shaffer, Multifunctional structural energy storage composite supercapacitors, Faraday Discuss 172 (2014) 81–103, https:// doi.org/10.1039/C4FD00055B.
- [30] H. Qian, A.R. Kucernak, E.S. Greenhalgh, A. Bismarck, M.S.P. Shaffer, Multifunctional structural supercapacitor composites based on carbon aerogel modified high performance carbon fiber fabric, ACS Appl. Mater. Interfaces. 5 (2013) 6113–6122, https://doi.org/10.1021/am400947j.
- [31] I. Corni, M.P. Ryan, A.R. Boccaccini, Electrophoretic deposition: from traditional ceramics to nanotechnology, J. Eur. Ceram. Soc. 28 (2008) 1353–1367, https:// doi.org/10.1016/j.jeurceramsoc.2007.12.011.
- [32] H.C. Hamaker, Formation of a deposit by electrophoresis, Trans. Faraday Soc. 35 (1940) 279–287, https://doi.org/10.1039/TF9403500279.
- [33] J. Hagberg, H.A. Maples, K.S.P. Alvim, J. Xu, W. Johannisson, A. Bismarck, D. Zenkert, G. Lindbergh, Lithium iron phosphate coated carbon fiber electrodes for structural lithium ion batteries, Compos. Sci. Technol. 162 (2018) 235–243, https://doi.org/10.1016/j.compscitech.2018.04.041.
- [34] C. Wang, J. Li, S. Sun, X. Li, F. Zhao, B. Jiang, Y. Huang, Electrophoretic deposition of graphene oxide on continuous carbon fibers for reinforcement of both tensile and interfacial strength, Compos. Sci. Technol. 135 (2016) 46–53, https://doi.org/ 10.1016/j.compscitech.2016.07.009.
- [35] H. Diao, A. Bismarck, P. Robinson, M.R. Wisnom, Production OF continuous intermingled CF/GF hybrid composite via fibre tow spreading technology 9 (2014).
- [36] K.K.C. Ho, S.-R. Shamsuddin, S. Riaz, S. Lamorinere, M.Q. Tran, A. Javaid, A. Bismarck, Wet impregnation as route to unidirectional carbon fibre reinforced thermoplastic composites manufacturing, Plast. Rubber Compos. 40 (2011) 100–107, https://doi.org/10.1179/174328911X12988622801098.
- [37] A.V. Delgado, F. González-Caballero, R.J. Hunter, L.K. Koopal, J. Lyklema, Measurement and interpretation of electrokinetic phenomena (IUPAC technical report), Pure Appl. Chem. 77 (2005) 1753–1805, https://doi.org/10.1351/ pac200577101753.
- [38] D.C. Henry, A. Lapworth, The cataphoresis of suspended particles. Part I.—the equation of cataphoresis, Proc. R. Soc. Lond. Ser. Contain. Pap. Math. Phys. Character. 133 (1931) 106–129, https://doi.org/10.1098/rspa.1931.0133.
- [39] W. Weibull, Statistical Theory of Strength of Materials. Generalstabens Litografiska Anstalts Förlag, Stockholm, 1939.
- [40] W. Weibull, A statistical distribution function of wide applicability, ASME J. Appl. Mech. 18 (1951) 293–297.
- [41] M. Mehrali, E. Sadeghinezhad, S.T. Latibari, S.N. Kazi, M. Mehrali, M.N.B.M. Zubir, H.S.C. Metselaar, Investigation of thermal conductivity and rheological properties of nanofluids containing graphene nanoplatelets, Nanoscale Res. Lett. 9 (2014) 15, https://doi.org/10.1186/1556-276X-9-15.
- [42] W. Yu, H. Xie, A review on nanofluids: preparation, stability mechanisms, and applications, J. Nanomater. 2012 (2011), e435873, https://doi.org/10.1155/ 2012/435873.
- [43] E. Fitzer, H. Jäger, N. Popovska, F. Von Sturm, Anodic oxidation of high modulus carbon fibres in sulphuric acid, J. Appl. Electrochem. 18 (1988) 178–182, https:// doi.org/10.1007/BF01009259.
- [44] S. Dul, L. Fambri, C. Merlini, G.M.O. Barra, M. Bersani, L. Vanzetti, A. Pegoretti, Effect of graphene nanoplatelets structure on the properties of acrylonitrile–butadiene–styrene composites, Polym. Compos. 40 (2019) E285–E300, https://doi.org/10.1002/pc.24645.
- [45] J. Jiang, X. Yao, C. Xu, Y. Su, L. Zhou, C. Deng, Influence of electrochemical oxidation of carbon fiber on the mechanical properties of carbon fiber/graphene oxide/epoxy composites, Compos. Part Appl. Sci. Manuf. 95 (2017) 248–256, https://doi.org/10.1016/j.compositesa.2017.02.004.
- [46] R. Kötz, M. Carlen, Principles and applications of electrochemical capacitors, Electrochimica Acta 45 (2000) 2483–2498, https://doi.org/10.1016/S0013-4686 (00)00354-6.
- [47] A. Burke, Ultracapacitors: why, how, and where is the technology, J. Power Sources 91 (2000) 37–50, https://doi.org/10.1016/S0378-7753(00)00485-7.

- [48] J. Zhao, A.F. Burke, Electrochemical capacitors: materials, technologies and performance, Energy Storage Mater 36 (2021) 31–55, https://doi.org/10.1016/j. ensm.2020.12.013.
- [49] A. Javaid, K.K.C. Ho, A. Bismarck, J.H.G. Steinke, M.S.P. Shaffer, E.S. Greenhalgh, Improving the multifunctional behaviour of structural supercapacitors by incorporating chemically activated carbon fibres and mesoporous silica particles as reinforcement, J. Compos. Mater. 52 (22) (2018) 3085–3097, https://doi.org/ 10.1177/0021998318761216.
- [50] L.E. Asp, K. Bouton, D. Carlstedt, S. Duan, R. Harnden, W. Johannisson, M. Johansen, M.K.G. Johansson, G. Lindbergh, F. Liu, K. Peuvot, L.M. Schneider, J. Xu, D. Zenkert, A structural battery and its multifunctional performance, Adv. Energy Sustain. Res. 2 (2021) 2000093, https://doi.org/10.1002/aesr.202000093.
- [51] R. Reece, C. Lekakou, P.A. Smith, A structural supercapacitor based on activated carbon fabric and a solid electrolyte, Mater. Sci. Technol. 35 (2019) 368–375, https://doi.org/10.1080/02670836.2018.1560536.
- [52] N. Shirshova, H. Qian, M.S.P. Shaffer, J.H.G. Steinke, E.S. Greenhalgh, P.T. Curtis, A. Kucernak, A. Bismarck, Structural composite supercapacitors, Compos. Part Appl. Sci. Manuf. 46 (2013) 96–107, https://doi.org/10.1016/j. compositesa.2012.10.007.
- [53] M.G. Huson, J.S. Church, A.A. Kafi, A.L. Woodhead, J. Khoo, M.S.R.N. Kiran, J. E. Bradby, B.L. Fox, Heterogeneity of carbon fibre, Carbon 68 (2014) 240–249, https://doi.org/10.1016/j.carbon.2013.10.084.
- [54] J. Sun, F. Zhao, Y. Yao, Z. Jin, X. Liu, Y. Huang, High efficient and continuous surface modification of carbon fibers with improved tensile strength and interfacial adhesion, Appl. Surf. Sci. 412 (2017) 424–435, https://doi.org/10.1016/j. apsusc.2017.03.279.