Surface Modifications of Carbon Fiber Electrodes for Structural Supercapacitors

Joaquín Artigas-Arnaudas[a,*], *Bianca K. Muñoz*[a], *María Sánchez*[a], *Javier de Prado*[a], *M. Victoria Utrilla*[a] *and Alejandro Ureña*[a]

[a] Materials Science and Engineering Area, Escuela Superior de Ciencias Experimentales y Tecnología, Universidad Rey Juan Carlos, Calle Tulipán s/n, 28933 Móstoles (Madrid) Spain

Abstract

Structural electrodes for supercapacitors based on woven carbon fiber were made from different surface modification approaches, such as spray coating with carbon nanoparticles (graphene nanoplatelets and multiwall carbon nanotubes, GNP and MWCNT, respectively) and direct synthesis of carbon aerogel (CAG) on the surface of the carbon fabric. Suitability of the different modification techniques was stablished based on the results from cyclic voltammetry and single fiber tensile test. Highest capacitance was achieved by the synthesis of CAG although mechanical properties were negatively affected. These treatments produced a good combination of mechanical and electrochemical properties, which suggests these electrodes are suitable for multifunctional applications. In particular, capacitance was improved by increasing the surface area of commercial carbon fiber fabric while keeping its mechanical properties. The best combination of properties was achieved by deposition of GNP by spray coating.

* Corresponding author: Tel: +34914884621 joaquin.artigas@urjc.es (Joaquín Artigas-Arnaudas)

Mechanical properties kept unaffected and capacitance was increased by an order of magnitude compared with the pristine carbon fiber.

Keywords

Structural supercapacitor, Multifunctional properties, Carbon aerogel, Graphene nanoplatelets, Energy storage.

1 Introduction

Carbon fiber has been extensively used for multiple structural applications for decades [1]. For example, epoxy resin and woven carbon fiber composites are excellent options for structural materials in the automotive, aerospace, and construction industries due to their outstanding mechanical resistance and special features [2,3]. The combination of mechanical and electrical properties also makes carbon fiber an ideal candidate for structural electrodes in multifunctional energy storage devices [4]. Carbon based electrodes are commonly used in energy storage applications such as supercapacitors and new modifications of carbon fiber to improve electrical properties are being developed due to demands for smart and multifunctional materials for energy storage [4–6]. In particular, electrical performance of supercapacitors is well known to depend on a high surface area to ensure high concentration of ions at the interphase (electrode-electrolyte) [7]. In order to increase the surface area of electrodes made of carbon fiber fabric, several surface modifications have been implemented, such as etching with alkaline or acid treatments [8,9], deposition and grafting of carbon nanotubes (CNTs) [10-15] or nanoparticles with synthesis of carbon aerogel (CAG) [16], metal nanowires [17-19], new combinations of these variations [20] and lithium phosphate [21]. However, the modification of carbon fibers using some of these treatments increases the specific surface area at a cost of worsening the mechanical properties of the fiber, in particular those procedures where high temperatures or

excessive oxidation procedures are involved. There are several examples in the literature where it has been observed a decreased in tensile strength when CNTs are introduced by chemical vapor deposition [22-24]. CNT growth conditions, fiber pretreatments and fiber morphology are some of the parameters that influence the single fiber tensile properties. This represents a serious drawback, especially when the carbon fiber fabric will be used as electrodes for structural applications. Moreover, for structural applications using woven carbon fiber can limit their complete surface modification on the faces of the fiber that are inside the fabric. Despite enormous efforts, obtaining electrodes of woven carbon fiber with both good electrochemical and mechanical properties is still far from being completely reached [4].

Most studies have focused on the macroscopic characterization of the carbon fiber fabric, and often only on the finished electrical device [16,17,20,25]. However, the micro- and mesoscale characterization are also crucial to assess the potential interfacial benefits of the fiber in the composites and to predict their final properties. These characterizations are not always performed as they required special equipment and it is more difficult to handle single fibers than full bundles or fabrics [26,27].

Tests of modified carbon fibers for applications in structural energy storage have shown mixed results. The characterization of single carbon fiber activated with an alkaline treatment showed a higher mechanical strength of the activated fiber (3960 MPa) compared to the non-activated one (3290 MPa) [8]. However, the tensile strength of single carbon fibers soaked in KOH declined with exposure time from 3600 MPa after a few minutes to nearly 2600 MPa after 3 hours [9]. Moreover, detrimental effects were found when the carbon fibers were treated under oxidative atmospheres. More recently, deposition of CNT on carbon fiber gave rise to an increase of the surface area while maintaining mechanical performance if electrodes were assembled on the final structural supercapacitor [10].

For other applications, carbon fibers modified with functionalized CNT were analyzed by single fiber-composite fragmentation tests. The deposition process improved the fiber/matrix interfacial adhesion [28]. In CNT modified-carbon fibers, single fiber tensile test showed that CNT introduced with the PopTube Approach (microwave) reduced strength by 8-10% [29], quite negligible in comparison with a 56 % reduction when CNT were introduced by chemical vapor deposition (CVD) [30]. In contrast, the introduction of carbon nanotubes on carbon fibers by a combination of alternating electric field with electrophoretic deposition process of amine-functionalized CNT did not show a decrease in the tensile strength of the specimens, enhancing the wettability and adhesion at the interphase in the reinforced composites [31].

These studies have explored new modifications on carbon fiber for different applications, but research comparing the electrochemical and mechanical properties of carbon fiber after deposition and carbon particles growths (CNT, graphene nanoplatelets (GNP) or CAG) for structural energy storage applications remains limited.

In the present work, the viability of different carbon fiber modification approaches and the establishment of their suitability for structural supercapacitor application are analyzed. The mechanical and electrochemical properties of the most promising carbon-based modifications on carbon fibers were studied: GNP, MWCNT and CAG. First, the increase in BET area for each modification was assessed. Then, the increase in capacitance related to the increase in BET was analyzed. Finally, the effect of capacitance increase on the mechanical properties of the fiber was evaluated.

2 Experimental procedure

2.1 Materials

AS4C 3k 5H (Five Harness satin weave) fabric, manufactured by *Hexcel*, was used in this work. Graphene nanoplatelets grade C with a surface area of 500 m^2/g (GNP500) and 750 m^2/g

(GNP750) were provided by *XG Science Ltd*. Multiwall carbon nanotubes *NC7000* (MWCNT) with a surface area up to 300 m^2/g were purchased from *Nanocyl*. N,N-Dimethylformamide (DMF), resorcinol, formaldehyde (37 wt% in H_2O) and KOH were purchased from *Sigma-Aldrich*. The binder polyvinylidene fluoride (PVDF HSV900) was supplied by *Kynar.*

2.2 Preparation of structural electrodes

Electrodes were prepared modifying the surface of carbon fiber by deposition of different nanoparticles (GNP or MWCNT) or by synthesis of a carbon aerogel.

2.2.1 Spray Coating (SC) of nanoparticles

Solvent dispersions of 3 wt% GNP500, 3 wt% GNP750 or 1 wt% MWCNT were prepared in DMF by ultrasonication for 30 min and sprayed on the surface of a 14 × 7 cm carbon fiber fabric with a manual spray gun *Kripxe 840-LP* at 1 bar and 20 cm distance. Fabric was washed with acetone before any particle deposition. Additionally, 1 wt% of PVDF was added to all dispersions before ultrasonication to ensure adhesion of nanoparticles to the carbon fiber. Deposition was performed once on one side on the fabric and dried at 100 °C for 10 min. Then the process was repeated on the other side. Finally, fabric was dried at 100 °C until solvent evaporation.

2.2.2 Synthesis of carbon aerogel

Carbon aerogel (CAG) and carbon aerogel reinforced with nanoparticles (CAG-GNP750 or CAG-MWCNT) were synthesized on the surface of carbon fiber fabric following a method adapted from previous studies [10]. Resorcinol-formaldehyde (RF) resin was synthesized using resorcinol (R) and formaldehyde (F) solutions as precursors with KOH as a catalyst (C). An aqueous solution was prepared with a R:C molar ratio of 1:50. Formaldehyde was added to form a R:F solution with a molar ratio of 1:2. Distilled water was added to keep the RF

concentration at 40 wt.%. After 2 h of agitation, 3 wt.% of GNP750 or 1 wt% of MWCNT were added to the RF resin and dispersed in a sonication bath for 15 min.

Carbon fiber fabric of 6 × 4 cm was soaked in the RF mixtures for 2 h and then pressed between two steel plates fixed with clamps. Then, fabric was placed in an oven at 80 °C for 24 h for curing. After polymerization, coated fabric was dipped in acetone for 48 h and then dried at 60 °C. Organic aerogel on carbon fibers was carbonized at 800 °C for 30 min in a vacuum atmosphere (< 10^{-6} mbar).

2.3 Surface morphology and area characterization

Specific surface area of the modified carbon fiber fabric was calculated by Brunauer, Emmett and Teller (BET) method based on N_2 adsorption-desorption isotherms recorded with a Micrometrics ASAP 2020 analyzer. Fabric surface characterization was also performed evaluating the images form Scanning Electron Microscopy (SEM, *S-3400N* from *Hitachi*) and Field Emission Gun SEM (FEG-SEM, *Nova NanoSEM FEI 230* from *Philips*). Samples were previously coated by a 6 nm layer of gold for proper characterization.

2.4 Electrochemical characterization

Cyclic voltammetry (CV) tests on modified carbon fibers were performed at room temperature with a three-electrode cell, using a Ag/AgCl reference electrode and a platinum counter electrode in 3M KCl aqueous electrolyte. The working electrode consisted of a single tow partly immersed into the electrolyte and electrically contacted at the dry end. Tows were measured and weighted before the test and active mass (m_a) of the working electrode was determined from the immersed length.

Experiments were conducted using an *Autolab PGSTAT302N* system. Different scan rates (from 1 to 100 mV/s) were tested on a representative specimen from each condition. Specific

capacitance (C_{sp}) was calculated with Equation (1). Representative capacitance results were calculated using a potential window (ΔV) from -0.1 V to 0.1 V and a scan rate (s) of 5 mV/s.

$$C_{sp} = \frac{\int_{V_0}^{V_f} I \, dV}{s \cdot \Delta V \cdot m_a} \quad (1)$$

Electrochemical capacitance behavior of the structural electrodes was also compared using a quantitative assessment of the CV curves [32]. Hysteresis index (HI) along the potential window of the CV curve describes the capacitor behavior. It was calculated at the maximum difference in current at the same potential (HI1) and the average different in current along the CV curve (HI2). Values of HI1 and HI2 range from 0 (no hysteresis) to 1 (ideal capacitor).

2.5 Mechanical characterization

Single fiber tensile tests were performed to mechanically characterize the electrodes. Tests were carried out according to the standard ASTM C1557-14 using an in-situ tensile test machine from *Deben UK Ltd.* with a load cell of 2 N.

Following the standard protocol, a single fiber was separated from the bundle with extreme care and glued with LOCTITE 401 at either end onto a paper tab (Figure 1). A mounting platform was designed to ensure the alignment of the single fiber on the paper tab. The platform consisted of a central alignment area where the paper tab was fixed with two lateral supports aligning the fiber. It was manufactured by FFF 3D printing (FFF, Fused Filament Fabrication) with 100 µm layer thickness to achieve the level of precision required.

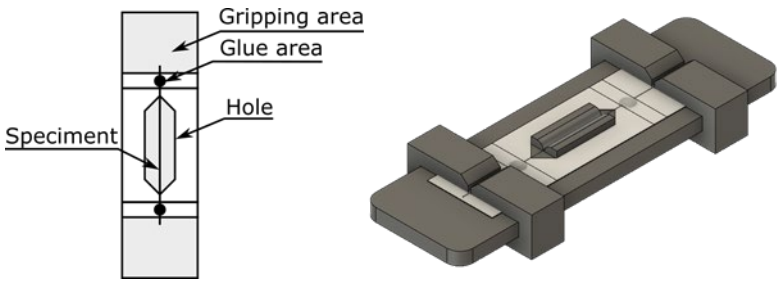

Fig. 1 Paper tab (left) and mounting platform (right) for single fiber tensile test

After the fiber was glued, the tab was removed from the mounting platform, placed on the tensile test machine and the lateral tab areas were cut. Tests were performed at a crosshead speed of 1 mm/min to achieve strength of fracture within 30 s and a gauge length of 15 mm. At least 15 measurements were conducted for each condition. Compliance of the system was calculated with carbon fiber specimens at gauge lengths of 10, 12 and 15 mm. At least three tests were performed for each gauge length.

Statistical evaluation of tensile strength results was performed with two-parameter Weibull distribution [33], described by Equation 2. Cumulative probability of failure (P_F) of single carbon fiber depends on specimen length (L), tensile strength (σ_f), Weibull scale parameter (σ_o) and reference gauge length (L_o).

$$P_F = 1 - exp\left[-\frac{L}{L_o}\left(\frac{\sigma_f}{\sigma_o}\right)^m\right] \tag{2}$$

The Weibull shape parameter or modulus (m) was determined by plotting of the rearranged two-parameter Weibull distribution of Equation 3 [34].

$$ln\left(ln\left[\frac{1}{1-P_F}\right]\right) = m\,ln(\sigma_f) - m\,ln\left(\sigma_o\left(\frac{L_o}{L}\right)^{1/m}\right) \tag{3}$$

Due to the variability in mechanical properties of advanced ceramics, the test procedure was evaluated on the non-treated carbon fiber with single fiber tensile tests on 40 specimens. As the statistical evaluation of the tensile test for non-treated carbon fibers shows expected values,

sample preparation and test procedures were considered suitable for mechanical characterization. Therefore, the number of tested specimens was reduced to 15 for the other conditions studied in order to allow faster characterization.

3 Results

3.1 Surface morphology of electrodes

Both the nanoparticle type and the deposition technique influenced surface morphology (Figure 2). As supplied, the carbon fiber had a uniform texture with almost no defect or pore on the surface (Figure 2a).

In general, particles deposited by spray coating were homogeneously distributed on the fabric surface (Figure 2b, c and d), although some agglomerates were observed in the gaps between fibers. The GNP did not strongly increase the surface area of the fabric, because the particles tended to lay with their basal plane facing the fiber surface (Figures 2b and c). Similar results were found in previous studies of GNP deposition on glass fabric [35]. On the other hand, MWCNT particles tended to tangle (Figure 2d) reducing the exposed area and increasing the presence of agglomerates.

Direct synthesis of CAG on the fabric produced a rough surface (Figure 2e), with a uniform layer of CAG covering the fibers and the inter-fiber gaps. Nanoparticles (GNP750 or MWCNT) added to the CAG showed a good dispersion, producing some agglomerates in located regions (Figures 2f-2i).

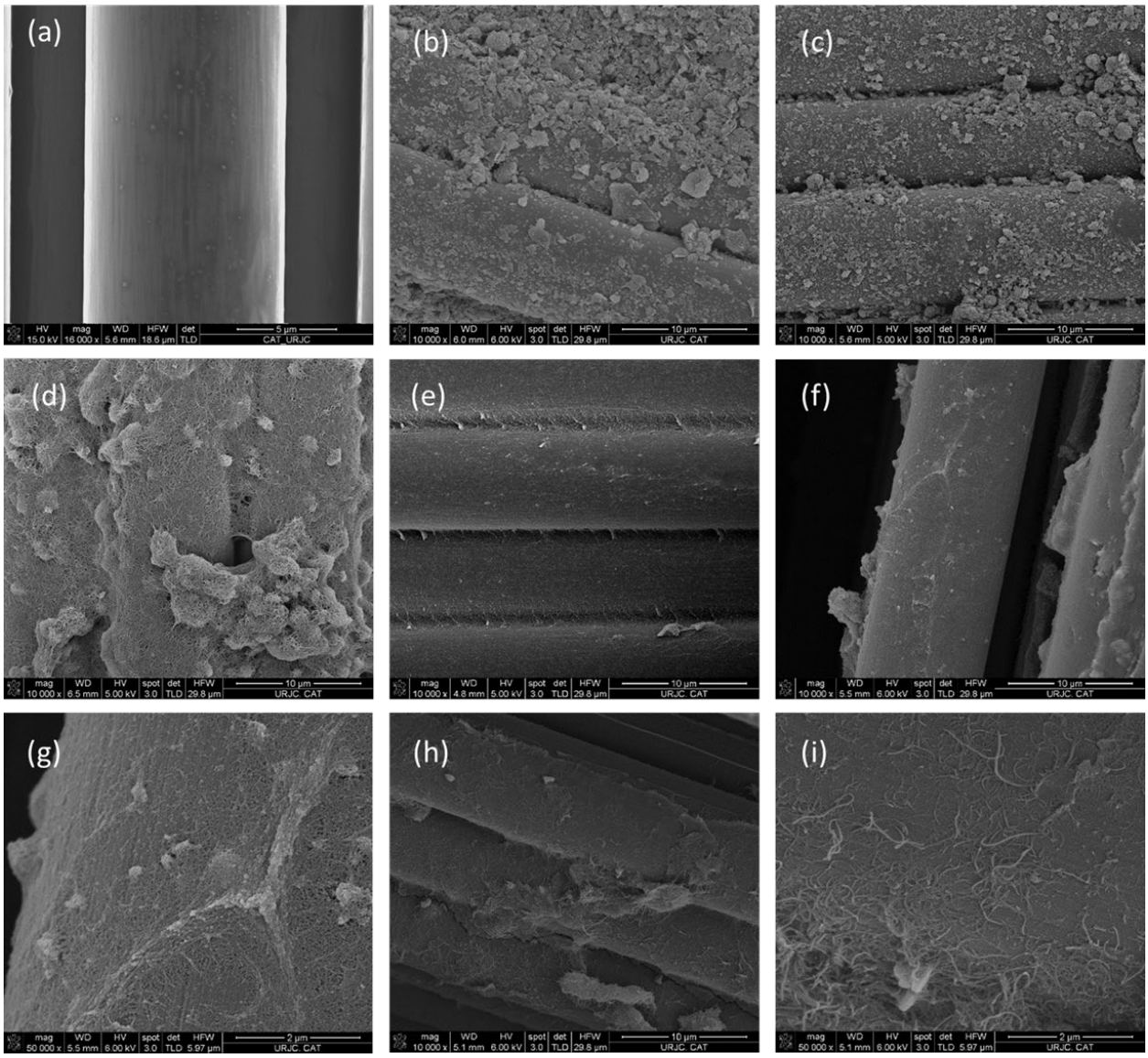

Fig. 2 FEG-SEM images of (a) reference carbon fiber, as well as carbon fiber modified with (b) SC-GNP500, (c) SC-GNP750, (d) SC-MWCNT, (e) CAG, (f,g) CAG-GNP750, (h,i) CAG-MWCNT

Increase of surface area was achieved with the modification of the carbon fiber (Table 1). Initial surface area in WCF was low without significant contribution from micro and mesopores. Particles with higher initial surface area (GNP750) increased the surface area of carbon fibers significantly more than GNP500 and MWCNT. The greatest increase of surface area was achieved with the synthesis of CAG.

Table 1 Specific surface area (S_{BET}), micro- and mesopores surface area (S_{micro}, S_{meso}) and specific capacitance (C_{sp}) of reference fiber and modification conditions.

Sample	S_{BET} (m^2/g)	S_{micro} (m^2/g)	S_{meso} (m^2/g)	C_{sp} (F/g)
WCF	0.04	-	-	0.017
SC-GNP500	2.29	0.37	1.92	0.073
SC-GNP750	4.72	0.11	4.61	0.408
SC-MWCNT	0.53	0.44	0.09	0.015
CAG	54.61	23.46	31.15	4.35
CAG-GNP750	63.95	28.18	35.78	2.55
CAG-MWCNT	66.18	27.93	38.26	3.95

Our results suggest two factors are important for the use of nanoparticles modification of carbon fiber. 1) Agglomerates of particles reduced the increase in surface area. Use of binder improve the adherence of the nanoparticles but also promotes this undesired reduction of exposed area. 2) An excess of particles also reduces the increase in surface area. MWCNT were particularly prone to both factors, which created a more compact coating and reduced the formation of mesopores on the surface. GNP performed best by showing less agglomerates and excess of particles. The synthesized CAG layer also had a good morphology, but it is important to keep the CAG layer thin to improve the ion diffusion and electrolyte penetration [36].

Agglomerates also limited the increase of surface area of CAG-GNP750 and MWCNT. The dispersion of particles during the CAG preparation was not enough to break all the agglomerates. Longer dispersion time will start the curing process of the RF resin due to the heat generated by ultrasonication.

3.2 Electrochemical properties of electrodes

An increase in scan rates from 1 to 100 mV/s caused a decrease in the capacitance (Figure 3a). Shapes of CV curves were symmetric and smooth. This indicated a behavior of the electrodes typical of capacitive materials and the absence of redox peaks, i.e., a lack of electrochemical reaction on the carbon electrodes [37]. The decrease of capacitance with the scan rate is typical from carbon-based electrodes and is associated with micropore blocking and their ionic resistance [38,39].

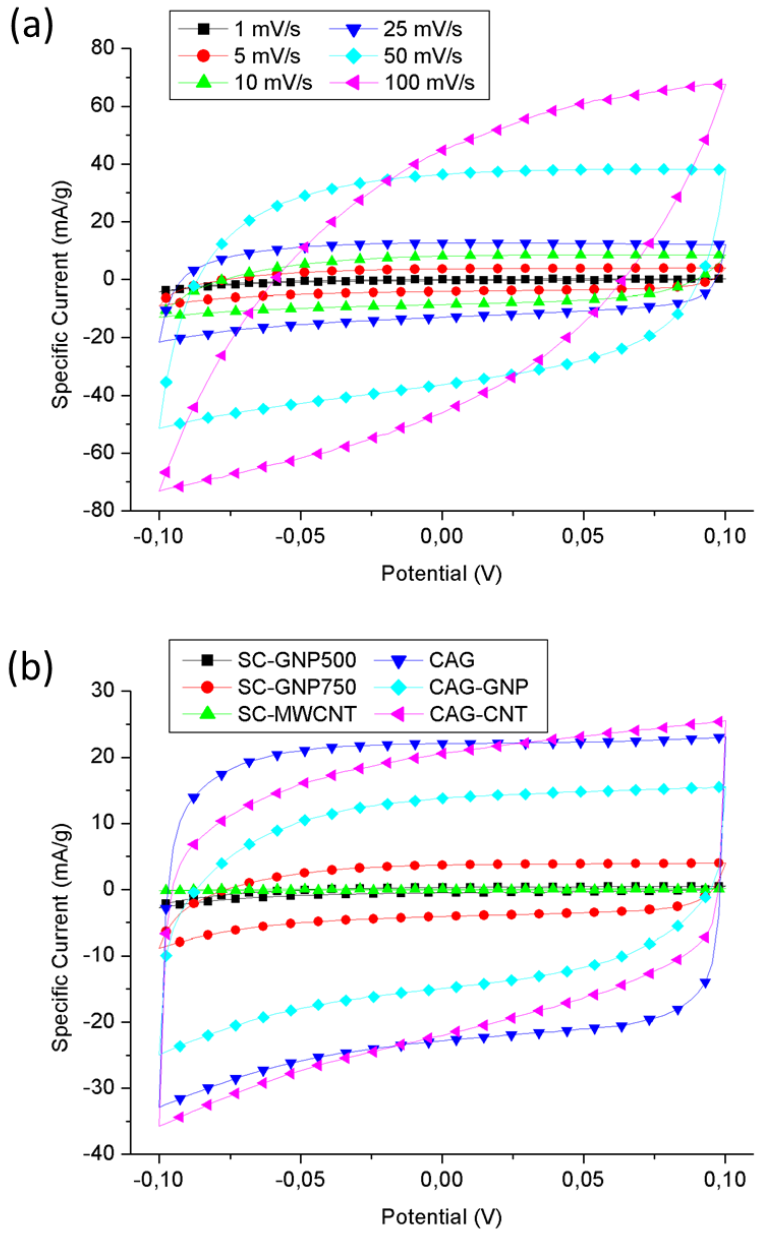

Fig. 3 CV curves of SC-GNP750 at different scan rates (a) and carbon fiber modifications at 5 mV/s (b)

A comparison of the different surface modification techniques at a scan rate of 5 mV/s (Figure 3b) showed that non-treated carbon fibers had very low capacity to store energy, as expected due to its small surface area. Deposition of nanoparticles on the surface of the carbon fiber fabric increased both its surface area and specific capacitance (Table 1). The deposition of GNP significantly increased capacitance more than MWCNT because carbon nanotubes tend to tangle and agglomerate. The mesopores contributed significantly to the capacitance increase.

The lack of mesopores that connect with micropores reduced the exposed area to the electrolyte. The highest increase of capacitance was achieved with the synthesis of CAG on the surface (Table 1), due to its higher surface area and a better contribution of both micro and mesopores. The addition of GNP750 or MWCNT to the CAG did not cause an additional increase of capacitance maybe due to these particles could be blocking some of the channel that connect different pores.

The type of particle influenced the increase of capacitance. Theoretically, this increase should be related to the increase in specific surface area [7]. In line with this, deposition of any of the tested GNP led to a higher increase in capacitance than MWCNT. GNP particles have a greater number of edges than MWCNT, which enhances the specific capacitance because electrochemical interaction with the electrolyte is higher on the edges of the carbon sheets than on the basal plane [40]. Polymeric PVDF binder added to sprayed particles limited the capacitance results, as it reduced electrical conductivity of the layer deposited on the electrodes. The highest values of capacitance and surface area were achieved by CAG. Capacitance obtained with CAG was close to the values achieved by previous studies, regarding the surface area of the samples [16]. Despite the high initial surface area of GNP750 and MWCNT, their addition to CAG did not show increase of capacitance due to the negative effect of agglomerates on the increase in capacitance. Addition of well dispersed GNP particles to CAG has shown increase in capacitance of supercapacitors structures [20].

Maximum and average HI for CAG modified fabric were 0.84 and 0.77, respectively, for CAG modified fabric, 0.61 and 0.50 for SC-MWCNT and 0.33 and 0.30 for SC-GNP750. The HI index of the different electrodes prepared with CAG were similar to the values of other carbon fiber electrodes studied before [9] but spray coated electrodes were not close to the ideal values for supercapacitors [32].

3.3 Mechanical properties of electrodes

Mean values of strength and elastic modulus (Table 2) were similar to the properties published by the manufacturer. Tensile strength was the mechanical property with higher standard deviation, up to 22% deviation from the mean value. Statistical evaluation of tensile strength with Weibull modulus (Figure 4) showed values expected for non-treated carbon fiber tensile test results [41].

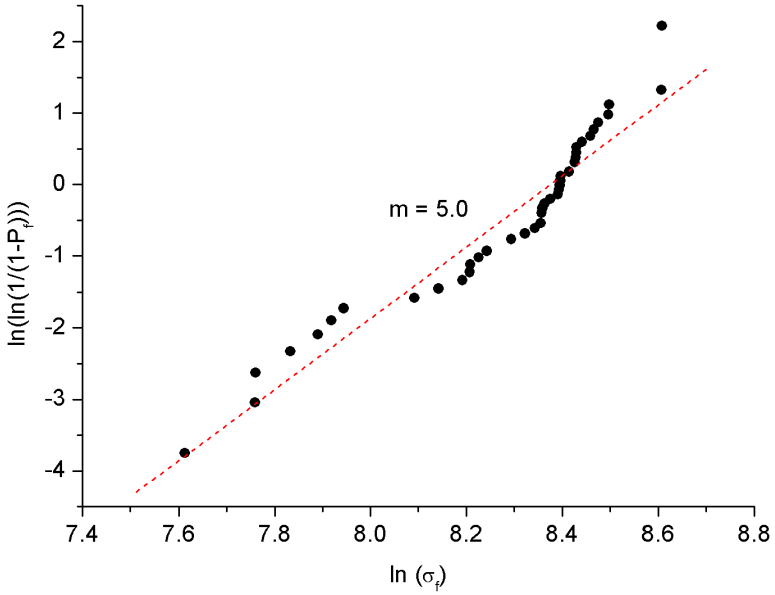

Fig. 4 Statistical distribution of single fiber tensile test results for pristine carbon fiber

Mechanical properties were not affected by most of the modifications of the fibers (Table 2). Sprayed particles were anchored by PVDF binder that created an adhesive bond without creating defects on the surface that would compromise mechanical behavior. A reduction of up to 32 % of tensile strength was caused by the synthesis of CAG on the surface of the fibers. This could be due to defects on the carbon fiber surface created during the calcination process. For example, RF resin used as base for the CAG contains oxygen on its chemical structure that could react with the carbon fiber at the high temperatures used during the process. Tensile strength of CAG-carbon fiber electrodes has not been studied, but previous studies of shear

strength [16,20] suggest improvements of the interface strength that might improve the overall mechanical behavior.

Standard deviation of tensile strength was considered suitable as the Weibull modulus for all the samples were similar between them and close to the expected values [41].

Table 2 Mechanical properties and Weibull modulus (*m*) of carbon fiber and modification conditions

Sample	σ_f (MPa)	E (GPa)	*m*
WCF	4035 ± 830	200 ± 25	5.0
SC-GNP 500	3614 ± 429	193 ± 22	10.4
SC-GNP 750	3848 ± 859	191 ± 12	5.1
SC-MWCNT	3789 ± 830	194 ± 8	4.9
CAG	2475 ± 547	180 ± 14	5.3
CAG-GNP750	3048 ± 517	202 ± 15	6.5
CAG-MWCNT	2992 ± 674	196 ± 13	4.5

3.4 Multifunctional electrode suitability

Multifunctional electrodes for structural applications require a combination of good capacitance and mechanical properties. SC-GNP750 electrodes presented a good combination of both properties. Capacitance of these electrodes was lower than the CAG, but mechanical properties were similar to those of the original carbon fiber. The advantages of SC deposition are that (1) it did not affect mechanical properties and (2) it is a technique that allows more flexibility than direct synthesis, e.g., modification on a larger surface of fabric is possible without a high increase of manufacturing costs. It is also easier to adapt the geometry of the electrodes to the requirements of the final component.

By contrast, CAG electrodes face four significant limitations. First, they have reduced mechanical properties, although the tensile strength values achieved are still high enough for other structural applications. Second, the size of the electrodes is small for a structural component. Third, its implementation is difficult and expensive, as it required calcination at 800 °C in a vacuum atmosphere. And fourth, geometry of the electrodes is limited by the rigidity of the CAG layer on the fabric.

4 Conclusions

Multifunctional electrodes for structural applications were produced using carbon fiber. Surface modification of carbon fiber fabric increased energy storage capacitance, by overcoming the lack of surface area of the original carbon fiber. Particle size and modification technique had a high influence on the increase in surface area, which drove increased capacitance. Electrodes produced by spray deposition of GNP750 showed enough capacitance for energy storage while maintaining the mechanical properties of the original carbon fiber. Further optimization of the limiting effect of the polymeric binder on the capacitance would produce good electrode candidates for structural applications such as in electric vehicles. CAG surface modification showed the highest capacitance, which made them good electrodes for supercapacitors. However, reduction on its mechanical properties limited its structural applications although its multifunctionality cannot be completely discarded, as its mechanical properties remained sufficient.

Acknowledgements

This work was supported by the Agencia Estatal de Investigación of the Spanish Government (project MULTIFUNC-EVs PID2019-107874RB-I00) and Comunidad de Madrid regional government (project ADITIMAT-CM (P2018/NMT-4411)).

Declarations

Funding

This work was supported by the Agencia Estatal de Investigación of the Spanish Government (project MULTIFUNC-EVs PID2019-107874RB-I00) and Comunidad de Madrid regional government (project ADITIMAT-CM (P2018/NMT-4411)).

Conflicts of interest/Competing interests

The authors have no conflicts of interest to declare that are relevant to the content of this article.

Availability of data and material

All data generated or analysed during this study are included in this published article.

References

[1] S.-J. Park, M.-K. Seo, Carbon Fiber-Reinforced Polymer Composites: Preparation, Properties, and Applications, in: Polym. Compos., Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, 2012: pp. 135–183. https://doi.org/10.1002/9783527645213.ch5.

[2] K.K. Sairajan, G.S. Aglietti, K.M. Mani, A review of multifunctional structure technology for aerospace applications, Acta Astronaut. 120 (2016) 30–42. https://doi.org/10.1016/j.actaastro.2015.11.024.

[3] P.K. Mallick, Fiber-Reinforced Composites, CRC Press, 2007. https://doi.org/10.1201/9781420005981.

[4] N. Forintos, T. Czigany, Multifunctional application of carbon fiber reinforced polymer composites: Electrical properties of the reinforcing carbon fibers – A short review, Compos. Part B Eng. 162 (2019) 331–343. https://doi.org/10.1016/j.compositesb.2018.10.098.

[5] C. González, J.J. Vilatela, J.M. Molina-Aldareguía, C.S. Lopes, J. LLorca, Structural composites for multifunctional applications: Current challenges and future trends, Prog. Mater. Sci. 89 (2017) 194–251. https://doi.org/10.1016/j.pmatsci.2017.04.005.

[6] R.F. Gibson, A review of recent research on mechanics of multifunctional composite materials and structures, Compos. Struct. 92 (2010) 2793–2810. https://doi.org/10.1016/j.compstruct.2010.05.003.

[7] B.E. Conway, Electrochemical Supercapacitors, Springer US, Boston, MA, 1999. https://doi.org/10.1007/978-1-4757-3058-6.

[8] 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 A Appl. Sci. Manuf. 46 (2013) 96–107. https://doi.org/10.1016/j.compositesa.2012.10.007.

[9] 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.

[10] 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.

[11] H. Qian, E.S. Greenhalgh, M.S.P. Shaffer, A. Bismarck, Carbon nanotube-based hierarchical composites: A review. J. Mater.Chem. 20 (2010) 4751-4762. https://doi.org/10.1039/C000041H.

[12] J. Karger-Kocsis, H. Mahmood, A. Pegoretti. All-carbon multi-scale and hierarchical fibers and related structural composites: A review. Compos. Sci. Tech. 186 (2020) 107932. https://doi.org/10.1016/j.compscitech.2019.107932.

[13] Lavagna L, Nisticò R, Musso S, Pavese M. Functionalization as a way to enhance dispersion of carbon nanotubes in matrices: a review. Mater. Today Chem. 20 (2021) 100477. https://doi.org/10.1016/j.mtchem.2021.100477.

[14] L. Lavagna, D. Massella, M.F. Pantano, F. Bosia, N.M. Pugno, M. Pavese, Grafting carbon nanotubes onto carbon fibres doubles their effective strength and the toughness of the composite. Compos. Sci. Tech. 166 (2018) 140-149. https://doi.org/10.1016/j.compscitech.2018.03.015.

[15] Lavagna L, Massella D, Pavese M. Preparation of hierarchical material by chemical grafting of carbon nanotubes onto carbon fibers. Diamond and Related Materials 80 (2017) 118-124. https://doi.org/10.1016/j.diamond.2017.10.013.

[16] 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.

[17] B.K. Deka, A. Hazarika, J. Kim, Y.-B. Park, H.W. Park, Multifunctional CuO nanowire embodied structural supercapacitor based on woven carbon fiber/ionic liquid–polyester resin, Compos. Part A Appl. Sci. Manuf. 87 (2016) 256–262. https://doi.org/10.1016/j.compositesa.2016.05.007.

[18] B.K. Deka, A. Hazarika, Ob. Kwon, D.Y. Kim, Y. Bin Park, H.W. Park, Multifunctional enhancement of woven carbon fiber/ZnO nanotube-based structural supercapacitor and polyester resin-domain solid-polymer electrolytes, Chem. Eng. J. 325 (2017) 672–680. https://doi.org/10.1016/j.cej.2017.05.093.

[19] B.K. Deka, A. Hazarika, J. Kim, N. Kim, H.E. Jeong, Y.-B. Park, H.W. Park, Bimetallic copper cobalt selenide nanowire-anchored woven carbon fiber-based structural supercapacitors, Chem. Eng. J. 355 (2019) 551–559. https://doi.org/10.1016/j.cej.2018.08.172.

[20] A. Javaid, M. Irfan, Multifunctional structural supercapacitors based on graphene nanoplatelets/carbon aerogel composite coated carbon fiber electrodes, Mater. Res. Express. 6 (2018) 016310. https://doi.org/10.1088/2053-1591/aae862.

[21] 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.

[22] H. Qian, A. Bismarck, E. S. Greenhalgh and M. S. P. Shaffer, Carbon nanotube grafted carbon fibres: A study of wetting and fibre fragmentation. Composites, Part A, 41 (2010) 1107-1114. https://doi.org/10.1016/j.compositesa.2010.04.004.

[23] Q. H. Zhang, J. W. Liu, R. Sager, L. M. Dai and J. Baur, , Hierarchical composites of carbon nanotubes on carbon fiber: Influence of growth condition on fiber tensile properties. Compos. Sci. Technol. 69 (2009) 594–601. https://doi.org/10.1016/j.compscitech.2008.12.002.

[24] R. J. Sager, P. J. Klein, D. C. Lagoudas, Q. Zhang, J. Liu, L. Dai and J. W. Baur, Effect of carbon nanotubes on the interfacial shear strength of T650 carbon fiber in an epoxy matrix. Compos. Sci. Technol., 69 (2009) 898–904. https://doi.org/10.1016/j.compscitech.2008.12.021

[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, Electrochim. Acta. 370 (2021). https://doi.org/10.1016/j.electacta.2021.137746.

[26] A. Castellanos-Gomez, A simple method to characterize the electrical and mechanical properties of micro-fibres, Eur. J. Phys. 34 (2013) 1547–1554. https://doi.org/10.1088/0143-0807/34/6/1547.

[27] J. Xu, W. Johannisson, M. Johansen, F. Liu, D. Zenkert, G. Lindbergh, L.E. Asp, Characterization of the adhesive properties between structural battery electrolytes and carbon fibers, Compos. Sci. Technol. 188 (2020) 107962. https://doi.org/10.1016/j.compscitech.2019.107962.

[28] M. Li, Y. Gu, Y. Liu, Y. Li, Z. Zhang, Interfacial improvement of carbon fiber/epoxy composites using a simple process for depositing commercially functionalized carbon nanotubes on the fibers, Carbon N. Y. 52 (2013) 109–121. https://doi.org/10.1016/j.carbon.2012.09.011.

[29] W. Guin, J. Wang, X. Zhang, J. Smith, Carbon nanotube-reinforced hybrid composites enabled by the PopTube approach, Proc. Am. Soc. Compos. 29th Tech. Conf. (2014).

[30] Q. Zhang, J. Liu, R. Sager, L. Dai, J. Baur, Hierarchical composites of carbon nanotubes on carbon fiber: Influence of growth condition on fiber tensile properties, Compos. Sci. Technol. 69 (2009) 594–601. https://doi.org/10.1016/j.compscitech.2008.12.002.

[31] E. Moaseri, M. Karimi, M. Maghrebi, M. Baniadam, Two-fold enhancement in tensile strength of carbon nanotube–carbon fiber hybrid epoxy composites through combination of electrophoretic deposition and alternating electric field, Int. J. Solids Struct. 51 (2014) 774–785. https://doi.org/10.1016/j.ijsolstr.2013.11.007.

[32] M. Kosmulski, P. Próchniak, C. Saneluta, M. Kosmulski, P. Próchniak, · C Saneluta, Quantitative assessment of hysteresis in voltammetric curves of electrochemical capacitors, Adsorption. 15 (2009) 172–180. https://doi.org/10.1007/s10450-009-9169-6.

[33] W. Weibull, A Statistical Distribution Function of Wide Applicability, J. Appl. Mech. Vol. 18 (1951) 293–297.

[34] K. Naito, J.-M. Yang, Y. Tanaka, Y. Kagawa, The effect of gauge length on tensile strength and Weibull modulus of polyacrylonitrile (PAN)- and pitch-based carbon fibers, J. Mater. Sci. 47 (2012) 632–642. https://doi.org/10.1007/s10853-011-5832-x.

[35] R. Moriche, A. Jiménez-Suárez, M. Sánchez, S.G. Prolongo, A. Ureña, Graphene nanoplatelets coated glass fibre fabrics as strain sensors, Compos. Sci. Technol. 146 (2017) 59–64. https://doi.org/10.1016/j.compscitech.2017.04.019.

[36] L.L. Zhang, X.S. Zhao, Carbon-based materials as supercapacitor electrodes, Chem. Soc. Rev. 38 (2009) 2520. https://doi.org/10.1039/b813846j.

[37] Y. Zhu, H. Hu, W. Li, X. Zhang, Resorcinol-formaldehyde based porous carbon as an electrode material for supercapacitors, Carbon N. Y. 45 (2007) 160–165. https://doi.org/10.1016/J.CARBON.2006.07.010.

[38] J. Wang, X. Yang, D. Wu, R. Fu, M.S. Dresselhaus, G. Dresselhaus, The porous structures of activated carbon aerogels and their effects on electrochemical performance, J. Power Sources. 185 (2008) 589–594. https://doi.org/10.1016/J.JPOWSOUR.2008.06.070.

[39] K.-L. Yang, S. Yiacoumi, C. Tsouris, Electrosorption capacitance of nanostructured carbon aerogel obtained by cyclic voltammetry, J. Electroanal. Chem. 540 (2003) 159–167. https://doi.org/10.1016/S0022-0728(02)01308-6.

[40] A. Ambrosi, T. Sasaki, M. Pumera, Platelet Graphite Nanofibers for Electrochemical Sensing and Biosensing: The Influence of Graphene Sheet Orientation, Chem. - An Asian J. 5 (2010) 266–271. https://doi.org/10.1002/asia.200900544.

[41] T. Tagawa, T. Miyata, Size effect on tensile strength of carbon fibers, Mater. Sci. Eng. A. 238 (1997) 336–342. https://doi.org/10.1016/S0921-5093(97)00454-1.