

## STRUCTURAL POWER COMPOSITES FOR HYBRID VEHICLES (STORAGE)

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### Abstract

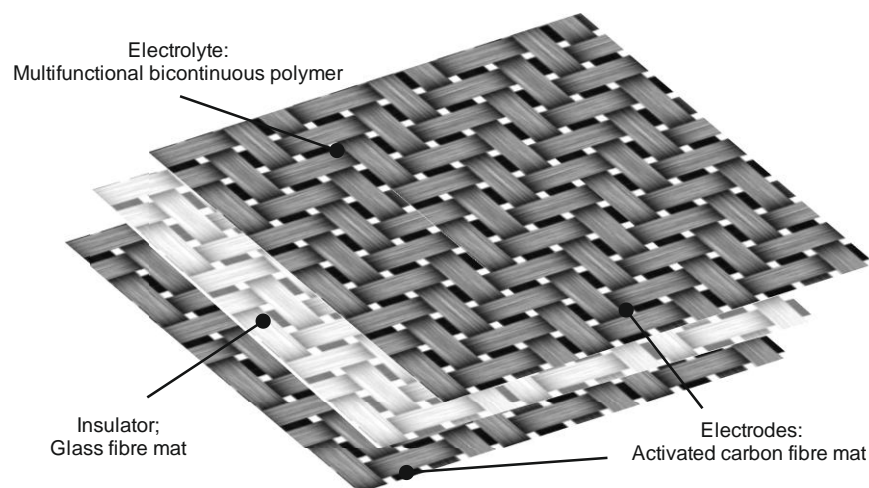
*Composite engineers have made considerable strides forward in the development of new constituents, architectures and processing routes, leading to an unprecedented ability to tailor and optimise the properties of the resulting composites. Recently there has been interest in developing multifunctional materials which exhibit dual, and distinctly different, capabilities. Structural power composites; multifunctional materials that carry mechanical loads whilst storing (and delivering) electrical energy, are the focus of this paper. The progress made by the STORAGE consortium, who have been using structural power materials for hybrid automotive applications, is presented. In particular, the progress made in the constituent development, the resulting composites, systems and demonstration is discussed.*

### 1 Introduction

Current engineering design demands efficient material utilisation; weight and volume are at a premium on many components and any material that does not contribute to the load-carrying capacity is structurally parasitic. For example, consider an electric vehicle that consists of structural materials, electrical systems, power sources, etc; the total weight is limited, and therefore compromises are made on parameters such as range, performance and durability. The conventional approach to system design pursues optimisation of the individual components by using materials with improved specific properties. The alternative is to formulate multifunctional materials that can perform two or more functions simultaneously. This design approach is in its infancy and faces considerable design and material synthesis challenges [1][2], requiring the combination of disparate and often cross-cutting phenomena. However, recently composite engineers have made considerable strides forward in the development of new constituents, architectures and processing routes, leading to an unprecedented ability to tailor and optimise the properties of the resulting materials [3]. The focus of the work reported here are *structural power composites*; multifunctional materials that carry mechanical loads whilst storing (and delivering) electrical energy. In such a material the constituents simultaneously and synergistically undertake two roles; electrical energy storage and carry mechanical load [4][5]. This should be distinguished from a *multifunctional structural* approach, in which distinct constituent components are packaged together to minimise mass or volume; for example, embedding thin batteries into a composite laminate [1][6][7]. Carbon fibre composites are an attractive starting point for structural power materials as carbon is commonly used both for electrodes [8] and as high performance structural reinforcements. Although the forms of carbon used for these applications are

different, combination of these roles can be achieved by appropriate modification of the fibres. Similarly, polymers can be used both as a structural matrix and as an electrolyte [9].

STORAGE [10] is an EU funded project focused on the development of structural power composites for hybrid cars. Academic institutes (Imperial College London and Chalmers) and research providers (Swerea SICOMP, BAM and INASCO) are providing the fundamental science and development. Material and device scale-up is being undertaken by ETC, Nanocyl and Umeco and Volvo Car Corporation are implementing the technology. STORAGE has been focused on three different types of energy storage; structural batteries, structural capacitors and structural supercapacitors, although the focus here is the latter. Conventional supercapacitors typically have energy and power densities of 5 Wh kg<sup>-1</sup> and 0.2-10 kW kg<sup>-1</sup> respectively [11]. They consist of two electrodes which sandwich an ionically-conducting but electronically insulating separator all of which is embedded within an electrolyte [12]. The energy is stored by the accumulation of charges at the boundary between electrode and electrolyte; the nanometre charge separation gives high capacitance. The amount of stored energy is a function of the available electrode surface, and the ion size and concentration.



**Figure 1.** Illustration of architecture of the structural supercapacitor

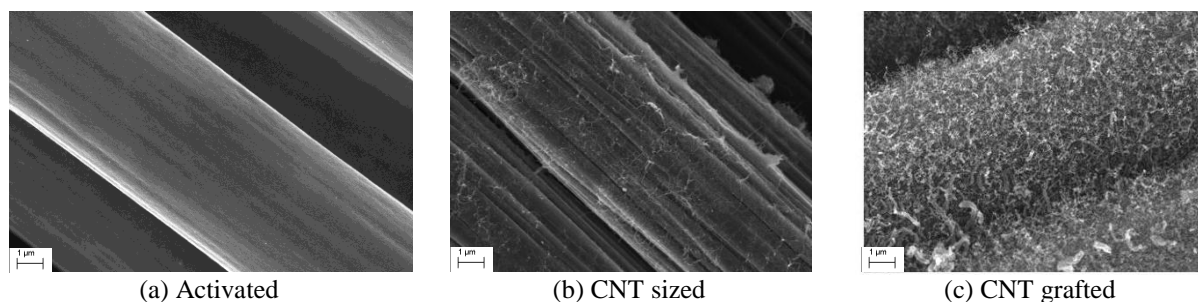
Figure 1 shows the configuration of the structural supercapacitor; this consists of woven carbon fibre (CF) reinforcements/electrodes which sandwich a woven glass fibre (GF) separator, all of which is embedded within a multifunctional matrix/electrolyte. The objective of this paper is to provide background into the development of structural supercapacitors and report on the progress made by the STORAGE consortium. The paper will discuss the developments in the constituents; the reinforcements and the matrix, and then present the development of the composites. In parallel with these material developments, the systems issues are presented, leading to the development of prototype devices. Finally, the insights gained are presented, and a review of the future hurdles in utilising these materials is given.

## 2 Constituent Development

### 2.1 Reinforcement Development

As can be seen in Figure 1, the requirements of the two reinforcement constituents; the electrodes (carbon-fibres) and the separator, are very different. Firstly, the electrodes are not only required to have excellent stiffness and strength, but also a high (electrochemical) surface area to enhance electrical energy storage; the amount of charge stored is generally proportional to the specific surface area [13]. The baseline electrodes chosen for STORAGE

was T300 carbon fibres (5HS weave) and several strategies were pursued to enhance the electrical properties (Figure 2). Firstly, activation was investigated (Figure 2a), in which the fibres were exposed to KOH to increase their surface area via the formation of mesopores. This approach succeeded in increasing the fibre surface area by over two decades, without any loss in mechanical performance. In fact, there is evidence [14] that the activation process mechanically enhances the fibre/matrix interface, but this was to the detriment to ionic access to the fibre pores. Ultimately, the multistage batch process which activation entails was not amenable to scale-up so it was not pursued further in STORAGE.



**Figure 2.** Different carbon fibre modification strategies

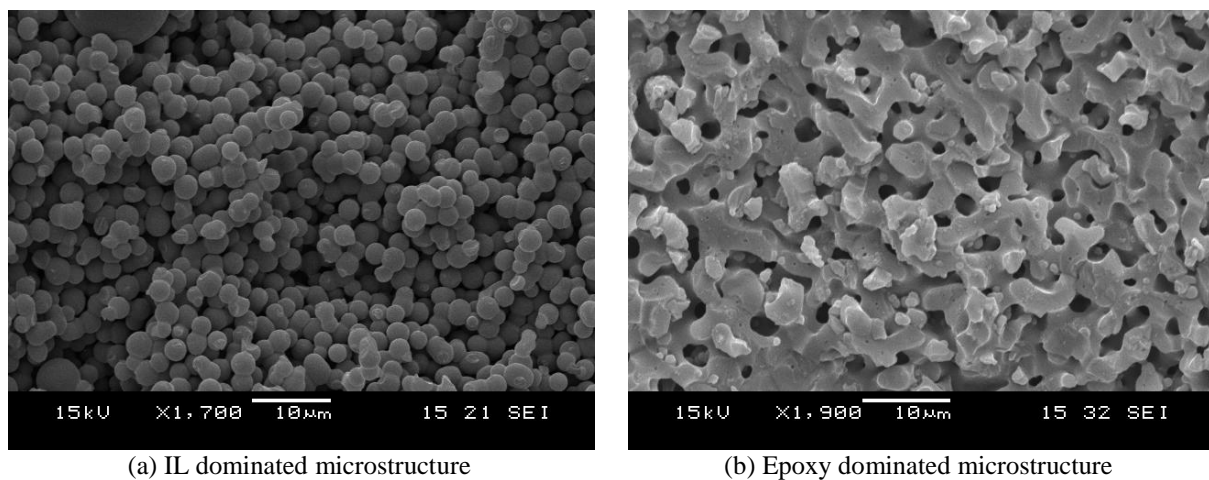
The next two approaches, led by Nanocyl, were to add a size (Figure 2b) or graft (Figure 2c) the fibres with carbon nanotubes (CNTs). The motivation was that this would not only provide increased surface area, but also the CNTs would provide mechanical support to the surrounding matrix, thus enhancing both compressive and delamination properties [15]. CNT sizing (Figure 2b) entailed immersing the weave in a solution of CNTs and then pyrolysing in an inert atmosphere to bind the CNTs to the fibre surfaces. Although this process was scalable, the bond between the CNTs and the fibres was relatively weak. The second approach was to grow CNTs in-situ onto the fibre surfaces using a catalytic decomposition of gaseous reactants over a catalytic precursor at a moderate temperature, as has been pursued by a number of researchers [15]. This approach results in intimate bonding of the CNTs to the host fabric, although costly and challenging to scale-up. Both these approaches increased the surface area by a factor of over two decades, and led to increases in specific capacitance. A final approach pursued in STORAGE has been to embed the carbon fibres in a carbon aerogel (CAG), and then infuse the matrix into the resulting laminate. This provides huge increases in surface area (nearly 500 times) and results in considerable increases in capacitance. Furthermore, initial studies [16] have demonstrated that CAG provides mechanical support to the carbon fibres, enhancing the resultant composite properties. Although challenging to scale-up, CAG does provide an elegant synergy between enhanced surface area and improved mechanical performance, and is the best way forward for future reinforcements.

The second aspect of the reinforcement, the separator, was originally considered to be a fairly trivial task; essentially identification of a material which is thin (to minimise the distance the ions need to migrate) and light (to minimize the weight penalty). However, it also needs to be impervious to the carbon fibres; i.e. not allowing any stray fibres to bridge the electrodes. Finally, it needs to provide a good interfacial bond to the electrodes to inhibit delamination. Initial studies assessed different glass fibre weaves, but unfortunately as the weight (and thickness) of the weave reduced, gaps were present at the interstitial sites in the weave, leading to short circuiting of the electrodes. Non-wovens were considered, such as papers or felts, but these offered no mechanical advantage and promoted delamination development. In addition, polypropylene films, such as those used in conventional supercapacitors and

batteries, were considered. Although these provided excellent electrical performance, they led to poor bonding, with delamination developing even during handling. For STORAGE, two layers of Umeco Style 120 glass fibre (plain weave) have been chosen as the separator. However, optimisation of this separator warrants further study, perhaps utilising technologies such as spread tows of non-conducting high performance fibres.

## 2.2 Multifunctional Matrix Development

The multifunctional electrolyte is perhaps the most challenging aspect of this class of material, since it must allow ion diffusion and provide mechanical stiffness and strength to ensure efficient load transfer and lateral support to the fibres, thus inhibiting microbuckling [17]. Prior to STORAGE various approaches have been taken [5][18], including polymerised vinyl ester derivatives of poly(ethylene glycol) in which lithium salt was dissolved, sometimes further enhanced by using fillers such as fumed silica [19]. Although this provided some enhanced capacitance, the mechanical properties were poor. The strategy for STORAGE has been to mix different constituents together to promote a bicontinuous structure at the sub-micron scale. Therefore, mixtures of a structural epoxy with an ionic liquid (IL) to provide the ions has been investigated. In addition, a third constituent, a lithium salt, was introduced to add further ions to the matrix and thus enhance the electrical performance. Different matrix formulations were formulated at Imperial College London, synthesised at Umeco, and then mechanically and electrically tested at BAM (Germany) and Chalmers (Sweden) respectively. The resulting studies have shown that modifying the ratio between these constituents led to a change in the microstructure of the matrix (Figure 3).



**Figure 3.** Different matrix microstructures with respect to the ratio of IL:Epoxy

When the IL was dominant, the structure was dominated by a beadlike morphology (such as that shown in Figure 3a) which exhibited good ionic conductivity but poor mechanical properties. Increasing the structural epoxy reversed this trend, and led to the formation of an open cell porous structure (such as that shown in Figure 3b). Furthermore for a given proportion of IL, as the lithium salt concentration increased the porous microstructure was promoted. Ultimately, based on these parametric studies, a 50:50 ratio of epoxy:IL (by weight) was chosen for composite fabrication, with two different lithium salt concentrations. It had been originally envisaged that both resin infused and prepregging routes would be pursued in STORAGE. However, a complicating effect which had not been anticipated was that the IL accelerated the epoxy cure kinetics, narrowing the processing window of the resulting matrix. Therefore, resin infusion was abandoned as a processing route; in the longer

term prepregging is perhaps a more attractive route anyway because it provides a means to 'lock-in' the mechanical and electrical properties of the resulting composites.

### 3 Composite Characterisation

#### 3.1 Composite fabrication

Clearly development and optimisation of the constituents does not necessarily lead to the best composite configuration. As is widely recognized, the interface between the fibres and matrix is critical to the properties, and this is particularly the case for multifunctional composites where very different aspects of performance are being optimised. The interfacial strength controls delamination resistance and consequently the damage tolerance [17]. However, it is within this interface that the energy can be stored in the form of the electrical double layer around the fibres. Therefore, an important phase in STORAGE has been the fabrication and characterization of the composite laminates. Umeco have been fabricating laminates using the range of different reinforcements described in Section 2.1, and using two different matrix formulations as described in Section 2.2. The basic laminate (cell) chosen for study has been a CF/GF<sub>2</sub>/CF configuration, which has a thickness of about 1mm; subsequent laminates were essentially multiples of this repeating cell. After fabrication the laminates were sealed in metalized film under vacuum to ensure negligible moisture could be absorbed during storage.

#### 3.1 Mechanical Testing

Firstly, considering mechanical testing, it was recognised that matrix or fibre/matrix interface dominated properties should be the focus of the study. However, since the composite had a woven rather than unidirectional architecture, characterisation of such properties were challenging. Therefore,  $\pm 45^\circ$  tension on a single cell (i.e. CF/GF<sub>2</sub>/CF) to characterise the in-plane shear stiffness and strength was chosen. Longitudinal compression tests (on monolithic CF laminates in a  $0^\circ/90^\circ$  lay-up) was pursued on (CF<sub>4</sub>)<sub>S</sub> configurations. Finally, interlaminar tests (DCB and ILSS) are being undertaken to characterize the CF/GF interface. These were 16 ply laminates with a [CF/GF<sub>2</sub>/CF<sub>2</sub>/GF<sub>2</sub>/PTFE/CF<sub>2</sub>/GF<sub>2</sub>/CF<sub>2</sub>/GF<sub>2</sub>/CF] stacking sequence. It was recognized that to characterize the CF/GF ply interface the PTFE insert could not be inserted at the mid-plane (since such a laminate would be unbalanced). Therefore, the decision was taken to grow the delamination just off the mid-plane, and use the measured toughness as a ranking rather than absolute value of delamination resistance. Finally, one aspect of these materials which is not a primary concern for conventional structural composites is the effect of short-term moisture exposure on the electrical and mechanical properties. Therefore, during characterisation, a methodology has been formulated which ensures the influence of moisture is accounted for.

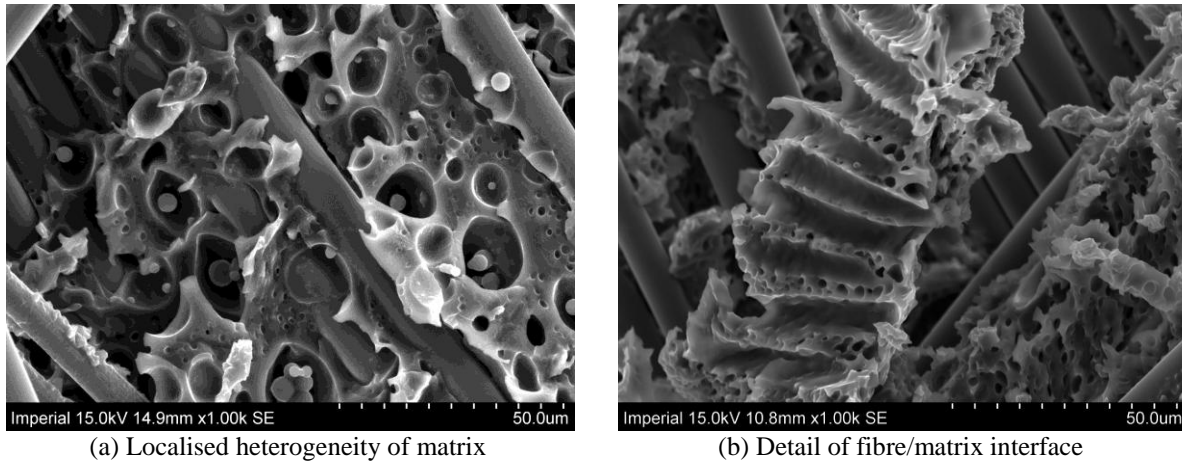
#### 3.2 Electrical and Crashworthiness Testing

Cyclic voltammetry has been used for characterisation of the electrical performance, with the laminates modelled as a simplified electrical equivalent circuit. The charge is stored in a capacitor of capacitance  $C_{SP}$ , in parallel with a resistance,  $R_P$ , and in series with a resistor  $R_S$  (equivalent series resistance). A high performance supercapacitor requires large values of  $C_{SP}$  and  $R_P$  and a low value of  $R_S$ . The energy and power densities ( $\underline{E}$  and  $\underline{P}$ ) are given by

$$\underline{E} = \frac{1}{2} C_{SP} U_{int}^2 \text{ and } \underline{P} = \frac{U_{int}^2}{4R_S} \text{ respectively, where } U_{int} = \frac{R_P}{R_P + R_S} U_{applied} \text{ and } U_{applied} \text{ is the voltage}$$

applied across the laminate. Preliminary electrical testing has shown the energy densities to be reasonable, but the power densities appear to be low.

An important aspect of these materials is the need to consider crashworthiness. When a structural power component is penetrated or damaged there may be a risk that the electrical energy could violently dissipate, leading to rapid heating or fire, evolution of toxic fumes and electric shock. Therefore research is underway to understand the processes that occur during such scenarios. The approach is to utilize nail penetration tests as used for conventional batteries, and characterise the heat and voltage across the laminate as this happens. It is recognized that the current energy storage is relatively low, and therefore the approach has been to put a conventional supercapacitor in series with the laminate. Consequently, as the laminate short circuits during penetration, energy from the conventional supercapacitor will be released through the laminate, mimicking a higher performance material.



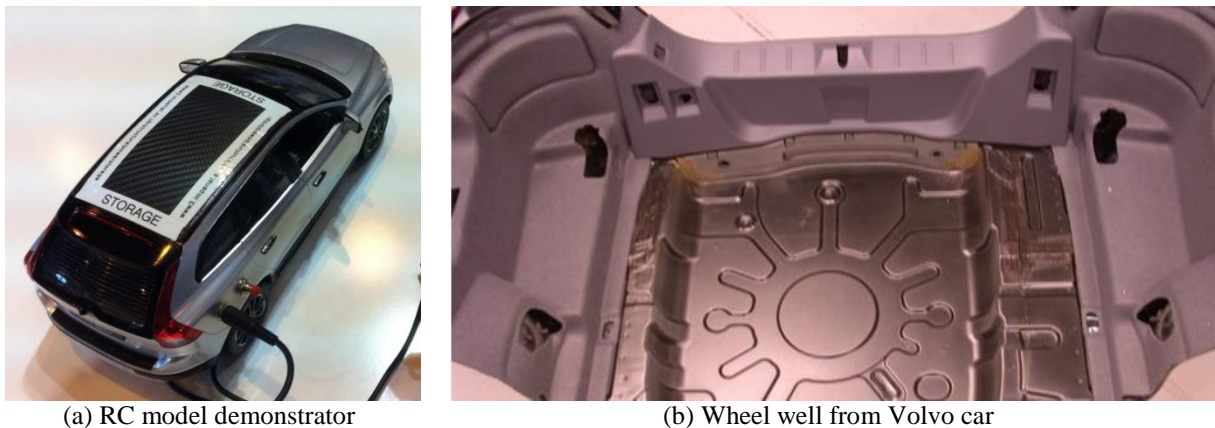
**Figure 4.** Fractographic observations from the CF/GF interface from a  $\pm 45^\circ$  tension test.

To date the characterisation has only just begun but some interesting fractographic observations have started to emerge (Figure 4). These images are from the CF/GF ply interface of a laminate which had been tested in  $\pm 45^\circ$  tension. Figure 4a mirrors some of the microstructures shown in the bulk matrix (Figure 3), but note that there is a degree of heterogeneity, with some regions exhibiting excessive IL (beadlike structure), whilst this was surrounded by regions containing structural epoxy dominated morphology (porous structure). It was also noted that there appeared to have been two levels of porosity in the matrix. Figure 4b shows the fibre/matrix interface, which is clearly very important regarding performance. This shows that the structural epoxy has tended to form a sheath around the fibres, which is beneficial for mechanical performance, but perhaps will tend to inhibit migration of the ions to the fibre surfaces. These particular observations support some of the preliminary electrical measurements regarding low power densities of these materials.

#### 4 System Issues and Demonstration

In parallel with the material development, engineering issues are being addressed. It has been recognised that these materials will require a completely different approach to design and assembly as compared to convention (monofunctional) materials. In particular, by changing the matrix constituents, the relative dominance of the electrical and mechanical performance can be tailored; this research is not developing a single material, but a spectrum of materials to suit particular applications. Such design requirements are amenable to a multiobjective optimisation approach such as that suggested by Ashby [20], where the relative dominance of the mechanical and electrical requirements are modelled using an exchange constant.

There are additional practical issues which are being advanced through STORAGE. These include concerns as to how to electrically connect the laminates with the surrounding systems. Although the electrical performance is currently quite modest, as they start to approach the electrical performance of existing conventional devices it is anticipated that electrical currents in the order of 10's of amps will need to be drawn. Lightning strike protection technologies perhaps already provide some background for addressing this problem. Connectivity also impacts on scale-up, since as the size of the components increase, the resistive heating losses in the carbon fibre electrodes will start to dominate. A further issue is associated with finishing and joining of these materials. Of particular concern is that any mechanical cutting or drilling could potentially lead to carbon debris bridging the electrodes and thus negating the electrical performance. Initial studies have suggested that cutting using a dry saw does not lead to such difficulties, but processes such as drilling can cause such self-discharging.



**Figure 5.** Fractographic observations from the T300 5HS / 50:50 (IL:epoxy)

The overall focus of STORAGE is to produce demonstrators using these structural power materials. To date, as well as a number of flat laminates for electrical and mechanical characterisation, a small demonstrator component has been made in the form of the roof of a radio controlled model car (Figure 5a). Ultimately, the central focus is to design, manufacture and assess a wheel well component made from these materials (Figure 5b), which is anticipated to be completed in June 2013.

## 5 Concluding Remarks

Structural power materials have the potential to make a significant impact on composite engineering, but the challenges in developing and maturing this technology are considerable. In this paper the work which has been done on developing structural supercapacitors was reported. Since January 2010, the STORAGE consortium have made significant strides forward in developing these materials, including identification of new reinforcement architectures (carbon aerogel reinforced weaves) which provide an elegant solution to enhancing both the surface area (for improved electrical performance) and supporting the compliant multifunctional matrix (for improved mechanical performance). Optimisation of the matrix constituents, and the influence the formulation has upon the matrix microstructure (and thus the mechanical and electrical properties) has been gleaned. In parallel to fabrication and characterisation, system issues have been addressed, with the aim of producing a demonstrator component (wheel well). The preliminary results are encouraging; the best energy and power densities for these devices are approximately 2 Wh kg<sup>-1</sup> and 90 W kg<sup>-1</sup> [16].

There are still considerable challenges which need to be addressed for this technology. Although it is anticipated that the carbon aerogel architecture will provide energy densities akin to those of conventional supercapacitors (the order of 5 Wh kg<sup>-1</sup>), the low power density of these devices is still a hurdle. Optimisation of the separator lamina and formulation of the matrix are needed, and will be driven by the design requirements particular to a given application. Other issues include scale-up of the technology, multifunctional design methodology, moisture control (both during processing and when in-service), robust electrical connection and assembly/joining of these components. Furthermore, before they can be used in service, characterisation of long-term performance (both electrical and mechanical) needs to be undertaken. However, if these issues can be addressed, the potential benefits of these materials will be immense and far reaching.

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