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A critical review of structural supercapacitors and outlook on future research challenges

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ABSTRACT

Structural composites and electrochemical energy storage underpin electrification of transportation, but advances in electric vehicles are shackled by parasitic battery mass. The emergence of structural power composites, multifunctional materials that simultaneously carry structural loads whilst storing electrical energy, promises dramatic improvements in effective performance Here, we assess the literature on structural supercapacitors, not only providing a comprehensive and critical review of the constituent (i.e., structural electrode, structural electrolyte and structural separator) developments, but also considering manufacture, characterisation, scale-up, modelling and design/demonstration. We provide a rigorous analysis of the multifunctional performance data reported in the literature, providing the reader with a detailed comparison between the different structural supercapacitor developments. We conclude with insights into the future research and adoption challenges for structural supercapacitors. There are several significant hurdles which must be addressed to mature this technology. These include development of a processable structural electrolyte; optimisation of current collection to facilitate device scale-up; identification of load-transmitting encapsulation solutions; standard protocols for characterisation and ranking of structural supercapacitors and; predictive multiphysics models for structural supercapacitors. Through addressing such issues, these emerging multifunctional materials will deliver a novel lightweighting strategy that can contribute to managing the ongoing climate crisis.

1. Background and motivation

Structural composites and energy storage underpin transportation [1,2]. However, advances in electric cars and aircraft are shackled by parasitic battery mass: i.e., to increase range, more batteries are needed but these add additional weight. Battery mass can now account for as much as 26% of the weight of an electric car [3]. Conventional battery performance can be increased, but gains are slow, whilst many of the new chemistries present considerable sustainability, safety and longevity issues [4]. This challenge is even more daunting for aerospace: the parasitic mass means that conventional battery technologies are not anticipated to be capable of propelling a fully electric airliner until the end of the century [5]. However, the emergence of *structural power composites*: multifunctional materials that simultaneously carry mechanical load whilst storing electrical energy [6], provides a means to resolve this quandary and offer a novel lightweighting strategy to that can contribute to managing the ongoing climate crisis [7].

Electrochemical devices can be classified via the balance between their specific energies and powers. Electrostatic capacitors provide high power but very low specific energies, and hence are not useful for most energy storage contexts. At the other extreme are batteries, providing high specific energy but low specific power. They store energy through chemical processes which are governed by thermodynamic and diffusive phenomena. In the context of structural power, the electrochemistry of batteries leads to considerable challenges for scale-up, including volumetric changes during charge/discharge, and for high energy density systems, very significant, irreversible moisture sensitivity. Supercapacitors offer a compromise between specific energy and power and

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can be partitioned into electrochemical double layer capacitors (EDLCs), pseudocapacitors and the combination (hybrid-capacitor) [8]. Conventional EDLCs consist of two high surface area electrodes which sandwich a thin, ionically conducting but electrically insulating separator, all of which is immersed within an electrolyte. Charge storage is exclusively physical, occurring via electrostatic adsorption at the interfaces between the electrodes and electrolyte [9–11]. Pseudocapacitors enhance the storage capacity by utilising faradaic processes at the electrode/electrolyte interface, though often operating over a wide voltage range. Hybrid capacitors combine both an electro-double layer electrode and an electrochemical electrode to give higher energy storage than a conventional EDLC but better power than a battery.

This review focusses on structural supercapacitors. There are several definitions as to what is deemed to be a multifunctional material, such as a structural supercapacitor [13–15], but this review adopts that suggested by Wetzel [16]. *Conventional* is deemed to be the Current Off The Shelf (COTS) classical approach in which a system consists of an assembly of monofunctional components which are physically isolated from each other. *Embedded* (Fig. 1a) are COTS monofunctional components embedded within each other, thus providing mass and/or volume savings through efficient packaging. Beyond this is *Conformable* in which the device flexibility is such that it can formed into the component. In the context of structural supercapacitors, conformable devices often utilise nanocarbons as the electrodes with liquid or gel electrolytes, manifested in laminated (Fig. 1b) or fibre architectures (Fig. 1c). They can tolerate high bending deformations (although not necessarily high strains) and are sufficiently durable to cope with environmental factors and repeated deformation. However, they do not offer high stiffness or strength under direct loading. Finally, *Structural* refers to a material which is intrinsically multifunctional, undertaking two roles, without any monofunctional constituents. Structural supercapacitor composites utilise a stiff/strong structural fibre as a scaffold for the electrode (Fig. 1d) with a stiff structural electrolyte, resulting in a device which can carry significant mechanical load. This configuration usually uses carbon fibres as the structural scaffold. For brevity, it is this latter class (Fig. 1d) which is the focus of this review, with brief details of *Embedded* (Fig. 1a) and *Conformable* supercapacitors (Fig. 1b and c) given in the ESI.

Reviews on structural batteries and supercapacitors are presented elsewhere [1,6,12,15,17] with reviews specifically on structural supercapacitors given in Refs. [18–21]. Such reviews have focussed on constituent development (electrodes, electrolytes and separators) with negligible consideration of manufacture, characterisation, scale-up, modelling and design/demonstration. Furthermore, although these reviews collate the reported data, rigorous comparative analysis of the multifunctional performance across the datasets is lacking. The aim of the current review is to address such issues. The aspiration is to provide a detailed comparison between the different structural supercapacitor developments and then insights into research and adoption challenges.

2. Performance data on structural supercapacitors

To distil and contrast the reported data, Table S1 and Table S2 in the ESI detail the reported device descriptions and performance from the literature. Where reported, the specific electrochemical capacitances have been collated, alongside the specific energy and power densities. The mechanical performance is tabulated as modulus and strength (under tension, in-plane shear and/or flexure). The reported specific energies and powers are very dependent on the electrolyte and voltage window chosen, and, in some cases, represent extrapolations, so are in general not directly comparable. Table S1 collates the data associated with specific performance (i.e., gravimetric) of structural supercapacitors, partitioned into carbon fibres and non-carbon fibre types. However, some literature only reports the areal or volumetric performance, and these data are collated in Table S2. It is difficult to directly compare gravimetric (Table S1) and volumetric (Table S2) performance since data associated with the constituent and device densities have not been reported. Whilst presenting data using structural electrolytes, some researchers have also shown data on the device using a liquid electrolyte. This approach provides useful comparisons of the electrochemical performance when changing from a monofunctional (i.e., liquid electrolyte) to a multifunctional device (i.e., structural electrolyte) [22].

Due to the relative immaturity of this field, there are several challenges associated with collating and comparing such data. Most notably, there is enormous variation in the approach, with some researchers having reported capacitance normalised by the electrode mass (indicated by an asterisk in Table S1) whilst others report capacitance normalised by the device mass (indicated by a dagger in Table S1). This same problem, in fact, permeates the pure electrochemical energy storage device field, as recently discussed [23]. Whilst both measures

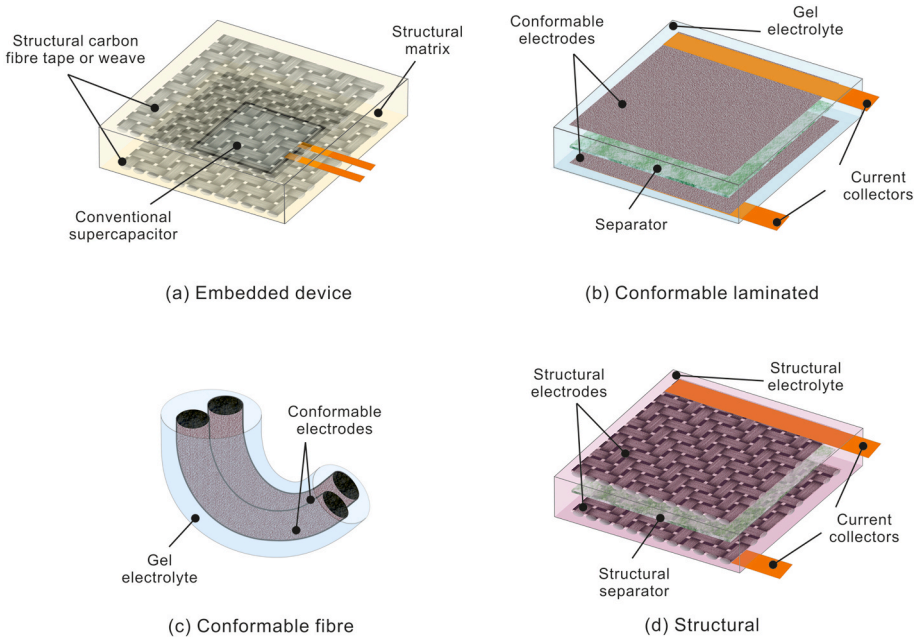


Fig. 1. Different structural supercapacitor embodiments [12].

have legitimate uses, the use of electrode mass normalisation gives higher values that may be misleading if used to consider device multi-functionality. Similarly, for the mechanical performance, some researchers have only reported the mechanical (tensile) performance of the fibres in the 'dry' state (i.e., without the electrolyte) rather than the whole device (including matrix): such instances have been indicated by a superscript 'a' in the Tables. Other reporting ambiguities are indicated in the Table legends. One clear outcome from this review is the need for a protocol to compare data from across the literature [22], and hence to identify the most promising routes to realising high performance structural supercapacitors.

3. Constituents

The following Sections describe the constituents of structural supercapacitors: structural electrodes (Section 3.1), structural electrolytes (Section 3.2), separators (Section 3.3), as well as materials for current collection (Section 3.4) and encapsulation (Section 3.5). The relative masses of each of the constituents in a typical device are illustrated in Fig. 2. The electrolyte has been further partitioned into the masses associated with both the structural and liquid phases, with only the latter being present in conventional devices.

The mass associated with encapsulation is not considered since its contribution is ambiguous: it is conceivable that a multicell assembly could have a single encapsulation layer (see Section 3.5). Current collectors provide a considerable proportion of the mass for conventional devices, since the electrode is deposited onto the current collector. For structural supercapacitors, the electrolyte dominates the device mass: increasing the electrode mass (by reducing the electrolyte) would enhance the device stiffness.

3.1. Electrodes

3.1.1. Plain carbon fibre electrodes

Using plain woven carbon fibres (WCF) as electrodes (Fig. 3a) is challenging because their very low fibre surface area (~0.2 m^2/g) translates into low capacitance. Snyder [25–28], used pristine fibres in liquid and structural electrolytes: IM7 carbon fibres in 1M $LiPF_6$/EC/EMC liquid electrolyte provided the highest capacitance (3.2 F/g, normalised by active mass) [26]. A similar study with PEGDGE/EMITFSI, as a structural electrolyte, with a woven glass fibre separator achieved 6 mF/g (normalised by device mass) but poor mechanical properties (G_{12} = 306 MPa) [29]. Studies on pristine WCF with PEGDGE/lithium bis(trifluoromethanesulfonyl)imide/PC and Celgard separators, gave good mechanical performance (E_{11} = 19 GPa) but poor capacitance [30–32].

3.1.2. Activated carbon fibre electrodes

Activation of carbon fibres (ACF) improves electrode surface area (Fig. 3b), with chemical activation in KOH the best means to maintain mechanical properties whilst enhancing capacitance [33]. In aqueous electrolyte (KCl), this route led to a considerable improvement in specific capacitance over that of WCF (0.06–2.63 F/g) and a negligible drop in stiffness and strength. The device performance of WCF has been compared to that of industrially activated carbon fibres (IACF), as used in conventional devices, using Celgard (PP) separators with both liquid (PC/LiTFSI) and structural (epoxy/LiTFSI) electrolytes [28,34]. The IACF gave a superior capacitance, but with very high resistivity and poor mechanical properties compared to WCF. Devices using ACFs with gel (PAN/PC/EC) and structural (PEGDGE/LiTFSI and PEGDGE/LiTFSI/E-MIMTFSI) electrolytes with glass fibre separators gave a capacitance of 52 mF/g (normalised by device mass) but this improved capacitance was accompanied with a reduction in compressive performance [34]. Similar studies with ACF using cellulose separators with liquid ($TEABF_4$/PC) and structural ($TEABF_4$/PC/epoxy) electrolytes showed that the specific capacitance, normalised by device mass, dropped from 30.4 F/g (liquid electrolyte) to 0.094 F/g (structural electrolyte), whilst increasing the proportion of epoxy in the structural electrolyte led to a considerable drop in capacitance but large improvements in flexural performance [35]. ACF with structural electrolytes (PEGDGE/LiTFSI/EMITFSI) showed that the introduction of silica particles led to improvements in both device mass normalised capacitance (46 mF/g to 60 mF/g) and in-plane shear modulus (292 MPa–1760 MPa) [36,37]. Finally, an alternative architecture was paired yarns of ACF, coated in gel electrolyte and then woven into a fabric, achieved 18.6 F/g (normalised by active mass) [38]. The tensile moduli (100 GPa) and strength (1956 MPa) were reported, but normalised by fibre, rather than yarn, cross-sectional area.

3.1.3. Nanocarbon decorated carbon fibre electrodes

An alternative approach to increase the electrode surface area relies on coating the primary carbon fibres with nanocarbon particles; this strategy has the potential advantage of improving mechanical performance, since nanocarbon coated interfaces can improve adhesion and load transfer. The introduction of carbon nanotubes (CNTs) into WCFs, by grafting (Fig. 3c) or sizing (Fig. 3d), was evaluated with a structural electrolyte of epoxy/LiTFSI/EMIMTFS [6,39]. The capacitance was poor, with the CNT grafted CF presenting the best performance of 10 mF/g (normalised by device mass) whilst the CNT sized CF presented the best mechanical performance. A reductive dissolution method has been used which gave a capacitance of 13.26 F/g and 0.173 F/g for the liquid and structural electrolyte, respectively (normalised by active mass), with the latter achieving tensile modulus and strength of 17.2 GPa and 245 MPa, respectively [40]. Comparisons between WCF, MWCNTs and their hybrids using a liquid electrolyte (PEO/EC/$LiClO_4$) have presented active mass normalised capacitances of 3.78 F/g, 12.49 F/g and 2.6 F/g, respectively [41]. Other studies have grown CNTs onto a steel mesh with a Kevlar separator, comparing liquid ($LiBF_4$/$BMIBF_4$) and structural (epoxy/$LiBF_4$/$BMIBF_4$) electrolytes [42]. The capacitance of the liquid electrolyte device (35 mF/g, normalised by device mass) was over twice that of the structural electrolyte, although the latter had mechanical properties (E = 6.2 GPa, X_T = 85 MPa).

Although CNTs offer good connectivity and accessibility, graphene related materials may offer higher electrochemical surface areas than

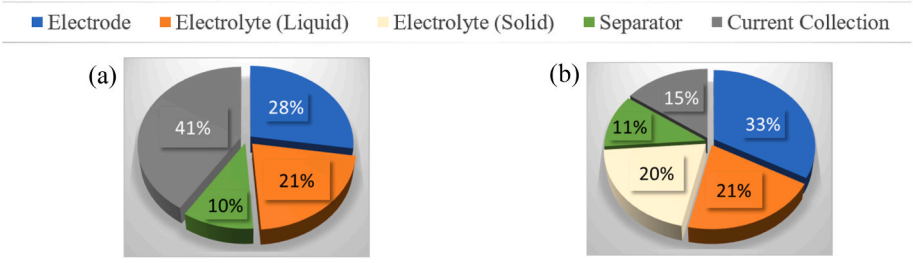


Fig. 2. Relative proportion (by mass) of constituents in single cells, excluding encapsulation, of (a) conventional supercapacitor [24]; (b) typical structural supercapacitor [22].

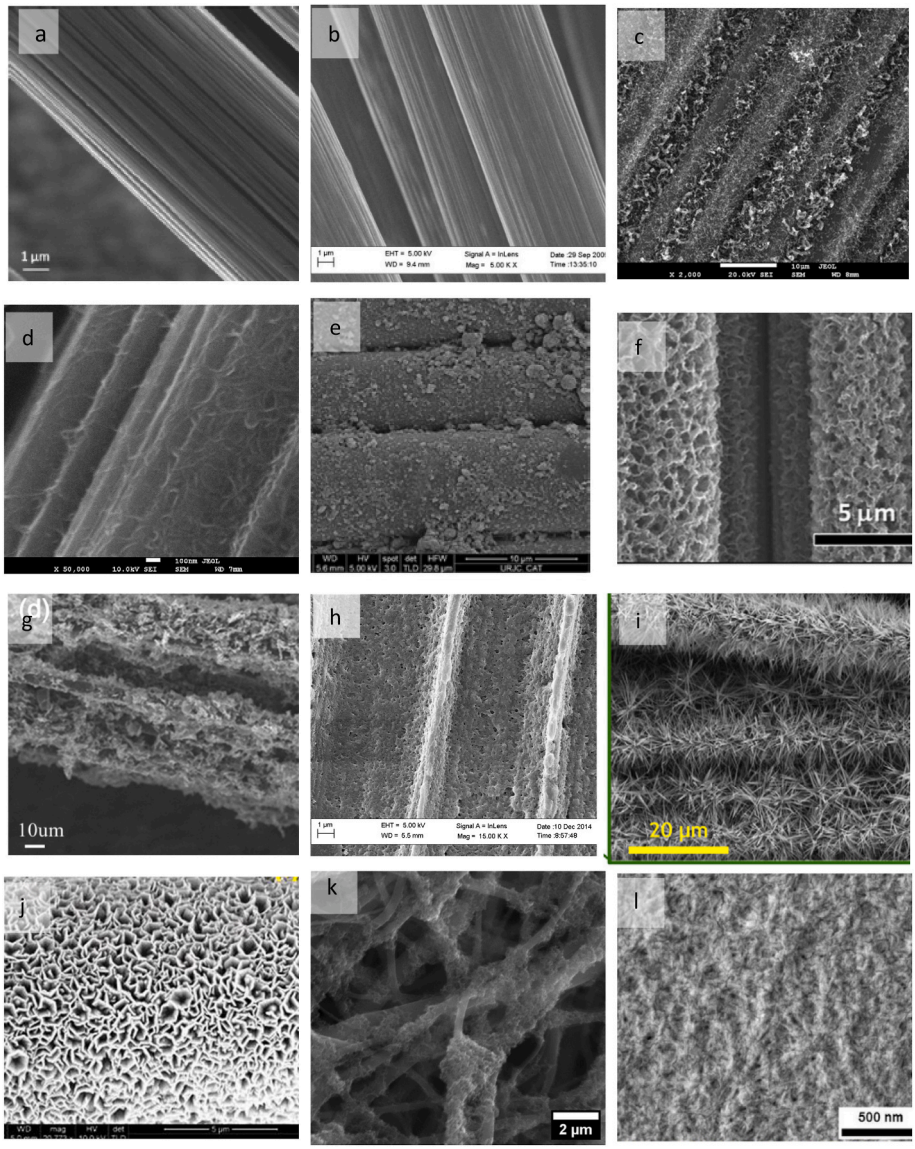


Fig. 3. Different structural electrodes: (a) Plain CF [47]; (b) Activated CF [33]; (c) CF + CNTs [6]; (d) CF + CNT sized [6]; (e) CF + rGO [48], Springer, © 2021; (f) CF + GNP [45]; (g) CF + G/AC [49], Elsevier, © 2018; (h) CF/CAG [50]; (i) WCF/NiCo nanowires [51], Elsevier, © 2018; (j) WCF/ZnO [52], Elsevier, © 2017; (k) CNF/CNT [53]; (l) ANF [54], ACS, © 2017. All images were reproduced with permission from the corresponding publisher where necessary.

multiwall nanotubes. WCF coated with reduced graphene oxide (rGO) (Fig. 3e) or graphene nanoplatelets (GNPs) (Fig. 3f) have been investigated [43–46]. Capacitances of 59 mF/g (normalised by device mass) were obtained using an epoxy/$LiClO_4$/PC structural electrolyte [43] whilst using an epoxy/PEGDGE/EMIMTSFI/TiO_2 electrolyte led to a three-fold improvement in specific capacitance over that of the plain WCFs [44]. Electrophoretic deposition of GNPs onto CF with a PEGDGE/$EMIBF_4$ structural electrolyte was used to produce a 'separator-free' supercapacitor with a capacitance of 623 mF/g (normalised by active mass) and tensile modulus and strength of 26 GPa and 350 MPa, respectively [46]. Inclusion of graphene does not depress the mechanical performance [44]. Urea activated graphene nanoflakes (GNFs) deposited onto WCF with PEGDGE/EMIMTSFI and GF separators enhanced the device mass normalised capacitance (31 mF/g to 48 mF/g) and Young's modulus (19 GPa–21 GPa) [45].

There have been studies using both CNT and GNP decorated WCF electrodes, but only using liquid electrolytes [48,55]. Whilst the CNTs offered little enhancement in capacitance, the GNP imbued a significant improvement (410 mF/g, normalised by active mass) compared to that of the plain WCF (20 mF/g, normalised by active mass). Dry fibre tests showed that the decoration with the nanocarbon led to a slight reduction in tensile modulus and strength compared to that of the pristine WCF. WCF have been decorated with rGO and porous activated carbon to produce a 'carbon concrete' film electrode (Fig. 3g) [49]. This electrode had a capacitance of 150 F/g (normalised by active mass) whilst mechanical testing of dry electrodes demonstrated that nanocarbon decoration had a negligible influence on the tensile modulus and strength.

3.1.4. *Carbon aerogel/carbon fibre electrodes*

An alternative route for improving electrode surface area has been to fill as much of the matrix space as possible with a carbon aerogel (CAG) (Fig. 3h), which is achieved by infusion of the WCF with a polymer precursor, followed by pyrolysis [22,47,50,56–58]. Using EMIMTFSI, this supercapacitor with WCF/CAG achieved a capacitance of 1.73 F/g (normalised by device mass) [22], whilst for a structural electrolyte (PEGDGE/EMIMTFSI), capacitances up to 603 mF/g are reported [47]. WCF/CAG electrodes with epoxy/EMIMTFSI and a polyester/ceramic veil separator gave a capacitance (normalised by device mass) of 1120 mF/g [58]. CAG has a Young's modulus of 25 GPa [59], thus providing improved load-transfer between the fibres for soft matrices, enhancing

in-plane shear performance [22,50]. However, although high tensile modulus (E_{11} = 33 GPa) has been reported [22], the CAG processing depresses the fibre tensile strength [22,48]. Adding GNP to WCF/CAG with an epoxy/$LiClO_4$/PC structural electrolyte presented a capacitance (normalised by device mass) of 354 mF/g and a shear modulus of 2640 MPa [60]. Spread tow CF/CAG has presented a capacitance (normalised by device mass) of 3.1 F/g in liquid electrolyte (EMIMTFSI) and 1.4 F/g in structural electrolyte (epoxy/EMIMTFSI) [61]. An alternative strategy using amorphous carbon has been to coat WCF in activated carbon particles (AC) rather than monolithic CAG, using the same structural electrolyte and separators as [57]. This gave C = 1.56 F/g (normalised by active mass), but a drop in tensile and in-shear performance with the introduction of AC: E = 23 GPa, X_T = 258 MPa, G_{12} = 480 MPa [62].

3.1.5. PANI decorated carbon fibre electrodes

An alternative approach has been to decorate ACF with conductive polymers, such as polyaniline (PANI), to increase energy density by introducing a redox active component. However, ACF/PANI tested with a structural electrolyte (epoxy/$LiClO_4$/PC) [63] only demonstrated modest capacitances of 22 mF/g (normalised by device mass). Similarly, WCF decorated with MWCNTs and PANI with an epoxy/LiTf/EMIMTFSI structural electrolyte gave a capacitance of 212 mF/g (normalised by device mass) and flexural modulus and strength of 2.9 GPa and 21.3 MPa, respectively [64].

3.1.6. Metal oxide or chalcogenide decorated carbon fibre electrodes

There is a large body of work using WCF decorated with metal oxides or metal chalcogenides to imbue pseudocapacitance to the structural supercapacitor. The most widely used additive is manganese dioxide (MnO_2) [56,65–69]. Carbon fibres decorated with MnO_2 nanowires in 1M Na_2SO_4 liquid electrolyte gave an almost four-fold (41.3 F/g, normalised by active mass) improvement in capacitance over pristine WCFs [65]. WCF decorated with MnO_2 and GNP with both 'semi-solid' (PVDF-HFP/$BMIMBF_4$) and structural (PVDF-HFP/$BMIMBF_4$/epoxy) electrolytes, demonstrated active mass normalised capacitances of 165 F/g and 15 F/g, respectively [66]. The tensile performance of the device with the structural electrolyte was twice that with the 'semi-solid' electrolyte. WCF coated with MnO_2 and silane sizing in a structural electrolyte (epoxy/BMIMTFSI) achieved a capacitance (normalised by active mass) of 10.5 F/g and tensile moduli and strength of 14 GPa and 397 MPa, respectively [69]. Other approaches include using WCF decorated with NiCo nanowires (Fig. 3i) [51]. This achieved a capacitance of 595 mF/cm^2 in an aqueous electrolyte (2M KOH), but only 5 mF/cm^2 in a structural electrolyte (PEO-b-P(S-co-DVB)/BMIMTFSI). Silver nanowires (AgNW) decorated WCF with an aqueous electrolyte (1M KOH) achieved a capacitance of 230 mF/cm^2 [70]. Similarly, WCF decorated with tin sulphide (SnS_2), carbon nanotubes and PANI [71] demonstrated an enormous capacitance of 891 F/g in liquid electrolyte (1M Na_2SO_4) whilst $NiCo_2O_4$ and polypyrrole (PPy) decoration gave a capacitance of 62 F/g in PVA/KOH gel [72]. However, it should be noted that these specific capacitances were considering only the mass of the active phase and not that of the carbon fibre scaffolds.

There have been several studies on decorating WCF with metal oxides or chalcogenides using structural electrolytes (polyester/$EMIMBF_4$/LiTFSI) [52,73–78]. These devices have reported capacitances (normalised by active mass) of 6.75 F/g for CuO [75], 16.96 F/g for ZnO (Fig. 3j) [52], 28.63 F/g for CuCoSe [76], 37.43 F/g for $NiCo_2O_4$ [79], 47.34 F/g for CuMnSe [77] and 13.88 F/g for N doped $ZnCuSe_2$-Mxene [78], and (normalised by device mass) 0.148 F/g for SnO_2 [73,74]. The metal oxide or chalcogenide generally improved tensile and in-plane shear performance over that of the monofunctional structural configuration (WCF/polyester). However, there were some ambiguities in the mechanical and electrochemical data in Refs. [52,75–78] which are discussed in detail in the ESI. The authors consider that the use of nanostructured metal oxides or chalcogenides within the matrix volume of the woven fibres is an encouraging approach that, similar to the carbon aerogel approach, in principle offers simultaneous improvements in both electrochemical and mechanical properties.

3.1.7. Alternative structural fibre electrodes

Hollow or porous carbon nanofibers (CNFs) may be used in place of WCF, offering much higher surface area and capacitance, but much lower tensile properties. Since all the mass is electrochemically active, they exceed the electrochemical performance of graphene or CNT decorated carbon fibres (Table S1). Porous CNF yarns in 6M KOH aqueous electrolyte achieved C = 138.2 F/g (normalised by active material), E = 38.1 GPa and X_T = 800 MPa [80]. Decorating these porous CNF yarns with Co_3O_4 has achieved C = 713.9 F/g using a PVA/H_2SO_4 gel electrolyte [81], whilst E = 26 GPa and X_T = 69 MPa were reported, but note that this was using the net, not gross, sectional area of the fibres. Activated and nitrogen doped CNF with a gel electrolyte (PVA/$(Zn(CF_3SO_3)_2)$), achieved C = 251 F/g, E = 14.4 GPa and X_T = 308.3 MPa [82]. Finally, structural supercapacitors using carbon nanofibre/nanotube (CNF/CNT) veils (Fig. 3k) in a PEGDGE/EMIMTFSI have been reported [53]. The CNF/CNT electrode had a superior capacitance 2.57 F/g (normalised by active mass) to that of the CNT (0.70 F/g).

Aramid nanofibers/rGO (ANF) veils have been used as the electrodes (Fig. 3l), although these have been characterised mechanically in the dry condition without electrolyte [54,83–86]. Such electrodes with PC/$LiClO_4$ [54] and 6M KOH [86] electrolytes achieved capacitances (normalised by active material) of C = 78 F/cm^3 and C = 226 F/g, respectively: the latter with mechanical properties of E = 13 GPa and X_T = 101 MPa. These ANF/rGO hybrids have been functionalised, using + NH_2 radicals [83] (C = 120 F/g, E = 9.9 GPa, X_T = 79 MPa), dopamine [84] (C = 83.2 F/g, E = 15.4 GPa, X_T = 117 MPa) and tannic acid [85] (C = 145 F/g, E = 25 GPa, X = 140 MPa), all characterised in liquid electrolyte (KOH). Grafting CNTs onto the rGO/ANF electrodes in KOH gave C = 169 F/g, E = 5.5 GPa, and X_T = 41.7 MPa [87]. Finally, alternative structural electrodes have been considered, including porous silicon [88–90], Ni foam [72] and graphitic carbon nitride [91], although the mechanical performance was poor.

3.2. Structural electrolytes

3.2.1. Introduction

Details of electrolytes used in conventional supercapacitors, and the critical parameters associated with them, are reviewed in Ref. [92], but modulus or strength are rarely considered to be important. However, the mechanical performance of structural supercapacitors is intrinsically linked to that of the structural electrolyte. Moreover, the electrolyte also dictates the electrochemical voltage window over which the device can operate as well as operating temperature, toxicity, flammability etc. The aspirational combination of properties for structural electrolytes includes a Young's modulus exceeding 1 GPa and an ionic conductivity exceeding 1 mS/cm. In fact, the required ionic conductivity depends on the electrolyte thickness (spacing between the electrodes) and hence is intrinsically linked to the device architecture. In fibre scale devices, a much thinner electrolyte-separator coating might be considered than in laminate designs, similar to the sub-micron coatings used in structural fibre batteries [6]. However, in full structural supercapacitor composites, ionic conductivity will still be needed either between the fibres, or throughout the inter-fibre (matrix) volume, on at least the ten micron scale. The mechanical performance of the structural electrolyte should ideally be considered at the length scales within the laminate, rather than by bulk measurements, since resin size effects are well established. Two main groups of electrolytes considered in this review are: (i) dual phase and (ii) solid, including composite solid electrolytes. A graphic representation of the mechanical (Young's modulus) and electrochemical (ionic conductivity) literature data on structural electrolytes is shown in Fig. 4.

Liquid electrolytes can be applied in structural power devices to investigate the intrinsic electrochemical performance of the structural

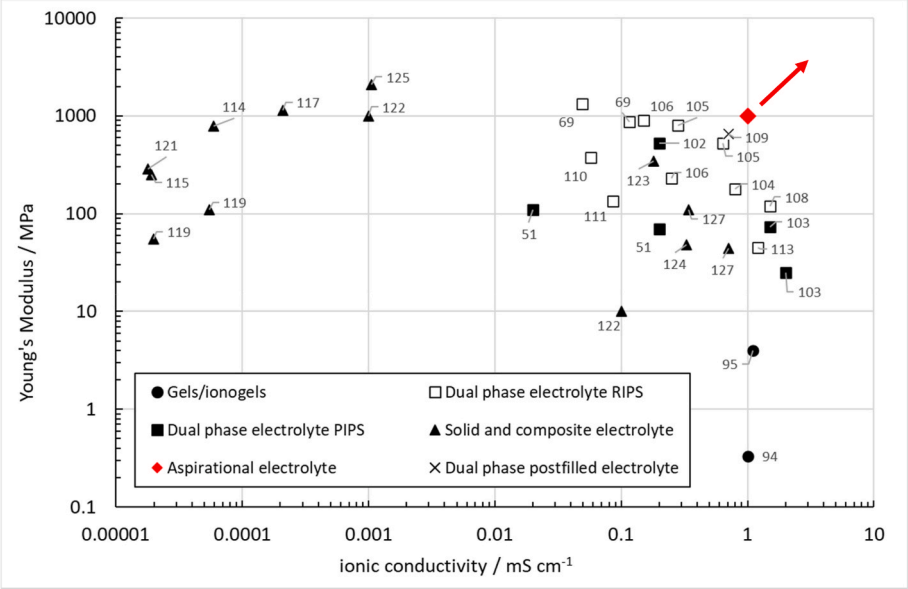


Fig. 4. Multifunctional performance of different structural electrolytes. N.B. labels correspond to reference numbers.

electrodes with both aqueous and organic electrolytes [22,86,93]. However, they do not provide mechanical support for the reinforcing fibres and therefore do not provide multifunctional structural supercapacitors: they are not considered further here. Similarly, for gel electrolytes, even though they are widely studied for energy storage devices, their relatively high ionic conductivity comes with insufficient mechanical performance for structural applications [94–96].

3.2.2. Dual phase electrolytes

Even though theoretical work has identified possible optimised microstructures for structural electrolytes, the ideal structural electrolyte is yet to be synthesised [97,98]. As shown in Fig. 4, dual phase electrolytes in which one phase, containing a liquid/gel electrolyte, is responsible for the ion conduction and another phase provides mechanical integrity, have the most promising characteristics [99]. Dual phase electrolytes can either be prepared in situ, where the electrolyte is a part of the initial reaction mixture, or by postfilling, when the structural phase of the electrolyte, in the form of a prefabricated motif, is backfilled with liquid electrolyte. Dual phase electrolytes formed in situ are usually synthesised using polymerisation induced (PIPS) or reaction induced phase separation (RIPS) methods which are straightforward for processing and scale up. In both cases the initial reaction mixture, comprising of a structure-forming precursor and a liquid electrolyte, is homogeneous. As the polymer starts forming, its solubility in the liquid electrolyte is reduced, resulting in the formation of a 3D network. The difference between the two competing reactions, polymer formation and phase separation, has a significant influence on the resulting microstructure and properties of the dual phase electrolyte.

Vinyl monomers are the main structure-forming precursors for PIPS reactions and the properties of the resulting electrolytes depend on multiple parameters, including the composition and reaction conditions [100–102]. The monomers used as a structure-forming precursor include styrene (S), divinyl benzene (DVB), methyl methacrylate (MMA) and multifunctional methacrylic monomers, as well as bisphenol A vinyl monomers [51,100,102,103]. The PIPS method, using the latter chemistry, has achieved storage moduli of 530 MPa and 750 MPa and ionic conductivities of 0.2 mS/cm and 0.15 mS/cm for an electrolyte synthesised using a thermal and UV initiation, respectively.

Due to their wide usage in conventional composites, the structural phase in electrolytes synthesised using RIPS has mainly comprised of epoxy resin. The composition of the ion conducting phase has varied and has included ionic liquids (ILs) [69,104–107], lithium salt solutions in organic solvents [108,109]; their combination [106,110] as well as other systems [111]. The addition of ILs to epoxy resin has resulted in electrolytes with the most promising combination of properties. An addition of 37% of BMIM-TFSI to epoxy has resulted in a structural electrolyte with a Young's modulus of 962 MPa and an ionic conductivity of 0.07 mS/cm [69]. The addition of a similar proportion (35%) of EMIM-TFSI to DGEBA led to a structural electrolyte with a slightly lower Young's modulus of 800 MPa but significantly higher ionic conductivity of 0.28 mS/cm [105]. This difference in ionic conductivity cannot be attributed solely to the difference in IL ionic conductivities, since that of BMIM-TFSI (3.5 mS/cm) is close to half that of EMIM-TFSI (8 mS/cm) [112]. This difference may be due to the structural electrolyte containing BMIM-TFSI having a more refined microstructure, demonstrating that the microstructure has a significant effect on the properties of the final structural electrolyte [69]. By varying the composition of the reaction mixture, it was possible to vary the microstructure of the structural phase from fused nodules to a bicontinuous structure and inversed nodules, with the ionically conductive phase infused through the pores in these microstructures [104,106,113]. The nodular microstructure presented a higher ionic conductivity in comparison to the other two microstructures, whilst structural electrolytes consisting of inversed nodules presented the highest mechanical performance but lowest ionic conductivity. The most promising combinations of properties were presented by electrolytes with a bicontinuous microstructure. Finally, the addition of the ionically conductive compounds usually has a plasticizing effect on the structural polymer phase, reducing the mechanical performance of the resulting electrolyte. This issue can be mitigated by the introduction into the system of solid particles, such as organoclay, nanosilica particles or even block-copolymers [105,110,111].

As shown in Fig. 4, a promising approach to control the electrolyte microstructure is to form the structural phase first by using a sacrificial porogen, which is then extracted, providing a motif that can be filled with a liquid electrolyte. This method permits high fidelity control of the electrolyte microstructure, negating the issue of the uncured structural phase interacting with the ionically conducting phase, and means different electrolytes may be used with the same structural phase. By varying the composition of the reaction mixture and liquid electrolyte used, ionic conductivities of 0.71 mS/cm [109] and 1.5 mS/cm [108] and Young's moduli of 650 MPa [109] and 120 MPa [108] have been

achieved. However, this complex, multistep process for synthesis of the structural electrolyte makes scaling up difficult and very energy- and resource-intensive.

3.2.3. Solid electrolytes

Solid electrolytes are single phase electrolytes where a salt is dispersed into the polymer matrix. Their main advantage is the absence of any volatile or flammable compounds and good mechanical properties, as defined by the polymer used. However, as can be seen in Fig. 4, the ionic conduction at ambient temperature is significantly lower than that of other electrolyte types. Since there are numerous methods to synthesise solid electrolytes, a wide range of polymers can be used, leading to electrolytes with a spectrum of mechanical properties. Using polymerisation in the presence of lithium salt as a preparation route, Snyder et al. [114,115] reported solid electrolytes with ionic conductivities of 1.6×10^{-5} to 1.7×10^{-3} mS/cm and Young's moduli of 562 MPa–15 MPa, respectively. However, a more common route for their preparation is through blending polymers with lithium salt with or without the need for the cure/reaction. As for dual phase electrolytes, epoxies and PEO are popular choices [116–121], with the former presenting a better balance between mechanical and electrochemical properties [116,117,122]. For example, by blending DGEBA with different proportions of succinonitrile and lithium salt, the ionic conductivity of the resulting electrolytes varied from 1×10^{-3} mS/cm to 0.1 mS/cm and Young's modulus from 1 GPa to 10 MPa, respectively [122]. Other examples of solid electrolytes include those based on cellulose acetate [123], PVA [124] and polyethylene terephthalate (PET) [125]. Finally, composite solid electrolytes should be considered, which consist of active or passive inorganic fillers and polymer matrices. Optimising the proportion and compatibility of these two constituents in the resulting electrolyte is a means to achieving good processability, ionic conductivity, excellent interfacial contact with the electrodes and durability (and hence potentially structural performance) of the electrolyte. Numerical studies have shown that a very high proportion (over 60%) of the ceramic phase is needed to achieve high stiffness and ionic conductivity [126]. Experimental research has shown that by increasing the TiO_2 content from 10% to 25%, the Young's modulus increased from 44 MPa to 110 MPa but with a reduction in ionic conductivities from 0.71 mS/cm to 0.34 mS/cm [127]. Muñoz et al. [117] used a blend of two epoxies with ionic liquid, showing that adding TiO_2 reduced the modulus of the electrolytes without affecting the ionic conductivity.

3.3. Separators

The role of the separator is to electrically insulate the electrodes from each other whilst permitting ion migration between them. The separator should be as thin and porous as possible to reduce the ion transport distance and tortuosity, and to minimise parasitic weight, although it typically accounts for about only 10% of the device mass (Fig. 2). From a structural perspective, the separator should be robust enough to cope with the processing conditions and to prevent shorting due to fibre penetration. At the same time, it must form a sufficiently strong bond with the electrodes to permit load transfer and avoid delamination [6,18]. On the other hand, Hubert [46] proposed a 'separator-free' device by casting and sandwiching the structural electrolyte between the electrodes but with a very low fibre volume fraction. From a practical perspective, to facilitate consolidation of the device and achieve reasonable fibre volume fractions, it is necessary to have a separator to negate shorting. As detailed in Table S1 and Table S2, separators for structural supercapacitors have drawn upon off-the-shelf products. Celgard (stretched polypropylene) membranes have been widely utilised and although these offer excellent electrochemical performance and robustness, they bond very weakly to the electrodes, leading to poor mechanical performance [26–29,47,49,83,128]. Cellulose or other filter papers are a common alternative [35,36,43,60,129], but have an inferior electrochemical performance compared to other separators, perhaps due to their pores being blocked by the structural phase of the electrolyte [29]. Glass fibre fabric separators are widely used: they contribute meaningful structural performance and permit ion transport [6,25,29,34,37,39,41,44,45,47,50,53,57,58,130]. The weave thickness is inversely proportional to the equivalent series resistance (ESR) [130] but if it is too thin, the sparse tow spacing can lead to shorting. Zhu [131] used two different separators with pristine WCF using a structural electrolyte (PEGDGE/Li salt), achieving 19 mF/g (a glass fibre weave) and 32 mF/g (Celgard), both normalised by device mass. Similarly [29] three different separators (glass fibre weave, Celgard and filter paper) were studied with a PEGDGE/EMITFSI electrolyte: the glass weave gave the best capacitance (6 mF/g, normalised by device mass) but the filter paper gave the best shear performance.

Polymeric fibre veils (such as polyester) which are reinforced with ceramic (alumina) particles [58] and thermoplastic electrospun nanoveils [132] have been investigated. These materials are robust but have inferior performance compared to that of glass fibre veils [41] or weaves [58]. Studies using CF/CAG electrodes with structural electrolytes based on epoxy/EMIMTFSI with polyester/ceramic veil separators led to a capacitance of 263 mF/g (normalised by device mass) [57], whilst using glass fibre woven separators, gave capacitances of 97 mF/g [57], 212 mF/g [22] and 1120 mF/g [58]. However, glass fibre separators present superior mechanical performance ($G_{12} = 790$ MPa [57] and 1700 MPa [22]) over that of polymeric separators. A promising alternative to glass is Kevlar [42,76,77,79]. A different approach has been to use vertically aligned nano alumina (VANS) [133], which demonstrated good interfacial bonding with conventional prepreg composite. The VANS were infused with P(VDF-HFP) and $TEABF_4$/PC between WCF electrodes. Although such electrodes provided negligible capacitance, the ionic conductivity of the VANS was superior to that of polymeric films.

3.4. Current collection

For conventional devices, current collectors can account for over 40% of the device weight [24], typically using copper or aluminium foils upon which a particulate electrode is deposited. Alternatives such as nickel, titanium, stainless steel and conductive polymers have been investigated, as well as using meshes, foams and etched films. Carbonaceous materials (e.g. CNT or GNP veils) have emerged as candidates, although these present challenges for joining to the electrical systems [134].

Very little work has focussed on current collection for structural supercapacitors, despite this having a profound impact on device scale-up [28,34]. Implicitly, the assumption has often been that the carbon fibres can provide the necessary conductivity; however, as the device size increases, the resistive losses become very significant. The problem is typically worse for structural supercapacitors than structural batteries, due to the focus on power density, which relates to ESR. Most research has used copper foil side strips as contacts, with little consideration having been given to the influence of current collection on device performance. Studies on structural batteries have used screen printing of conductive inks to develop tailored geometries of current collectors [135]. As illustrated in Fig. 5, scale-up of devices from 0.8 cm^2 (Swagelok) to 446 cm^2 (~A4 size) with edge strip current collectors leads to enormous reductions in electrochemical performance [61]. The specific energy fell from 1.75 Wh/kg to 0.83 Wh/kg, which was only partly recovered when covering the entire face with a copper mesh. However, the specific power fell dramatically, from 2.05 kW/kg (Swagelok) to 0.027 kW/kg (A4 size), and only slightly recovered when the copper mesh was used. This loss in performance has been attributed to the resistive losses, which can be partitioned into in-plane (longitudinal and lateral), out-of-plane, contact (electrode/current collector) and inherent current collector resistances. In-plane and out-of-plane resistivities are dictated by fibre/fibre contact in the electrode. Drawing on resistivity measurements, strategies have been formulated to reduce the power losses: contact resistance dominates for typical structural cells

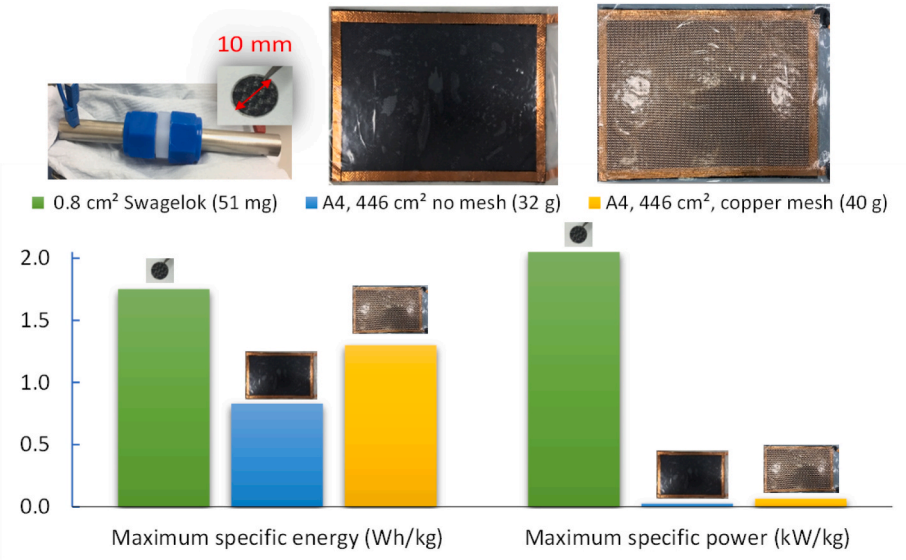


Fig. 5. Electrochemical comparison between small scale and A4 size structural supercapacitors using liquid electrolyte [61].

[136].

3.5. Encapsulation

The final constituent are materials for encapsulation, the role of which is to electrically isolate the cell from the surrounding systems, contain the electrolyte and protect it from the environment. The encapsulation should be light weight but robust, and can contain multiple (stacks of) cells, to minimise the parasitic mass. For structural supercapacitors, the encapsulation should also transmit mechanical loads across the device/encapsulation/system interfaces. For conventional devices, stainless steel or aluminium alloys are used, whilst for conventional pouch cells, the encapsulation consists of metallised polymeric films [137]. Other approaches for pouch cells for conformable devices include shrinkable tubes [138], elastomeric [139], silicone [140] or PVC [141] layers, although none of these will provide a load-transmitting layer. The literature on encapsulation of structural power devices has been sparse, with most researchers having used conventional pouch cells. Efforts have been made to use prepreg, such has glass-fibre epoxy. However, the ionic liquid in the multifunctional device can be leached out by the uncured (or even B-staged) epoxy, dramatically reducing the device performance [50,61], although such effects have not been observed by some researchers [142–145].

4. Device assembly and characterisation

4.1. Device manufacture

Most of the focus on structural supercapacitors has been on constituent development, whilst device assembly has relied upon conventional composite methods. However, the multifunctional nature of these materials presents additional challenges for fabrication which are rarely issues for conventional composites. Control and elimination of moisture during processing is perhaps the most critical hurdle for non-aqueous electrolytes. Most of these, such as ionic liquids, rapidly absorb water which degrades their subsequent electrochemical response. Exposure to voltages of over 1.23 V leads to performance losses, or in extreme cases, gas evolution. Structural supercapacitor electrodes tend to be high surface area materials and hygroscopic, which may carry unwanted moisture into the final device. Ideally, processing of structural supercapacitors should be undertaken in a moisture-free environment. In a laboratory context, glove boxes are often used, which may be difficult to combine with composite processing methods, particularly for larger components. For larger scale production, dry rooms as used for battery assembly, are likely to be used. The moisture problem is less severe for structural supercapacitors than that for structural Li-ion batteries, since devices can potentially be dried after assembly.

A further constraint on structural supercapacitor manufacture is the processing temperature. Whilst conventional thermoset composites are processed at below 200 °C, many engineering thermoplastic composites are processed above 350 °C. Usually the structural electrodes, and the associated active materials, can tolerate such high temperatures, although they are often brittle. Although many ionic liquids are stable to 300 °C, aqueous electrolytes and electrolytes such as polycarbonate are limited to below 100 °C. Except for glass fabrics, the most temperature-critical constituent is the separator, which is often thermoplastic. These materials frequently cannot be processed above 150 °C, since exposure to excessive temperatures leads to softening, distortion and closure of the separator pores. Note that temperature may be an issue for end-use, with applications such as aerospace having service temperatures ranging from −50 °C to 100 °C.

A further limitation is the pressure to which the devices are exposed during fabrication. Application of consolidation pressure is vital during assembly to remove voids, increase the fibre volume fraction (i.e., elevating modulus) and minimise the spacing between the electrodes. However, excessive pressure can lead to pinching of the separator between crests of the electrode weave, resulting in shorting. Adopting unidirectional tape or spread tow fabric can potentially alleviate this issue, but it is unlikely that a ‘separatorless’ device will be practical. Devices are typically only three plies thick and need to be very thin (fractions of a millimetre) to maximise electrochemical performance: this low thickness also ensures a sufficient number of cells can be stacked within a component to meet the electrical demands for typical platforms (usually in excess of 24 V). Thin devices make processing even more challenging, particularly when consolidating the device, and also make handling during lay-up difficult, promoting wrinkles etc. Finally, in thin devices, the resin skin which normally forms on the surface of composite laminates, can depress the overall fibre volume fraction.

Most device manufacture has focussed on flat panels, typically just a few centimetres in size. However, for industrial applications, curvature or changes in thickness are necessary, presenting difficulties for some of the electrode developments such as rigid carbon aerogels. The incorporation of current collectors prior to infusion ensures an intimate bond with the electrodes, but complicates device fabrication, exposing the current collector to uncured structural electrolyte and risking chemical interactions. The introduction of the structural electrolyte into the dry

laminate has drawn upon conventional composite processing methods. Due to the inclusion of low molecular weight electrochemical phases, such as ionic liquid, structural electrolytes tend to have lower viscosity than conventional matrices. However, the electrochemical phase can accelerate the cure of the structural electrolyte and constrain the processing time [146]. The low viscosity of the uncured structural electrolyte makes it amenable to resin infusion methods, such as RIFT or VARTM [20,60,89,93]. However, infusion results in large transport distances for the structural electrolyte, leading to poor microstructural control. Moreover, the active materials on the electrodes can lead to self-filtration and heterogeneities. An alternative route is to use RFI or prepregging, in which the structural electrolyte is filmed and then either stacked between or deposited on the electrodes and separator prior to assembly [58]. The drawback is that because the matrix space is partly occupied by active materials, complete electrode infusion is difficult.

4.2. Multifunctional performance

Characterisation of structural supercapacitors has drawn upon methods associated with conventional devices [8] and polymer composites. Electrochemical performance is established galvanostatic charge discharge (GCD), cyclic voltammetry (CV) and impedance spectroscopy (IS), which measure the capacitance, ESR and subsequently, power and energy densities. The response of the device is often fitted to a Randles circuit [8], consisting of a capacitance (C), ESR and a parallel resistance (R_p). The capacitance dictates the energy storage capacity whilst the ESR dictates the energy delivery rate. However, whilst conventional electrochemical devices are characterised using small devices, structural supercapacitors are larger and thus the measurements may be influenced by resistive losses (Section 3.4). Moreover, structural supercapacitors have inferior ion mobility to that of conventional devices, leading to sensitivities to charging rate and current densities. Finally, the soft structural electrolyte means that applied pressure will increase fibre-to-fibre contact, reducing the ESR. With no pressure, high variability manifests, whilst if the pressure is too high, shorting occurs [58].

Regarding mechanical testing, one of the challenges is the slenderness of the cells, resulting in the laminates falling outside the requirements for many of the standards. This non-standard geometry does not present difficulties for tensile or in-plane shear loading, and hence most of the literature has focused on these two loading conditions. Tensile performance is dominated by the fibre volume fraction, and so this loading condition provides little insight into matrix or interfacial issues whilst the need for a long gauge length can present difficulties when there is limited material supply. Since the greatest mechanical challenges for structural power composites typically arise from the demands of the structural electrolyte, in-plane shear testing is more relevant. This test provides a good insight into future performance, and a better guide to device development, as it reflects both fibre/matrix interface and matrix behaviour. Furthermore, the test piece is thin and quite short which makes it easier to test when material availability is limited.

To provide an insight into the comparative multifunctional performance from the literature (Table S1 and Table S2), specific capacitances versus mechanical parameters are plotted in the following Figures. Because the literature does not conform to any standard, these Figures have been partitioned into the following groupings.

- Devices using liquid electrolytes (normalised by active mass);
- Devices using structural electrolytes (normalised by active mass);
- Devices using structural electrolytes (normalised by device mass).

Unfortunately, since there is insufficient information to compare across these datasets, comparisons can only be made within these three groupings. In the following Figures the electrode type is indicated by a symbol, reflecting the different types described in Section 3.1, whilst the symbol colour indicates the electrolyte type. Finally, the reference associated with each datapoint is shown as labels in these graphs.

Firstly, the specific capacitance (normalised by active mass) using liquid electrolytes is plotted against the tensile modulus (Fig. 6a) and tensile strength (Fig. 6b). This dataset was typically generated using tows or veils immersed in liquid electrolyte, whilst the mechanical tests were undertaken on 'dry' electrodes: i.e., the measured mechanical properties do not correspond to the measured electrochemical properties. The data (Fig. 6) segregated into electrodes dominated by mechanical performance, and those dominated by electrochemical performance. Good multifunctional performance (and superior strength) was demonstrated using carbon fibres with GNP and activated carbon (AC) (E_{11T} = 236 GPa; X_T = 5300 MPa; C = 150 F/g) [49].

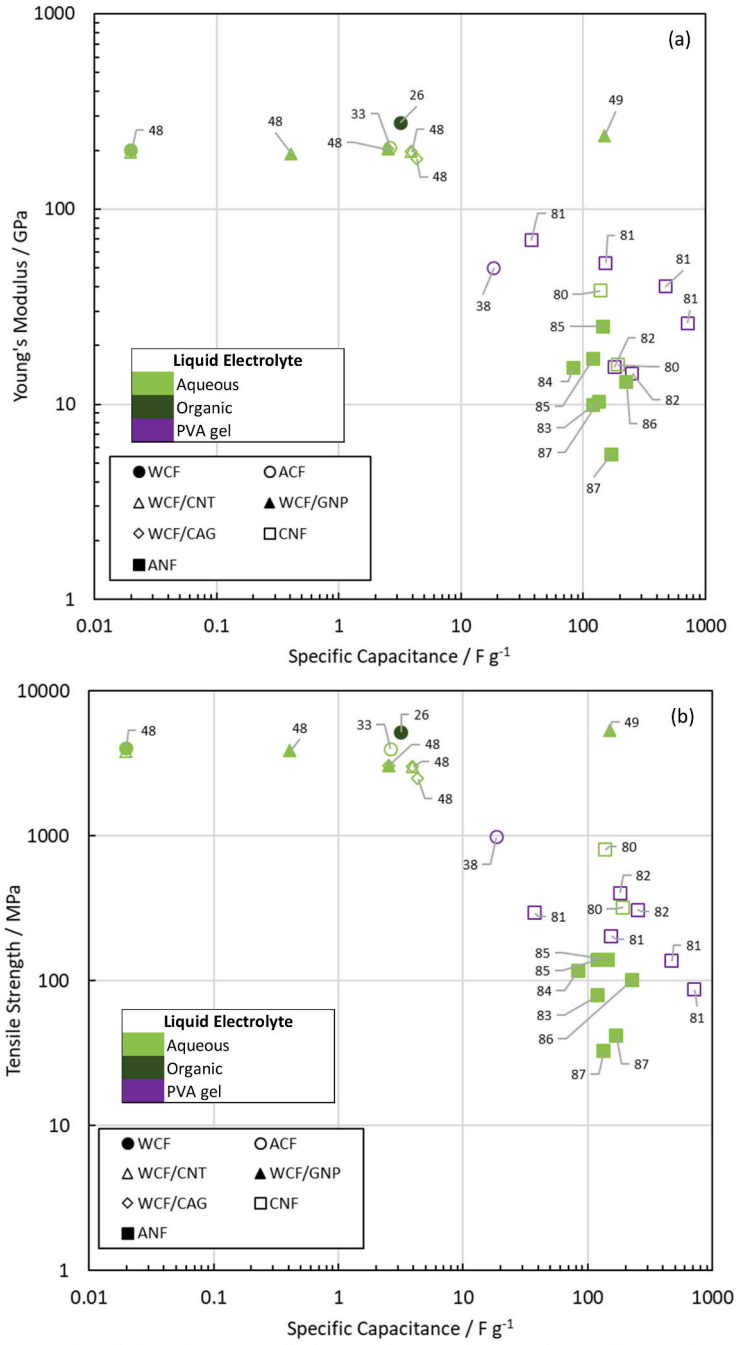
Regarding devices using structural electrolytes, Fig. 7a and b show the specific capacitance (normalised by active mass) plotted against the tensile modulus and strength, respectively. The best multifunctional performance was presented by WCF/CAG electrodes with an epoxy/EMIMTFSI electrolyte (E_{11T} = 33 GPa; X_T = 110 MPa; C = 1.57 F/g) [22] and WCF/GNP/MnO_2 electrodes with a PVDF-HFP/$BMIMBF_4$ electrolyte (E_{11T} = 11 GPa; X_T = 87 MPa; C = 165 F/g) [66]. Regarding strength, WCF/MnO_2/silane electrodes with an epoxy/BMIMTFSI electrolyte (E_{11T} = 14 GPa; X_T = 397 MPa; C = 10.5 F/g) [69] presented the best performance. All these materials offered improvements in both capacitance and mechanical properties compared to baseline devices. The in-plane shear performance versus specific capacitance (normalised by active mass) for devices using structural electrolytes are plotted in Fig. 8a (modulus) and Fig. 8b (strength). Although sparse, this plot identifies a balance between mechanical and electrochemical functions, again with WCF/CAG electrodes with an epoxy/EMIMTFSI electrolyte (G_{12} = 1.70 GPa; τ_{12} = 13.7 MPa; C = 1.57 F/g) [22] giving the best multifunctional performance. For the multifunctional data normalised by active mass, it should be noted that metal oxide and chalcogenide devices [52,75–79] were reported to have high multifunctional performance but they have been omitted from these multifunctional device plots due to concerns about the measurement conditions (see ESI). Nevertheless, the synergy between mechanical and electrochemical functions provided by metal oxide and chalcogenide networks within the matrix spacing is a promising approach for future structural supercapacitor electrodes.

Considering specific capacitance normalised by device mass, the tensile performance with structural electrolytes are shown in Fig. 9a (modulus) and Fig. 9b (strength). It is notable that the magnitude of the specific capacitance had significantly reduced compared to that in the previous graphs, indicating the importance of the non-active constituents on defining performance. Unlike the devices in liquid electrolyte (Fig. 6), the multifunctional performance presented a spectrum extending from mechanically to electrochemically dominated. Regarding modulus (Fig. 9a), the best performance was demonstrated using WCF/CAG with an epoxy/EMIMTFSI structural electrolyte (E_{11T} = 33 GPa; X_T = 110 MPa; C = 0.21 F/g) [22] although the tensile strength of this system was depressed. WCF with SnO_2 nanorods using a polyester/epoxy/$EMIMBF_4$/LiTFSI structural electrolyte had the highest strength (E_{11T} = 13 GPa; X_T = 450 MPa; C = 0.148 F/g) [73]. Finally, the shear modulus (Fig. 10a) and strength (Fig. 10b) of devices using structural electrolytes against the specific capacitance presented a broad spectrum of multifunctional performance. The best multifunctional (and electrochemical) performance was demonstrated by WCF/CAG with GNP in an epoxy/$LiClO_4$/PC structural electrolyte (G_{12} = 2.6 GPa; τ_{12} = 8.7 MPa; C = 0.35 F/g) [60].

5. Modelling, design and scale-up

5.1. Device modelling

Most structural supercapacitor research has been experimental although it should be noted that there have been numerical studies on



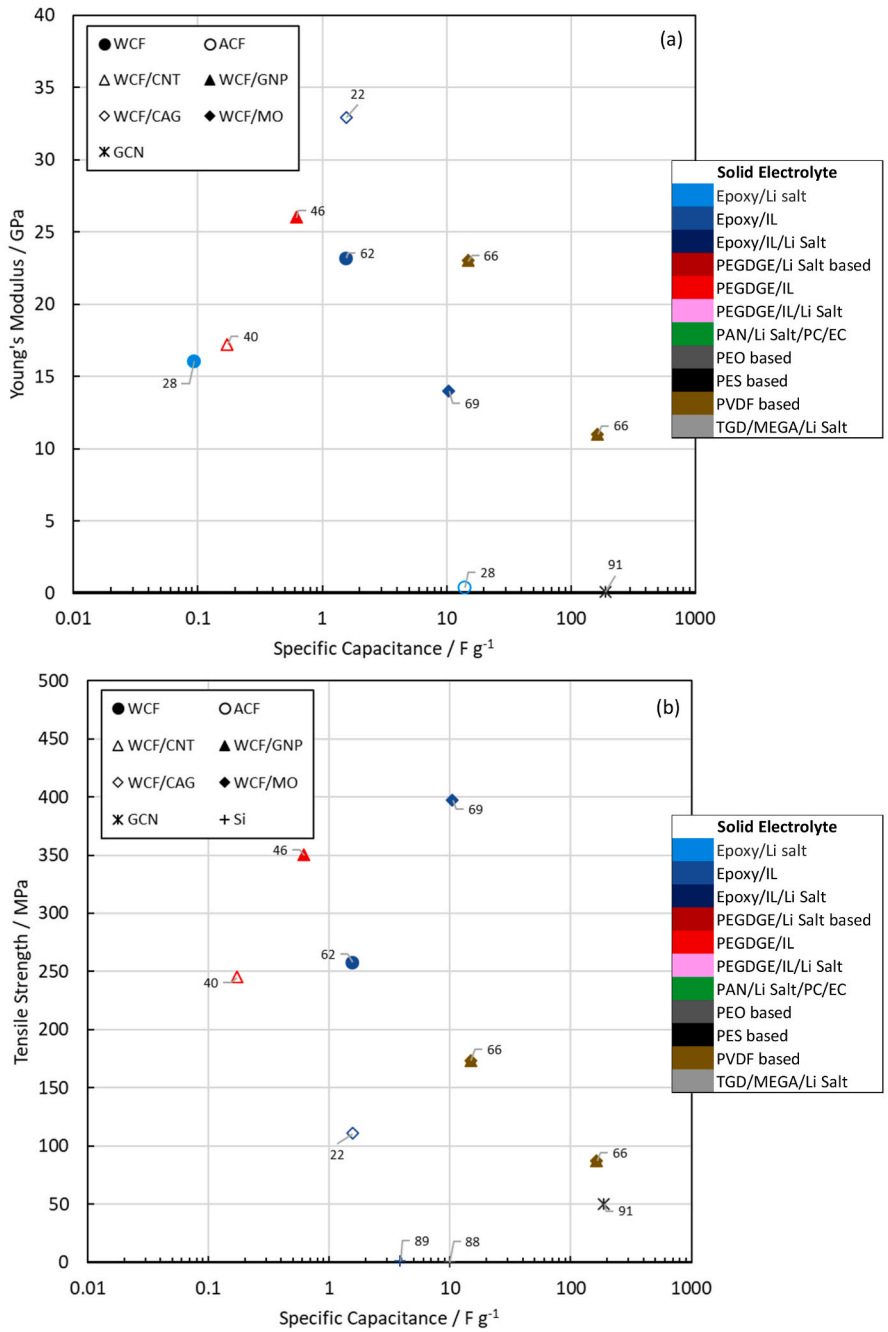
Key: ACF (Activated carbon fibre); ANF (Aramid nanofibre); CAG (Carbon aerogel); CNF (Carbon nanofibre); CNT (Carbon nanotube); GCN (Graphitised carbon nitride); GNP (Graphene nanoplatelet); MO (Metal oxide); PANI (Polyaniline); WCF (Woven carbon fibre).

Fig. 6. Specific capacitance (normalised by active mass) in liquid electrolyte versus (a) tensile modulus and (b) tensile strength for different electrodes. N.B. labels correspond to reference numbers.

structural batteries [147] and conventional supercapacitors [148]. Predictive models permit parametric studies into different constituents and architectures, and underpin certification of multifunctional components. With this in mind, multiphysics models that can predict coupling between mechanical and electrochemical functions will be essential. Most predictive models of conventional supercapacitors have focussed on the interfacial and transport phenomena associated with the device electrochemistry [149]. Although there is scope to draw on these models, the properties and scale of structural supercapacitors are quite different to that of conventional devices. The first step for such multiphysics models is to predict the detailed architecture following assembly, which not only dictates the fibre volume fraction (and hence the modulus), but also the electrode spacing (and hence the ESR) [150]. The resulting mesh is then used predict the mechanical and electrochemical response [59].

5.2. *Multifunctional design*

One of the core requirements of multifunctional composites is to provide a significant level of performance in two (or more) functions. In the context of structural supercapacitors, these functions are capacitance, and perhaps low ESR, whilst carrying mechanical load. Quantification of the multifunctional performance for minimum mass has been developed by defining a multifunctional efficiency, described as the sum

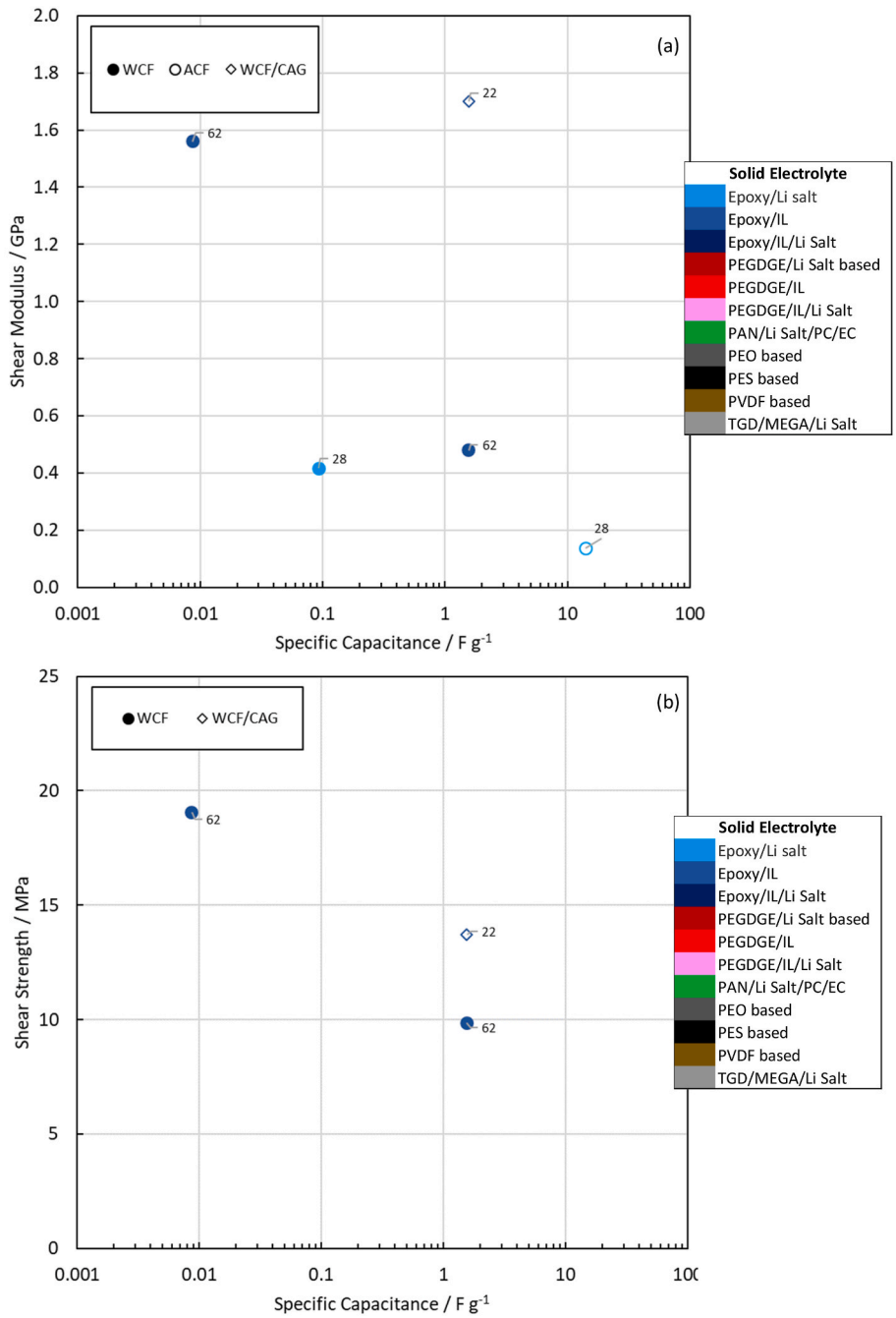


Key: ACF (Activated carbon fibre); ANF (Aramid nanofibre); CAG (Carbon aerogel); CNF (Carbon nanofibre); CNT (Carbon nanotube); GCN (Graphitised carbon nitride); GNP (Graphene nanoplatelet); MO (Metal oxide); PANI (Polyaniline); WCF (Woven carbon fibre).

Fig. 7. Specific capacitance (normalised by active mass) in structural electrolyte versus (a) tensile modulus and (b) tensile strength for different electrodes. N.B. labels correspond to reference numbers.

of energy and structural performance, each normalised by the equivalent monofunctional performance [151]. If the multifunctional efficiency exceeds unity, the multifunctional component will provide a weight saving over the monofunctional assembly. Several authors [6,17,18,20,21,151] have used this metric, or a development of it, to describe multifunctional performance. However, there are ambiguities associated with this approach, such as what to consider as the relevant conventional (monofunctional) components. An alternative methodology has assessed the 'residual' performance [152]. This metric equates the mechanical performance of a multifunctional device to that of a conventional laminate, and then assigns the 'residual' difference in mass to the electrochemical function. If the 'residual' mass is less than that of an equivalent monofunctional device, then the multifunctional material is deemed to have provided a weight saving.

There have been studies to develop the field of multifunctional design: i.e., resolving whether a multifunctional component offers a saving over the conventional assembly of monofunctional energy storage device and structure. The approach has been to audit the structural mass and the energy and power demands, and to then assess what specific energy and specific power the multifunctional material would need to provide to offer a saving over conventional systems. Very often, the introduction of multifunctional composites has wider implications for the overall system design, offering other savings, for example in cabling. This methodology has been used to evaluate the implications for aircraft cabins [153], future electric aircraft [154] and air taxis [155].



Key: ACF (Activated carbon fibre); ANF (Aramid nanofibre); CAG (Carbon aerogel); CNF (Carbon nanofibre); CNT (Carbon nanotube); GCN (Graphitised carbon nitride); GNP (Graphene nanoplatelet); MO (Metal oxide); PANI (Polyaniline); WCF (Woven carbon fibre).

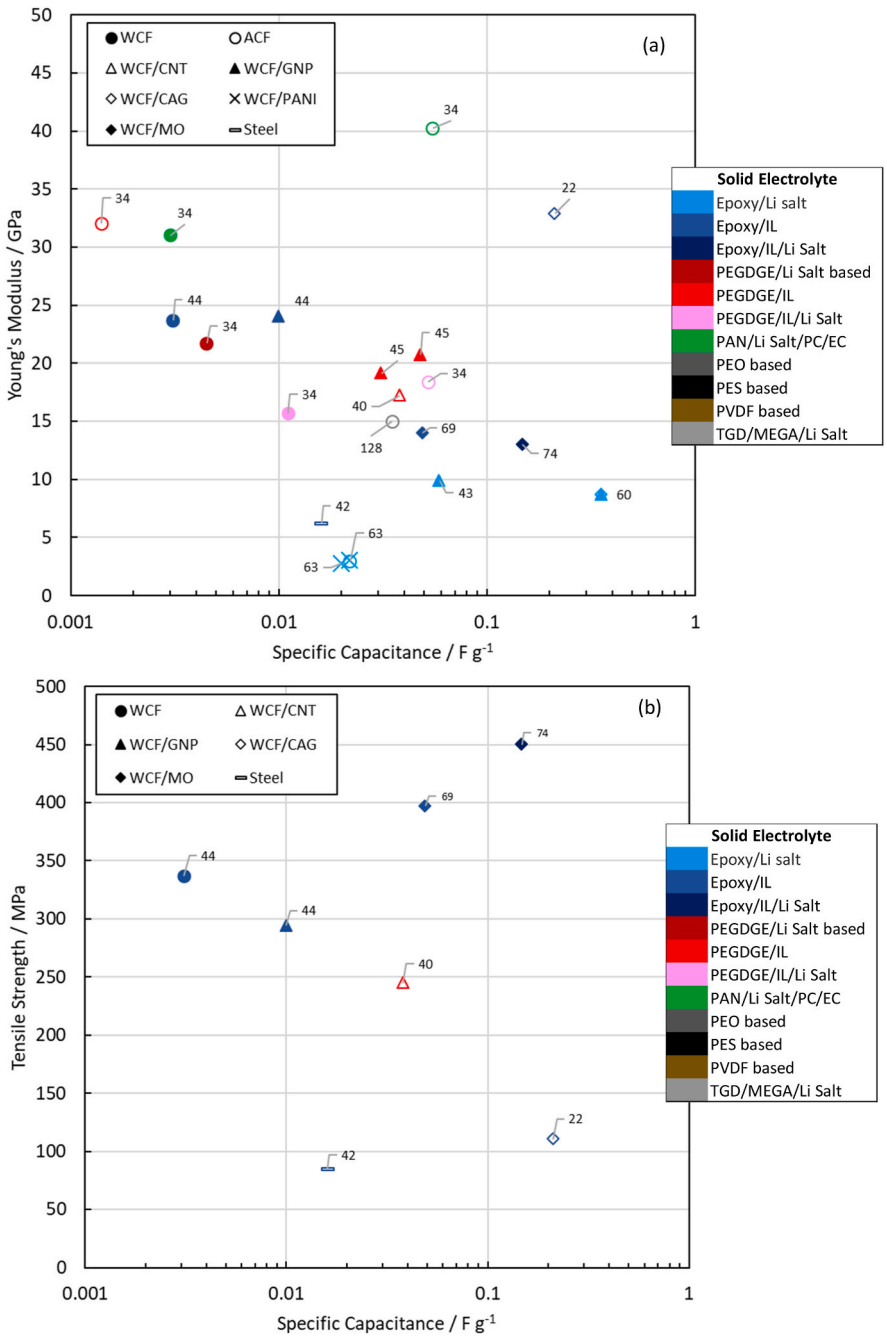
Fig. 8. Specific capacitance (normalised by active mass) in structural electrolyte versus (a) in-plane shear modulus and (b) in-plane shear strength for different electrodes. N.B. labels correspond to reference numbers.

5.3. Scale-up and demonstration

(a)

As discussed in Sections 3.4 and 3.5, scale-up of structural supercapacitors presents several hurdles. Where cells are stacked, the relative proportion of encapsulation can be reduced as compared to that for single cell devices. Since individual cells are typically limited to 3 V, multicell assemblies will be required to achieve the target voltages for end-use, and therefore the reproducibility of the nominally identical manufactured cells is important. Although the mechanical performance presents relatively little scatter [22], the electrochemical performance can vary considerably between nominally identical cells [58], resulting in an uneven voltage distribution. Most structural supercapacitors reported in the literature have presented single cells, typically lighting an LED: there has been relatively few multicell assemblies for industrially inspired demonstrators. Fig. 11a shows the development of a bootlid which contained four stacks, each of four A4 sized cells [156]. These were sandwiched between a precured outer skin and an internal skin, all cured at room temperature, with the final component lighting a series of LEDs.

A second demonstrator (Fig. 11b) was a C-section fuselage beam [157]. The cells, each about A5 size, were assembled into two stacks of four cells, which were interleaved into the web of the beam, and then sandwiched between two precured shells. The final beam was



Key: ACF (Activated carbon fibre); ANF (Aramid nanofibre); CAG (Carbon aerogel); CNF (Carbon nanofibre); CNT (Carbon nanotube); GCN (Graphitised carbon nitride); GNP (Graphene nanoplatelet); MO (Metal oxide); PANI (Polyaniline); WCF (Woven carbon fibre).

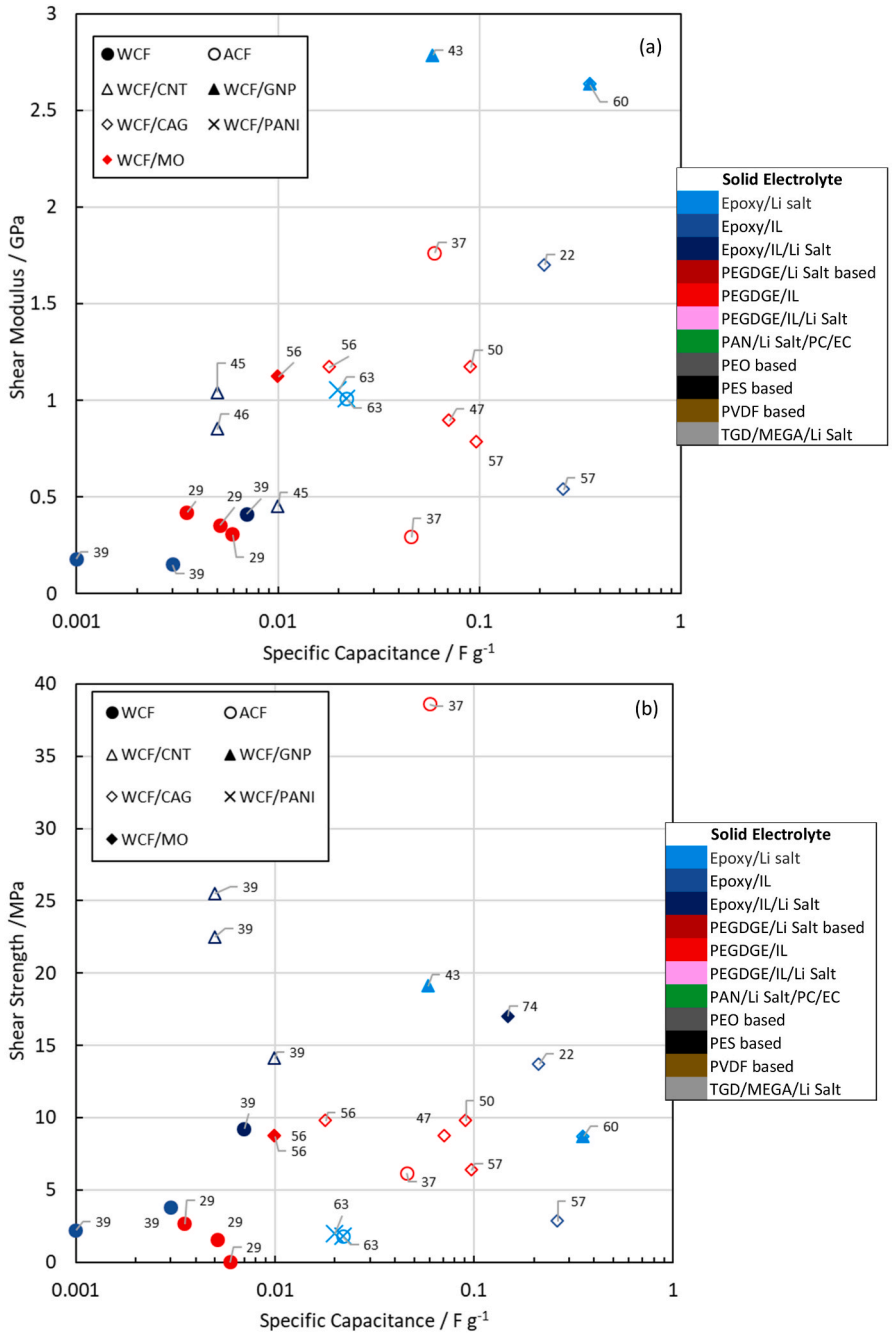
Fig. 9. Specific capacitance (normalised by device mass) in structural electrolyte versus (a) tensile modulus and (b) tensile strength for different electrodes. N.B. labels correspond to reference numbers.

demonstrated to open and close an A3 sized model aircraft door.

6. Outlook and concluding remarks

6.1. Constituents

Considering the constituents for structural supercapacitors, most of the research effort has been focused on electrodes, particularly using carbon fibres as the structural scaffold. Although non-carbon fibre-based electrodes have been developed (i.e., CNF and ANF), these have yet to be demonstrated as structural supercapacitors. Most electrode developments present a trade-off between mechanical and electrochemical performance, making advancing this technology challenging. However, the most promising configurations, WCF/CAG and WCF/MO, offer apparent synergies between mechanical and electrochemical functions. WCF/CAG presents a co-continuous high surface area microstructure, imparting high capacitance and effective ion access, but also partly fills the matrix space with a stiff phase, enhancing the mechanical performance. Metal oxide and chalcogenides apparently provide similar combinational benefits and potentially offer high specific capacitances [52,73–78]; full multifunctional device performance remains to be demonstrated (see ESI). Since many of these compounds are redox active or intercalation based systems, rather than EDLCs, they may have limited power performance. These electrodes have been explored at the



Key: ACF (Activated carbon fibre); ANF (Aramid nanofibre); CAG (Carbon aerogel); CNF (Carbon nanofibre); CNT (Carbon nanotube); GCN (Graphitised carbon nitride); GNP (Graphene nanoplatelet); MO (Metal oxide); PANI (Polyaniline); WCF (Woven carbon fibre).

Fig. 10. Specific capacitance (normalised by device mass) in structural electrolyte versus (a) shear modulus and (b) shear strength for different electrodes. N.B. labels correspond to reference numbers.

small scale (order of 100 cm^2), but the CAG-based system has already been built into larger demonstrators using processing techniques consistent with conventional composites. Full scale-up is yet to be demonstrated for these electrodes, but the CAG based system can be produced by processes consistent with conventional composites.

The most critical challenge to achieving true multifunctionality is the structural electrolyte (SE), since the best formulation is yet to be identified. Unlike structural electrodes, none of the proposed solutions offer synergies between functions, with dual phase RIPS and PIPS offering the best potential performance balance (Fig. 4). However, there are issues associated with scale-up, processing control of the SE microstructure upon introduction to the fibres and optimisation of the fibre/SE interface. Although, as reported in Section 3.2, there has been a significant effort in this field, this area still warrants further research.

More effort should be directed to the development of multifunctional separators, with particular focus on reducing thickness, enhancing porosity and improved mechanical bonding to the electrodes (without blocking the pores). Although structural lamina, such as glass fibres, have been adopted, membranes that are better optimised to maximise electrochemical performance would be preferable. Nanomaterials, such as nanocellulose [158], may offer a good solution due to their uniformity at low thickness and robustness.

Current collection is critical to scale-up of structural supercapacitors but has been largely neglected by the research community. Research

Fig. 11. *Multicell structural supercapacitor components (a) STORAGE Volvo S80 bootlid assembled from four stacks, each of four cells, within a CFRP skin* [156]*; (b) SORCERER C-beam showing individual cells, two stacks of four cells being integrated into the C-beam and connected to a desktop scale model of an aircraft door* [157].

focused on centimetre scale devices risks missing the importance of this issue. A key difference to conventional supercapacitors is that the integrity of the device comes from the fibres, not the metal current collector foil; so thin metal coatings can potentially be applied in optimised localised patterns. Non-metals, such as nanocarbons, may offer the best approach regarding compatibility, fatigue performance and avoiding corrosion. Finally, identifying a light weight and efficient solution for encapsulation of structural power devices is vital for maturing this technology. Current solutions are susceptible to the electrolyte leaching from the device. Encapsulation is perhaps a route by which to compact the device during use, and hence to enhance the electrochemical performance and inhibit delamination.

6.2. Device manufacture and characterisation

Except for aqueous electrolytes, the principal challenge associated with device manufacture is maintaining dry conditions during manufacture to ensure the electrochemical performance is maintained. This manufacturing constraint will have an impact and cost implication as to where structural supercapacitors can first find application, with small components (such as mobile devices, systems housings, and small elements for UAVs) being amenable to fabrication in dry environments. Developing new composite processes that can exclude exposure to moisture will be key to the translation of this technology to larger structural components, such as for aerospace, automotive and infrastructure. There may be scope for electrochemical drying to be used to manage and eliminate moisture ingress in structural supercapacitors. Device performance is also very sensitive to compaction conditions during processing: high compaction improves the fibre/fibre and current collector/electrode contact, hence reducing the resistivities. However, excessive pressure leads to electrode shorting, demonstrating the importance of the separator. Sensitivities to processing results in poor reproducibility between nominally identical devices. Therefore, the use of automated and robotic manufacturing processes may be beneficial, particularly if they can be undertaken under dry conditions. Moreover, using spread tow unidirectional tape architectures would reduce the electrode thickness and undulation, elevating the mechanical performance. Finally, the synthesis of the different active and high surface area electrode materials exposes the parent fibres to harsh conditions, removing the sizing (hence making them difficult to handle) and damaging them, which impacts on the modulus and strength of the resulting devices. In the long-term, rather than modifying off-the-shelf fibres purely optimised for monofunctional performance, the best approach would be to synthesise fibres with tailored surface properties for improved multifunctional performance.

The key outcome of this critical review is the need for standard methodologies to characterise and rank structural supercapacitors. For instance, the applied pressure during electrochemical testing should be described and defined. Constituent volume fractions and capacitance normalised by active material and device mass should both be reported. Applying such standards will permit robust and quantitative comparison between different configurations [22]. Regarding mechanical characterisation, no work has been undertaken on delamination of the electrode/separator interfaces in structural supercapacitors, despite toughness being a critical parameter for composite design.

6.3. Modelling, design and scale-up

By drawing on existing of models for conventional composites and electrochemical devices, numerical modelling could provide a compelling opportunity to advance structural supercapacitors. However, such models are complicated by the device being a thin hybrid composite and the compliant nature of the structural electrolyte. An aspiration is to deliver combined electrochemical-mechanical models which could, for instance, determine the influence of fibre volume fraction on the trade-offs between capacitance, ESR and mechanical performance. A further opportunity is using models to optimise current collection, which would underpin device scale-up.

Design tools for structural supercapacitors are relatively immature and need to be advanced to underpin industrial uptake. Such studies identify target material performance and motivate future research strategies. However, there is a fundamental quandary associated with the multidisciplinary aspect of structural supercapacitors. Efficient structural components rely on continuous load paths throughout the structure with minimal joints. However, from an electrochemical perspective, to minimise resistive losses, most power sources consist of stacks of small cells with many joints between them. To resolve this conflict, methodologies are needed to configure the multicell assemblies within a component to maximise mechanical load transfer and minimise electrical loses. The authors' aspiration is that of achieving larger continuous components (i.e., minimal joints): this would offer the best mechanical advantages for this technology. But key to delivering this would be to formulate and implement both efficient current collection strategies but also repair/replacement strategies.

There has been significant effort in constituent development for structural supercapacitors, but relatively little on device manufacture, characterisation, modelling and scale-up. There is considerable common ground between structural batteries and structural supercapacitors, particularly in the areas of structural electrolyte development, current collection, encapsulation, and fabrication. Hence, advances in structural

supercapacitor devices provide a stepping stone to addressing the generic challenges associated with other multifunctional structural materials [159]. This family of emerging multifunctional materials has the potential to make a considerable impact on fully electric transportation and beyond.

CRediT author statement

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Declaration of competing interest

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Data availability

Data will be made available on request.

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Appendix A. Supplementary data

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