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Multifunctional carbon fibre composites using electrochemistry

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ABSTRACT

Most products today have several functions, but these are achieved by integrating different monofunctional devices and/or materials in a system. Having several functions simultaneously in one single material has many potential advantages, such as a structural material that can also store energy, have self-sensing or self-healing capability or any other physical function. This would lead mass and resource savings, being more energy efficient and thus more sustainable. This paper presents a mini review on how carbon fibres can be used for integrating several functions simultaneously in a high-performance load carrying structural material using the electrical and electrochemical properties of carbon fibres. Through this carbon fibre composites can also store energy like a lithium-ion battery, be used as a strain sensor, have electrically controlled actuation and shape-morphing, and be used as an energy harvester.

1. Introduction

Reducing mass for improvements in system performance is a priority in a wide range of applications. Lowering the mass of electric vehicles can improve range while reducing the mass of handheld electronics such as mobile phones or power tools can improve their useability. Exploiting high performance materials such as carbon fibre (CF) composites in the structure of such products is one route to reduce the mass of load-bearing elements that require high specific stiffness and/or strength. However, the structure is often the subsystem with the highest mass contribution while other functions (e.g. energy storage, embedded sensors, and actuation mechanisms) are usually structurally parasitic as they add mass but no stiffness or strength to the structure. By combining several functions into one material, it is possible to create lighter and more resource-efficient products, capable of improving energy efficiency and useability [1].

Traditional approaches to engineering design most often use materials that perform one function, i.e. monofunctional materials. For example, the steel chassis of a car – despite being designed to provide stiffness and absorb energy during a crash – is still just a mechanical structure. Similarly, the battery pack in an electric vehicle provides energy storage but is structurally parasitic. Due to the monofunctional approach the same is true for many other products that combine a

mechanical structure with other functionalities (e.g. energy storage, sensing, actuation). Ideally, adding functionality to a material would not increase mass or mechanical complexity. Composite materials are well suited to provide multifunctionality since they are, by definition, a mix of different materials of different phases. CFs as a reinforcing fibre are particularly attractive as they can be used as both a high-performance structural material and simultaneously as an active component for other functions.

CFs are perhaps the most mechanically high-performing commercially available structural material in use today. CFs are thin carbonised filaments with a diameter generally between 5 and 7 μm . They are manufactured using a linear process, starting with a precursor (e.g. polyacrylonitrile (PAN), pitch, or bio-based polymers such as lignin [2]) which is spun and then carbonised in an inert atmosphere, followed by an optional graphitisation step. The resulting CF filaments have a carbon content of 90 % or more with varying portions of graphitic and disordered carbon depending on the precursor and heat treatment used. This morphology affects the CF stiffness, with elastic moduli typically in the range of 200–800 GPa [3], with higher degrees of graphitisation giving a higher modulus. The tensile strength is typically in the range 2–5 GPa, with tensile failure strain ranging from 0.7 to 2.5 %.

As well as their excellent mechanical properties, CFs have several other interesting properties. They have a very low or even negative coefficient of thermal expansion [4]. They are electrically conductive

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Abbreviations

BEV	Battery electric vehicle
CNF	Cellulose nano fibrils
CF	Carbon fibre
EGO	Exfoliated graphene oxide
K	Potassium
Li	lithium
LIB	lithium ion battery
LFP	lithium iron phosphate
Na	Sodium
NMC	Nickel manganese cobalt

OCP	Open circuit potential
PAN	Polyacrylonitrile
PEG	Polyethylene glycol
PEI	Polyethyleneimine
PIPS	Polymerisation induced phase separation
PVDF	Polyvinylidene fluoride
PECT	Piezo-electrochemical transducer effect
SBE	Structural battery electrolyte
SEI	Solid electrolyte interphase
SOC	State of charge
UD	Uni-directional
UHM	Ultra-high modulus

with an electrical resistivity in the order of $10^{-3} \Omega\text{cm}$, which is about 3 orders of magnitude larger than for many metals [5] but still enables CFs to be used as current collectors in energy storage devices [5]. They are also piezo-resistive (the electrical resistance changes with mechanical strain) [6] which allows CFs to be exploited as strain sensors. Due to their carbonaceous microstructure, CFs are electrochemically active: they can be charged with ions such as lithium (Li), allowing them to be used as an electrode material in a lithium-ion battery (LIB) [7,8]. During electrochemical charging, CFs undergo a reversible volume change, which when embedded in a composite laminate will cause stresses, something that needs to be mitigated. CFs also exhibit a voltage-strain coupling similar to piezo-electric materials. These properties make CFs a very interesting candidate for use in multifunctional materials.

This paper reviews the work carried out to demonstrate these properties and to show how they can be exploited to create multifunctional CF composites. The article begins with a section describing CFs electrochemical properties, which is followed by sections focussing on the functionalities of structural energy storage, strain-sensing, shape-morphing, and energy harvesting. However, there is no obvious physical reason why a material could not be conceived that could perform all five functionalities simultaneously. This, as well as perspectives on future work required to realise such multifunctional materials in commercial products, is discussed in more detail in the final section of the article.

2. Carbon fibre electrochemical properties

In commercial LIBs the negative electrode (the anode) consists of graphite particles. Li-ions intercalate between the graphene sheets and can theoretically store one Li-ion for every six carbon atoms (LiC_6) giving a theoretical capacity of 372 mAh/g that can be calculated from the stoichiometry. The idea of using CFs, being partly graphitised, as a negative electrode in a LIB is therefore not that far-fetched. A range of different CFs have been cycled electrochemically versus Li-metal in half cells [7,8], where the CFs are lithiated (Li-ions being inserted) and delithiated a number of cycles using different current rates. It was found that the fibres with higher graphitic content, ultra-high modulus fibres (UHM), did not perform all that well, whereas intermediate modulus fibres (IM) performed well [7]. The capacity of the UHM fibre M60J has been measured to be around 150 mA/g whereas the IM fibres T800 and IMS65 had capacities of 265 and 358 mAh/g, respectively [9], which then is close the theoretical capacity of graphite. To be noted, this was done at low current density corresponding to 10 h charge or discharge cycles (C/10). The relatively low capacity of UHM fibres is thought to be due the large crystal size and the turbostratic graphitic structure that obstructs radial transport and staging during lithiation. For lower modulus fibres the Li-ion insertion mechanism is closer to that of partly disordered (amorphous or hard) carbon [9], which suggests that their more disordered carbon structure is more favourable for Li-ion insertion. It has also been seen by NMR-measurements that Li-ions first occupy domains that lack ordered coordination (more amorphous carbon) while

at increasing Li content the more ordered domains (graphitic) become populated [10]. Most CFs appear to cycle stably electrochemically in half-cell set-ups but have higher first-cycle losses than graphite. One reason for that could be that the first-cycle losses are not only due to formation of the solid electrolyte interphase (SEI) on the surface of the fibres but also due to lithium being irreversibly trapped inside the CF [11]. The Coulombic efficiency was measured using high precision coulometry showing that some CF types have an efficiency surpassing even that of commercial graphitic negative electrode materials (so called meso carbon micro beads) [12], although some types of sizing, but not all, appeared to create chemical side reaction leading to more losses. All in all, it has been shown that CFs do work well as a negative electrode in LIBs.

Of great importance if CFs are used as a battery material is how the mechanical properties are affected by ion insertion. Measurement of the elastic modulus and tensile strength were performed on CF tows prior to electrochemical cycling, fully lithiated and fully delithiated. It was found that the stiffness did not change between the different states indicating the fibres did not suffer any permanent damage from electrochemical cycling. However, the tensile strength dropped after lithiation by 25–35 %, but after delithiation the strength recovered but was still about 5–10 % lower than for pristine fibres [13]. The decrease in strength rather depended on the amount of ions inserted into the fibre, with more (higher capacity) leading to larger strength drops [14]. The strength drop is thus linked to the strains caused by the volume expansions created by ion insertion. That the strength does not fully recover when the fibre was fully delithiated is another indication of trapped ions in the atomic structure of the CF. That the strength of CFs drop with ion-insertion is not really a show-stopper for multifunctional usage, at least for stiffness driven designs, since the stiffness does not change and the fibres do not seem to degrade from repeated electrochemical cycling.

Another interesting finding is that the radial modulus changes with ion insertion. By performing nano-indentation tests on uncycled, fully lithiated and fully delithiated fibres it was found that the radial elastic modulus doubled for the fully lithiated fibres, whereas the delithiated had approximately the same modulus as uncycled fibre [15].

The use of sodium (Na) or potassium (K) instead of lithium has seen a resurgence of interest lately due to concerns for the cost of Li as well as the reliance on critical minerals such as cobalt in LIBs. Cells made with Na- and K-ion chemistries have the same architecture as LIB's but using different electrode materials and avoids the need for e.g. cobalt and nickel, and are thus potentially more environmentally friendly chemistries. Na does not intercalate in graphite resulting in low capacity. Instead, hard carbons (carbons that cannot be graphitised) are used as the negative electrode [16]. Hard carbons are more less ordered, with a more randomly oriented microstructure consisting of interlacing, curved graphitic layers. K-ions do intercalate in graphite, but not as readily as Li-ions. Since CFs consist of a mix of graphitic and more amorphous domains it has been shown that both Na- and K-ions insert in PAN-based

CFs, however with a lower capacity than for Li-ions [17,18]. Similar to Li insertion, it was found that Na and K insertion also result in a decrease in tensile strength of the CF, but again mainly recovered after discharging [17,18]. Still, there is scope to make structural batteries using Na and K but that might require using different types of CFs with more amorphous structure.

Another more environmentally friendly approach is to use bio-based pre-cursors for making CFs, such as lignin and cellulose [19]. Such CFs are not yet commercially available but most probably will be in the very near future. But, lignin-based CFs also insert Li-ions with high capacity and up to 335 mAh/g has been reported [20]. Thanks to their more amorphous structures very high capacities, over 300 mAh/g [21], has been reached also with Na-ion insertion.

The work on electrochemical properties of CFs has shown that they will work as a LIB negative electrode material, and likely also for sodium-ion and potassium-ion batteries, as well as being a high-performance structural material which can also be used for current collection. CFs are in this respect a truly multifunctional material performing three different roles at the same time.

3. Carbon fibre based structural batteries

The fact that CFs both have high mechanical performance and are electrically conductive make them interesting for structural energy storage. A lot of research has been done on using CFs for structural supercapacitors [22]. However, supercapacitors rely on high conductive surface area and although CFs have a reasonably high surface area, around $0.2 \text{ m}^2/\text{g}$, it is far from sufficient for this kind of application. Efforts have been taken to increase the area of CFs using various surface activation techniques [23]. Some promising routes have been to use carbon nano tubes [24] or embedding the carbon fibres in a carbon aero gel [25]. Both these routes led to an increase in surface area of three orders of magnitude (to over $200 \text{ m}^2/\text{g}$) enabling high performance supercapacitor electrodes. Modified and augmented CFs have thus been proven to work as a multifunctional electrode material in structural supercapacitors.

The idea of CF based structural battery composites was first pursued by U.S. Army Research Laboratory, but they never succeeded in achieving any useable energy storage capacity [26]. The idea is appealingly simple but has turned out to be difficult to realise despite lots of efforts in the past 10 years or so. A schematic of a structural battery is shown in Fig. 1. It resembles a composite laminate and a LIB at the same time. It consists of a CF negative electrode, a positive electrode of CFs coated with a conventional active electrode material (e.g. lithium iron phosphate (LFP) or nickel-manganese-cobalt oxide (NMC)) and a porous separator, all embedded in an ion-conductive matrix material.

Such an assembly will have high structural performance thanks to

the CFs embedded in a polymer matrix. The CFs further act as current collectors so that the electrodes do not need to be covered by metallic sheets for current collection, which instead can be run through narrow metallic strips at discrete positions, saving mass. The separator must be electrically insulating and could also be structural, using for example aramid [28] or glass fibres, contributing to the overall stiffness and strength. Any such separator would need to be as thin as possible for satisfactory energy and power storage.

The structural battery electrolyte (SBE), i.e. the multifunctional composite matrix, also needs to have two functions, to transfer mechanical loads but at the same time be ionically conductive. Initial efforts utilized a homogeneous polymer thermoset containing ethylene oxide segments, that could coordinate Li-ions to facilitate ion transport, while the thermoset network provided a mechanical load transfer ability [29]. Although being a proof-of-concept that worked, this approach led to an unavoidable trade-off between ion conductivity and mechanical rigidity that limited the multifunctional performance [30]. The use of nanocellulose reinforcement in mechanically weak SBEs was shown to improve the overall multifunctional performance but deemed difficult to employ in a battery set-up due to processing limitations [31]. Another path of SBE's addressed both these issues by using a polymerisation induced phase separation (PIPS) approach to obtain a two-phase system on a nano-/micron scale where one liquid phase allowed for a good ion transport and the second solid phase gave mechanical integrity, a similar route to what has been used for structural supercapacitors [32]. The polymerisation process starts with a homogeneous mixture of lithium salts, conventional electrolyte solvents, and a difunctional methacrylate monomer (often denoted vinyl ester when used for composite applications) [33]. This mixture will, when polymerized, phase separate into a solid polymer phase and a liquid phase that both percolate on a nano-/micron scale. It was subsequently demonstrated that this process could be adapted to suitable thermal curing conditions in combination with battery constituents to form functioning half cells [34]. The multifunctional performance, i.e., elastic modulus and ionic conductivity, of a variety of SBEs was analysed using the finite element method [35] showing that substantial improvements can be achieved by topology optimisation.

CFs can then be mixed with the SBE using ordinary vacuum infusion techniques to form a unidirectional lamina with multifunctional performance [36]. This was done using spread tow Toray T800S fibres creating a thin lamina (about $45 \mu\text{m}$ thick) which was tested both electrochemically and mechanically. The electrochemical capacity was quite high, 230 mAh/g, at low charge/discharge rates (around C/10 corresponding 10 h). Mechanical tests were performed in longitudinal, transverse and off-axis direction completing the full stiffness matrix of the lamina. The longitudinal modulus was around 52 GPa, which is quite modest, mainly due to the low fibre volume fraction of around 18 %, which in turn was due to making one single layer with small thickness. It was shown later that this could be increased to over 100 GPa [37] becoming quite close to that of a unidirectional CF pre-preg layer (commercial pre-pregs with a similar fibre type has a longitudinal modulus of around 125–150 GPa). The transverse modulus was almost 2 GPa with a transverse strength of 12–14 MPa. It was further found that neither moduli nor strengths decreased after electrochemical cycling, implying that the volume changes due to electrochemical cycling did not affect the long-term mechanical performance of the material, although this was not tested for more than 10 charging cycles. There are several important conclusions from this study: the lamina is truly multifunctional, and mechanical properties do not seem to degrade with electrochemical cycling. The SEM pictures in Fig. 2 show fibres and fibre imprints in the SBE both before and after electrochemical cycling clearly indicating that the fibres have SBE residues on them enabling stress transfer and that the SBE is bi-continuous all the way into the CFs [36] enabling liquid contact to the CFs, creating a multifunctional interface. This was later tested experimentally by measuring the interfacial shear strength between the fibre and the SBE using a so-called droplet test,

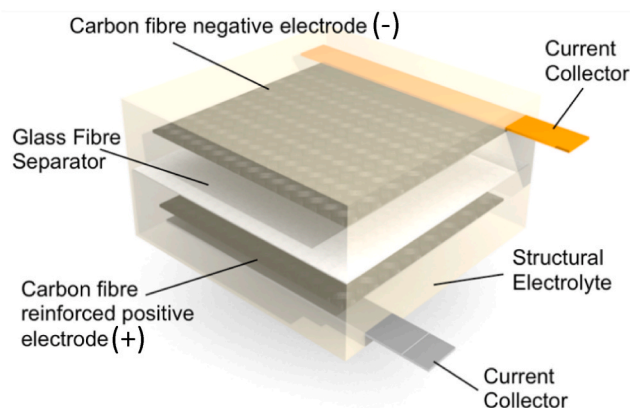


Fig. 1. Schematic of laminated structural battery composite [27]. Reproduced with permission under CC BY-NC-ND license, IOP.

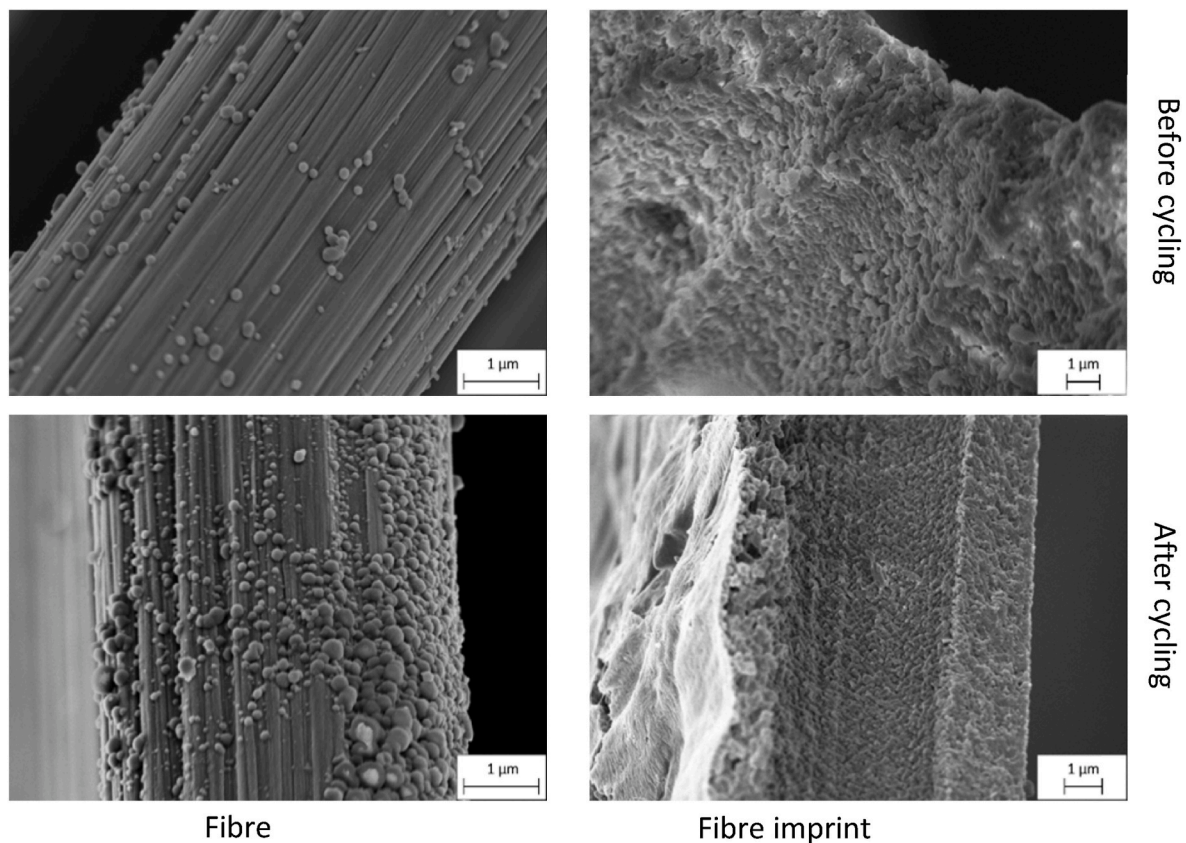


Fig. 2. SEM pictures of CFs combined with the SBE. (a) Non-cycled sample with matrix residue sticking to carbon fibres. b): Non-cycled sample showing SBE matrix with fibre imprint. c) Cycled sample showing SBE matrix residue sticking to carbon fibres. d): Cycled sample showing SBE matrix with fiber imprint. Reproduced with permission [36] under CC BY-NC-ND license, Elsevier.

confirming adhesion albeit with a lower strength than with a fully homogeneous polymer matrix system [38].

To realise a full battery cell of the type depicted in Fig. 1 there also needs to be a positive electrode. This is ongoing work but some progress has been made. The main idea is to coat CFs with active positive electrode material, which commonly come in the form of submicron size particles. The particles must then adhere to the CFs requiring a binder. The coating must also be electrically conductive making this somewhat complicated. Several different paths to obtain this have been pursued. Park et al. used an autoclave to infiltrate a slurry mix from LFP, carbon black and polyvinylidene fluoride (PVDF) into a CF fabric [39]. Using the same type of mix of materials CFs could also be coated using a dip-coating method [40]. Another route was to use electrophoretic deposition of LFP particles in a mix of PVDF binder and carbon black as a conductive additive [41]. This method created a quite homogeneous coating of each individual CF. The coated CFs showed good electrochemical capacity in the range 60–110 mAh/g with liquid electrolytes as compared with the capacity of LFP of around 150 mAh/g. These were, however, never tested with the SBE or in a full cell device. Another approach was to use exfoliated graphene oxide (EGO) as a binder in electrophoretic deposition resulting in a little higher capacity (around 130 mAh/g at C/10) [42]. These were subsequently tested as a full cell with a CF negative electrode reaching high energy storage capacity, over 200 Wh/kg based on the mass of the entire electrode, but this was done in liquid electrolyte so there was no mechanical performance. A powder impregnation (siphon impregnation) technique using a water-based slurry containing LFP and the water-soluble binder polyethylene glycol (PEG) showed a first discharge capacity of 151 mAh/g with capacity retention higher than 80 % after 100 cycles when cycled in liquid electrolyte [43]. Yet another approach was to use a layer-by-layer assembly of LFP and nano-cellulose fibrils (CNF) as binder creating

electrostatic adhesion from polyethyleneimine (PEI) [44]. The coated fibres were then carbonised at 450 °C turning the CNF binder into an electrically conducting carbon network. This technique has since been adopted to an infiltration technique resulting in higher LFP loading and a faster manufacturing process. For a more complete review of structural positive electrodes, see Ref. [45].

There are some research groups in the world looking into CF based structural battery composites of the kind discussed here, where every material constituent provides at least two functions, but have so far reported only poor to moderate multifunctional performances. Thakur and Dong [46] reported an energy density of 24 Wh/kg with an elastic modulus of only 0.29 GPa. Meng et al. [47] made a structural battery cell with an energy density of 1.4 Wh/kg and an elastic modulus of 7 GPa. In a later paper they achieved an energy density around 35 Wh/kg but still with a rather low modulus of around 2 GPa [48]. Liu et al. reported an energy density of 35 Wh/kg and an elastic modulus of 3 GPa [49]. So far, the best multifunctional results for a structural battery composite are an energy density of 24 Wh/kg and a modulus of 25 GPa, but that concept used a commercial LFP-based positive electrode [50]. This should be compared with today's commercial LFP-based batteries with an energy storage capacity of 130–150 Wh/kg and longitudinal modulus of an uni-directional (UD) CF composite of around 100–150 GPa. Still, showing a fully carbon fibre based structural battery, as depicted in Fig. 1, with good multifunctional performance has not been reported yet. More comprehensive and broader reviews on structural batteries can be found in Refs. [51,52].

For theoretical predictions of the multifunctional performance of structural batteries, multi-physics modelling is needed. Based on work on conventional batteries [53,54] a thermodynamically consistent modelling approach for the electro-chemo-mechanical properties of the laminated structural battery negative half-cell was developed [55]. It

showed that it is vital to account for the two-way coupling between the mechanical and electrochemical processes, which can be significant. This was later employed to study the electro-chemo-mechanical properties of the structural negative electrode accounting for the combined action from migration, stress-assisted diffusion, and convection in the electrolyte [56], and was found to successfully simulate continuous charge/discharge processes at different charge rates. It revealed that the convective contribution to the mass transport within the SBE has minor influence on the multifunctional performance for relevant mechanical loading situations [57]. Heat generation during galvanostatic cycling was found primarily associated with discontinuities in the electrical and chemical potentials at the fibre/electrolyte interface. This was later experimentally validated [58] with respect to the combined electrochemical and mechanical performance of CF/SBE half cells. The fibre expansion in the CF electrode gives rise to residual strains which were confirmed numerically. In a recent study, Larsson et al. demonstrated the need to consider finite strains to assess the internal stresses in the carbon fibre negative electrode. In that study, predominately compressive von Mises stresses up to 90 MPa were predicted in the structural battery electrolyte matrix as the fibres were fully lithiated [59].

Theoretical predictions on systems mass savings can be done using projected future multifunctional properties of structural batteries. However, how much depends on the system compared with. A structural battery replaces both a structural component and parts of a battery pack. A structural battery provides a mass saving if its mass is lower than the structure and battery pack combined, i.e. one multifunctional material replaces two monofunctional. Theoretical predictions show that there is substantial potential in structural batteries. For example, replacing a steel roof in a battery electric vehicle (BEV) could save up to 60 % mass on the roof since parts of the traction battery can be removed whereas replacing a CF hull structure in an electric ferry would only save about 10 % mass [60]. It can also be projected that making the casing for a lap-top as a structural battery could remove the need for a separate battery. In the BEV roof case it would also lead to a reduction of the environmental impact (LCA in CO₂-eq) [61]. Furthermore, the resulting reduced vehicle mass will bring more energy efficient electric vehicles to the market meeting consumer's demand for increased drive range [62]. Measuring multifunctional benefits is generally difficult and pedagogically complicated since a structural battery would in most cases have both lower structural and energy storage performance than the monofunctional counterparts (e.g. a CF-laminate and a commercial LIB). One way to make such comparisons is to evaluate what the performance of one of the monofunctional systems (structure or battery) must have so that the system has the same mass as the multifunctional system, called the residual performance methodology [63].

Combining structure and energy storage as a structural battery could potentially be used in any application which require a structure and electrical energy storage, such as road vehicles, aircraft, portable electronics and autonomous systems, completely or partly replacing conventional batteries. Still, showing a full carbon fibre based structural battery with good multifunctional performance has not been reported yet, but at least doubling (or tripling) what has been reported in the open literature so far should be possible in a not too far future reaching 75 Wh/kg energy storage capacity and 75 GPa longitudinal elastic modulus. That would lead to significant range improvements in e.g. electrical air-taxis [64] by having energy storage also in the structure.

4. Piezo-electrochemical transducer (PECT) effect enables strain sensing

There are many different methods for strain sensing in composite materials including piezo-electrics [65], optical glass fibres with Bragg gratings [66], polymer optical fibres [67] and piezo-resistive materials [68,69]. However, they all have disadvantages: piezo-electrics add parasitic mass to the structure; fibre optics could create unwanted stress concentrations in the material; and although promising piezoresistive

materials only offer a change in electrical resistance when strained – therefore limiting their applications to strain-sensing and damage detection.

Materials that change volume due to electrochemical reactions exhibit a change in equilibrium potential from mechanical strain. This is referred to as the *piezo-electrochemical transducer* (PECT) effect [70] and appears in ionically charged materials [71]. Similar to the piezo-electric effect, the PECT effect is a mechano-electro(-chemical) coupling that manifests itself as a change in electrical potential when a material is mechanically strained. It exists in several materials including silicon [72,73], aluminium [74], black phosphorus [75], and in LIB cells [70]. Carbon fibres also exhibit a PECT effect when inserted with alkali ions (Li, Na or K) [17,18,76]. The response is instantaneous and the electrical potential change is linear with applied mechanical strain [76].

Jacques et al. [76] showed that the PECT effect exists in lithiated CFs. CFs were placed in a pouch cell together with a lithium metal counter electrode and mounted in a tensile tester, before being loaded along the fibre direction. The cell open-circuit potential (OCP), the OCP being the potential or electrical voltage difference between the carbon fibre and the Li-metal counter electrode when no currents are running, was measured as function of an applied cyclic strain. The coupling factor, the ratio of change in OCP to applied strain, was found to peak around 50 % state-of-charge (SOC, 0 % SOC meaning fully delithiated and 100 % SOC fully lithiated) and reached around 1.5 V/unit strain [77]. The OCP response varied with SOC and a little surprisingly was the lowest for fully lithiated and fully delithiated states (0 or 100 % SOC). The CFs could only be loaded in tension though since a liquid electrolyte was used and compressive strains cannot be applied to a carbon fibre bundle without any structural support. The same type of experiment was later carried out for Na- and K-ion insertion using the same type of CF (Toray T800S) showing that the PECT response was much lower than for Li, with 0.15 and 0.26 V/unit strain for Na and K, respectively [18].

Embedding the CFs in a SBE enabled a laminate to be produced with structural integrity that could also be deformed in bending. This allowed the PECT effect to be measured in compression [78]. This was done in a three-layer set-up with two thin CF layers sandwiching a separator, which was then infused with the SBE. The two CF layers were then pre-charged up to a SOC of approximately 50 % using temporary Li metal counter-electrodes. The counter-electrodes were removed and the pre-charged laminate was then placed in a bending rig (Fig. 3a). A constant strain along the length of the beam was produced by forcing the laminate to bend with a constant curvature using clamps. It was found that the PECT response in compression was the same as in tension, but with opposite sign, as expected from theoretical predictions [55]. The OCP response from bending is shown in Fig. 3b.

The PECT effect could therefore conceivably be used to sense strain in a CF structure – given knowledge of the SOC and coupling factor between strain and OCP response – without adding parasitic mass.

Integrated sensing in lightweight CF composite structures is important, for example in aerostructures, wind-turbine blades, infra-structure applications and potentially also in future composite automobile structures to mention a few. By including a layer with a positive electrode, a coated CF layer, would enable the laminate to be recharged externally which would be needed since the system would self-discharge with time (just like a LIB does), and thus become both a battery and a sensor at the same time. In a structural battery subjected to external load the carbon fibres will exhibit the PECT effect enabling inherent strain sensing. To measure strain accurately the SOC must be known since the PECT response varies with SOC. Thus, some development remains before this technology is ready for use in practice.

5. Carbon fibre expansions used for actuation and shape-morphing

Structures that can change their shape by morphing are advantageous in a wide variety of applications. However, to shape-morph a

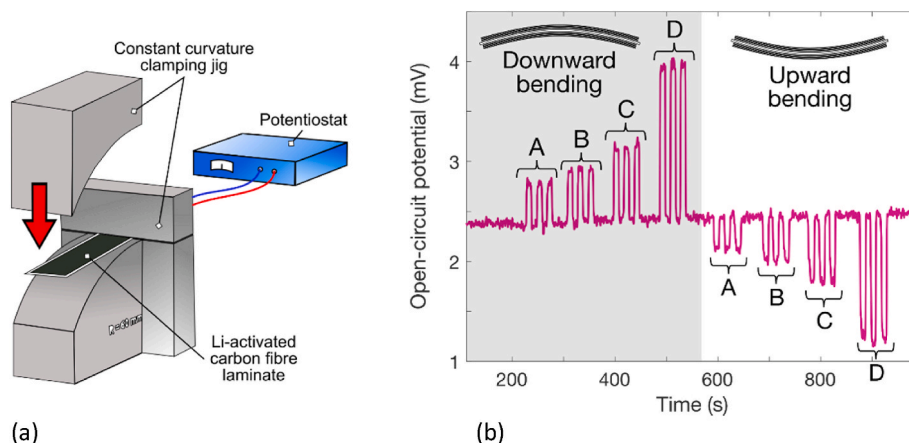


Fig. 3. Experiment showing the PECT effect in bending. (a) Experimental set-up bending a CF laminate to a known constant curvature and (b) the open circuit potential (OCP), or voltage response created from the PECT effect for different strain levels (A–D). Reproduced with permission [78] under CC BY-NC-ND license, American Chemical Society.

structure, actuators such as mechanical motors, hydraulics, and solenoids are needed to create the shape-change. Such systems and materials add parasitic mass and complexity. One route to reducing complexity is to use solid-state actuators such as piezo-electrics, shape-memory alloys, or pseudocapacitive materials, however these have some disadvantages. Piezo-electric materials typically work at high frequency but are mostly non-structural relying on adding patches of piezoelectric materials to the existing structure to enable shape-morphing [79]. Piezoelectrics also require high voltages to operate. Shape-memory alloys are also good actuation materials but need to be triggered by temperature or pressure changes [80]. Another interesting solution is to use pseudocapacitive actuation materials which provide high actuation force at low voltages [81–84]. However, such materials are often reliant on liquid electrolytes, preventing their use in structural applications. All the above-mentioned solid-state actuation materials require a constant trigger to maintain their deformation (e.g. a change in temperature), and revert back to their original form as soon as that trigger is removed. This in turn requires a supply of energy to maintain a given deformation.

Using volume expansions caused by ion-insertion in materials is an interesting way to create solid-state actuation that overcomes many of the above-mentioned challenges. It has the advantage of not only providing high actuation forces at low voltages but also presents the possibility of a zero-power hold, i.e. requiring no additional power to hold the deformation. It should be noted however that such actuators operate at low frequency and until recently have been limited structurally due to the use of liquid electrolyte for sufficient ion transport [85,

86].

When lithium ions are intercalated into graphite the volume increases of about 10 % [87]. Using CFs as the ion-insertion material for solid-state actuation has been proposed due to their favourable mechanical properties. Ion-insertion expansions have therefore been investigated in several studies. The expansion in the fibre direction was measured indirectly by applying a mechanical strain to CF bundles (Fig. 4a and b) and then cycling these electrochemically versus a Li-metal counter electrode [11]. The expansion in the fibre direction was measured as a load drop when the CFs were charged and expand (lithium insertion) followed by a load increase as the fibres were discharged and contract. By using a charge time of 1 h (1C) the CFs reached a capacity of 150 mAh/g and the measured axial expansion was around 0.3 %. However, lowering the charge rate to about C/10 the capacity reached around 300 mAh/g, and the reversible axial expansion increased to about 0.7 %. Despite this no mechanical degradation of the fibres was observed [13,14]. During the first cycle an irreversible expansion of around 0.2–0.3 % was observed, supporting the assumption that some Li-ions remain irreversibly trapped in the atomic structure of the CF after the first lithiation [11]. At first sight this number appears dangerously large since the failure strain of these CFs (T800 and IMS65) is only around 2 %. This explains some of the decrease in tensile strength when the CFs are lithiated but not necessarily all of it. Although the reversible expansion is almost half of the strain to failure of the uncycled fibre, the decrease in strength is less than that (25–35 %) and a plausible explanation is still pending [14].

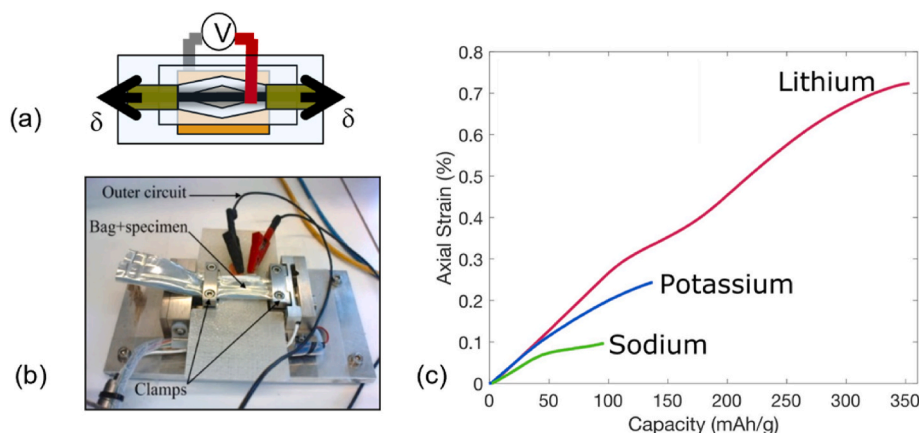


Fig. 4. (a) Schematic and (b) photo of a carbon fibre bundle in a half-cell setup mounted in a micro-tester subjected to a constant displacement. (c) Irreversible axial strain expansions of CFs from Li-, Na- and K-ion insertion. Data from Ref. [18] under CC BY-NC-ND license, Elsevier, and reproduced with permission from Ref. [90].

Volume expansion of CFs has also been measured with Na- and K-ion insertion [18] but even though Na- and K-ions have a larger ionic radius they still create lower expansions than Li-ions per capacity (amount of charge) as shown in Fig. 4. The clear bilinear strain vs capacity relationship seen for Na suggests a different storage mechanism in the CF microstructure, indicating that Na inserts more in ordered domains first before filling micropores at lower potentials. This is supported by the staging in the charge/discharge curves for Na-ion insertion in CFs [17, 88]. There is still, however, an on-going debate on these insertion mechanisms [89].

CFs also expand in the radial direction, in fact substantially more than in the longitudinal direction. The cross-section of the fibre expands up to 13 % when fully lithiated [11,15]. Despite this, it is less clear how this could be useful for structural actuation purposes given that the strength and stiffness of CFs are optimised along the fibre direction. Similar experiments to show radial expansion for Na- and K-ion insertion have not been reported yet.

CFs can be used as a linear actuator by exploiting the longitudinal expansions caused by ion insertion. Although such an actuator will be slow and the expansions from ion insertion are relatively small, very large forces can be created since CFs are very stiff. Such approaches have been taken using solid carbon materials for applications in MEMS (micro electromechanical systems) using graphite particles [91]. Actuators made from e.g. lead-zirconium-titanate (PZT) piezoelectric ceramic have an energy density of approximately 100 kJ/m^3 or a specific energy density of 14 J/kg . Assuming a CF with a modulus of 300 GPa that can irreversibly expand 0.5% when inserted with lithium ions the energy density is $(E\epsilon^2/2) 3750 \text{ kJ/m}^3$ and with a density of about 1750 kg/m^3 , the specific energy density is over 2000 J/kg . In fact, an expansion of only 0.5% corresponds to a stress of 1500 MPa , thus showing that very high forces could potentially be created. This can be achieved with a low electrical voltage of only a few volts with an inherent zero-power hold.

By combining the CFs with an SBE it is possible to create a shape-morphing laminate [37]. This was done the same way as with the PECT bending experiment, with partially pre-charged CFs on either side of a separator. The laminate layers were thin (about $40\text{--}50 \mu\text{m}$ for the CF layers and $20 \mu\text{m}$ for the separator), creating a laminate with a high longitudinal elastic modulus exceeding 100 GPa . By applying an electrical current Li-ions moved from one layer to the other, causing one layer to expand and the other to contract. This caused the laminate to bend significantly using small electrical currents at below 1.5 V [37]. By reversing the current bending was reversed. Large deformations were

obtained, and the material had a zero-power hold. A schematic of the setup and snap-shots of the morphing achieved are shown in Fig. 5.

It is thus possible to use electrochemically induced volume expansions in CFs to create both linear actuation and shape-morphing of a composite laminate with high mechanical performance. Although slow, it can create large forces, large deformation and is electrically controlled at low voltages, and does not require adding any materials for actuation.

Volume expansions of this magnitude are of course unwanted in structural battery applications and need to be mitigated or at least minimised. They could induce mechanical fatigue in the SBE leading to degradation of its properties. Using a modified version of classical laminate plate theory it was possible to show that in-plane deformations can be reduced by clever lay-up sequences in a structural battery, although all stress build-up cannot be completely avoided [92].

Morphing, although assumed to be rather slow could be of great interest trimming surfaces for fluid control in for example aircraft wings, wind-turbine blades, or other flow-control applications, leading to lower drag, higher efficiency and lower energy consumption. By adding a positive electrode and having two (or more) CF negative electrode layers, the CF layers can be controlled individually, expanding or contracting the layers without influencing each other. The material can then also be recharged using an external electrical circuit. Then it would also be possible, by altering the fibre angles of CF-layers, to create other forms of morphing [92], i.e. twisting and combined twisting and bending. An increase in deformation rate might be needed for practical use in some applications.

6. Energy harvesting using carbon fibres

An important complement to energy storage is harvesting energy from the surrounding environment [93]. Harvesting energy can supply power to functions needed in, e.g. autonomous systems. Piezoelectrics can be used to convert mechanical motion to electrical energy through their mechano-electrical coupling. These have previously been integrated in structural composite materials to add an energy harvesting function [94,95]. However, since piezoelectric materials are typically quite brittle, this approach adds parasitic mass to the structure. They are usually also restricted to operation at relatively high frequencies. Capacitive materials show great potential for energy harvesting with high efficiency and high power output [96], although most concepts rely on liquid electrolytes.

The PECT effect is also a mechano-electrical coupling that can be

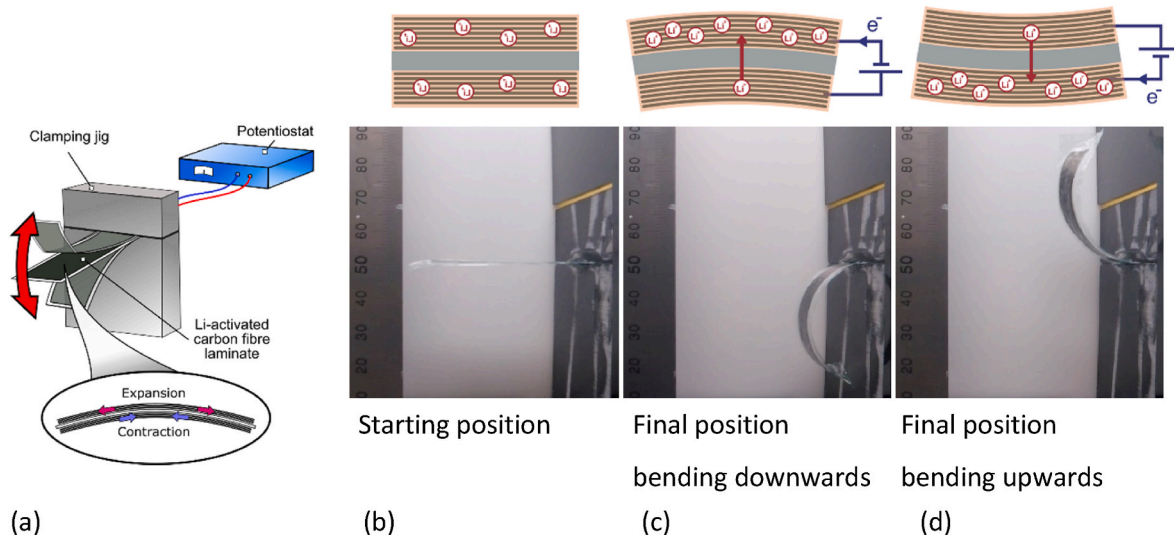


Fig. 5. (a) Schematic of set-up for shape-morphing experiment and photos of shape-morphing laminate created by axial expansions of CFs during lithiation and delithiation. (b) Before applying an electrical current. (c) Running the current one way then (d) running it in the opposite direction. Reproduced with permission [37] under CC BY-NC-ND license, National Academy of Sciences.

used for energy harvesting. This has been shown using prismatic LIB cells [70], silicon [73], aluminium [74], black phosphorus [75], and Prussian blue [97]. The harvested power is quite low, but it is hard to compare between the different approaches since the reported data are given with different metrics (W/g, W/cm², etc). Piezo-electrochemical energy harvesting works best in the low frequency range (e.g. < 10 mHz) with the best output having high strain rates (e.g. > 1×10^{-3} /s) and long hold-times (e.g. < 60s) [98].

Energy harvesting with ion inserting materials is possible by exploiting a combination of the PECT effect and volume expansions of the material caused by ion insertion. This was shown for both a standard battery cell [70] and a CF bundle in half cell with a Li-metal counter electrode in liquid electrolyte [77], using in principle the same approach. In the CF case, a CF bundle was charged, after which a mechanical load (strain) was applied, raising the electrical potential through the PECT effect. The CFs could then be discharged at a higher cell voltage than when charged; effectively harvesting electrical energy. The harvested energy comes from losses in mechanical work due to the reversible Li-ion insertion strain in the CFs during the harvesting cycle. Using CFs in tension led to a harvested power of 1 μ W/g of CF.

The more recent development of structural SBEs made it possible to show energy harvesting in a load bearing CF laminate. The set-up was similar to the sensing and shape-morphing experiments previously described using two pre-charged CF layers sandwiching a separator embedded in an SBE. This created a stiff (high in-plane modulus), but thin, unidirectional laminate with a longitudinal elastic modulus around 100 GPa. This laminate was then subjected to three separate tests. First, the PECT response was measured, as described previously (Fig. 3), by bending the laminate and measuring the OCP (no currents running). In the next experiment, the two CF-layers were subjected to the very same experiment but with the two carbon fibre layers being short-circuited after which an applied bending deformation resulted in a current running between the CF-layers (but with no electrical potential difference). This is known as the short-circuit current. In the third experiment, depicted in Fig. 6a, an external electrical load was placed in series with the two CF-layers, allowing a current to run through the resistor creating an electrical power according to methodology reported by Preimesberger et al. [99]. By matching the external electrical load (resistor) to the internal resistance of the source (the laminate), according to the maximum power theorem [100], an electrical power of approximately 18 nW/g could be harvested [78]. The results being shown in Fig. 6.

Although the expected power that can be harvested from ion-inserted CFs is rather small the energy “comes for free” from deformations and low frequency vibrations of a structure subjected to external loads. Though not really shown yet this should work in a rather

large frequency range from moderate to really low frequency and long hold-times. It could be useful in various autonomous applications where weight is sensitive, such as unmanned aerial vehicles, satellites, low power electronic devices, MEMS devices where energy could be provided to micro/nano-sensors or actuators, or sports applications with integrated sensors, requiring energy harvesting and storage, reporting fitness, health, and performance statistics. Similarly, engineering infrastructure can benefit from self-powered distributed sensing networks. Including a positive electrode is perhaps even more intriguing for this function since energy could be then harvested and stored in the material itself, where it is generated.

7. Outlook and concluding remarks

There are still several areas, both regarding constituents and architecture, that can and need to be improved to increase performance and most of them apply to all the functions described as they rely on the same physical/chemical foundation.

Contemporary CFs are made for one purpose: to be an efficient structural material. So far, no efforts have been made to make CFs with better multifunctional properties combining structural stiffness and strength, electrical conductivity and ion-insertion capacity. This would probably involve tailoring the manufacturing process to achieve a microstructure with an optimal balance between these three characteristics.

To improve both energy and power density in the battery function the electrodes and the separators should be as thin as possible. That would also improve the rate of actuation and shape morphing, and most probably also the power output from energy harvesting. Actually, smaller diameter CFs could do that, however, possibly creating larger first cycle losses due to increased surface area. New separators should be developed, being not only thinner but also adding to the structural stiffness and strength.

There are ongoing efforts on making CF-based positive electrodes using various kinds of concepts for coating CFs with active cathode materials e.g. Refs. [43,101]. This is perhaps the most imminent and important development at the moment. The methods need to be robust, the coating must adhere to the fibres well and be electrically conductive. For possible scale-up the coating method must be continuous as opposed to the currently reported methods mainly being batch processes.

The state-of-the-art SBE systems are still far from fully developed and understood, and there are on-going efforts to improve their performance further. Recent findings have for example revealed that these two-phase systems are more complex when it comes to the effect of the chemical composition and morphology on the ion transport ability. It is the

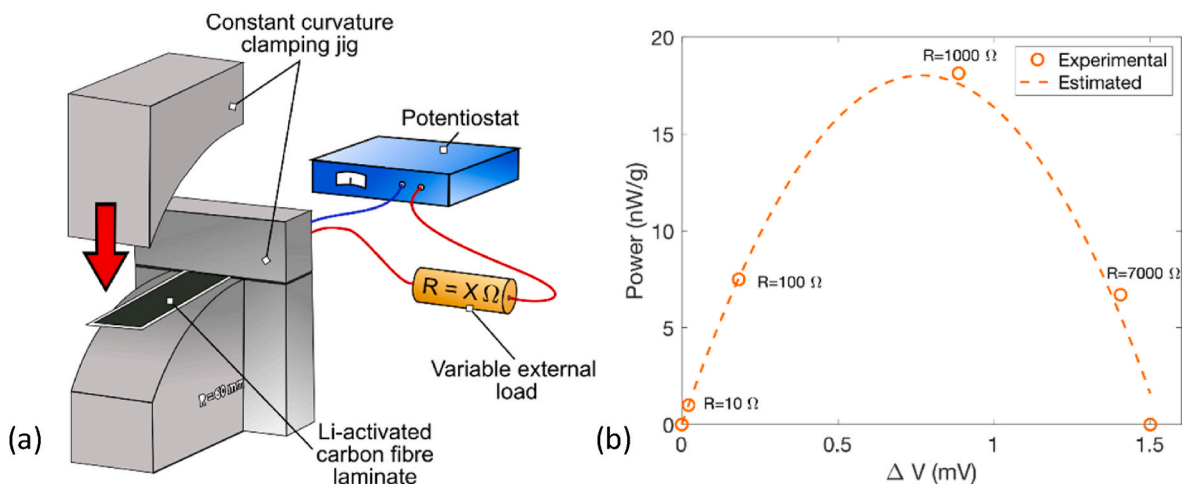


Fig. 6. (a) Schematic of energy harvesting experiment. (b) Measured power output for different electrical loads. Reproduced with permission [78] under CC BY-NC-ND license, American Chemical Society.

combination of all in-going constituents and how they interact that must be considered and here it is of great potential for further developments [102]. Another aspect is that the multifunctional performance should be better adopted to different specific applications where different properties are essential e.g. ductility, stiffness interface adhesion, etc.

There are also several future technical challenges. Although CFs are electrically conductive their resistance is much higher than for Cu or Al so to avoid large Ohmic losses some metal current collectors will be needed. It would, however, be sufficient to have metal current collectors in grids at specific distances, which will save considerable mass. One possible approach for this is to inkjet print current collectors on the CF electrodes [103].

The structural battery, or any other multifunctional laminate using this technology, must be encapsulated and protected from the surrounding environment. This is for two reasons: to avoid evaporation of the liquid part of the electrolyte in the SBE but more importantly to prevent moisture ingress which would very quickly degrade any electrochemical performance. This is a challenge shared with structural supercapacitors. Having fully solid SBEs would solve the evaporation problem but not moisture ingress. The encapsulation must thus also be multifunctional able to transfer stress to any surrounding structure. A good encapsulation method is still to be found.

No future technologies can really be accepted if it increases the environmental footprint. Based on estimated future performance values of a structural battery it was shown that the environmental footprint (in terms of lifetime CO₂-eq) could be reduced in e.g a BEV application [61]. More studies like this must be done in parallel with technological development to ensure that positive environmental impact is projected.

There are other paths to improved sustainability. Making high performing CFs from bio-based precursors, e.g. lignin and cellulose, would lower the environmental impact significantly. Much effort is ongoing at the moment in that area, e.g. Ref. [104]. As also discussed, both Na- and K-chemistries could potentially be used in the future. Na and K are much more abundant alkali metals than Li and avoids the use of cobalt. Work on lignin-based CFs have shown that their less ordered structure, being a hard carbon rather than a graphitised material, enables excellent electrochemical ion storage capacity not only with Li, but also with Na and K [20,21].

A grand future challenge is efficient manufacturing and upscaling. It has been shown that resin vacuum infusion methods can be used, i.e. using a dry fibre lay-up which is bagged and infused with a liquid SBE which is then cured at elevated temperature [34,36]. This is a well-established route for composites manufacturing. Some trials have been done using coextrusion technique to 3D-print CF-based structural batteries [46,105,106] which show some promise, but the electrochemical capacity was quite low and so were the mechanical properties. Some of the manufacturing steps probably needs to be performed in a moisture free environment imposing new challenges. Another is that the layers should be very thin for optimal performance. A third is that any single stray CF through the separator will lead to short-circuiting resulting in a loss of all the additional functions. Automated manufacturing with high precision is thus needed for both robustness and up-scaling. The multifunctional material also needs to be integrated into an otherwise monofunctional material building up the structure which would require electrical wiring, encapsulation and perhaps also compartmentalisation.

In some applications there will be temperature constraints since the rate of electrochemical reactions will be impaired with lower temperatures (typically sub-zero °C) and can create safety problems at high temperatures (typically above 50–70 °C) which are the same challenges as for commercial alkali-ion batteries. Safety is also to be considered since the material will be electrochemically active [107]. Another important aspect is how the long-term performance is affected by electrochemical cycling and mechanical loads simultaneously that could lead to material fatigue and electrochemical degradation. These issues are again common to commercial LIBs but with some additional

complexities. Material recycling must also be considered at some point for environmental reasons. The large mix of different constituents in these materials will make that a complex task to solve. Damage and subsequent repair are other challenges for future development along with component replacements. Multifunctional materials might have a lot of possible advantages but if a part of the structure is damaged several functions will fail at the same time!

Simple single function metrics to describe a material (e.g. electrical storage capacity, or elastic modulus) will not be sufficient to describe a multifunctional material. Instead, new metrics will be needed that will help designers understand the performance improvement across all functions at a systems level. Some initial work has been carried out on this [60,63], but more is needed to give designers tools to be able to assess the benefits multifunctional materials can bring to any given product. Multiphysics based simulations tools will also be necessary for designers integrating structural mechanics with electrical and electrochemical predictions.

This technology is still emerging and several of the functions described in this paper are not more than proof-of-principle and not shown to work in concert yet. Still, it seems possible to have all the five functions integrated in one single laminate, as schematically shown in Fig. 7. The future will tell if even more functions can be added, all without added mass or complexity, providing intriguing opportunities for lighter, more resource efficient, more energy efficient and more sustainable solutions.

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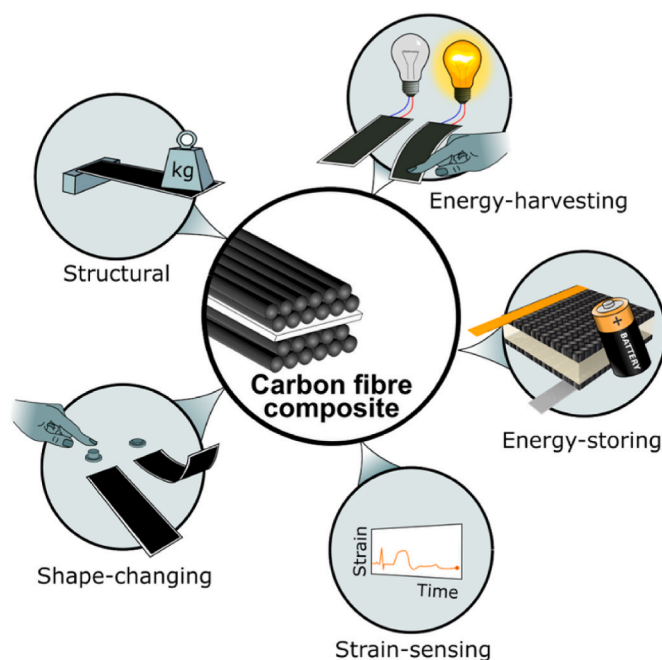


Fig. 7. Multifunctional carbon fibre composites from electrochemical activation. Five different functions in one material [90].

CRediT authorship contribution statement

Dan Zenkert: Conceptualization, Writing – original draft. **Ross Harnden:** Writing – review & editing. **Leif E. Asp:** Writing – review & editing. **Göran Lindbergh:** Writing – review & editing. **Mats Johansson:** Writing – review & editing.

Declaration of competing interest

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

Data availability

No data was used for the research described in the article.

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