



AFRL-AFOSR-UK-TR-2021-0012

Damage Tolerance and Durability of Structural Power Composites

Zenkert, Dan
KUNGLIGA TEKNISKA HOGSKOLAN
230 W 41ST STREET FL 7
NEW YORK, NY, 10044
US

06/21/2021
Final Technical Report

DISTRIBUTION A: Distribution approved for public release.

Air Force Research Laboratory
Air Force Office of Scientific Research
European Office of Aerospace Research and Development
Unit 4515 Box 14, APO AE 09421

REPORT DOCUMENTATION PAGE				Form Approved OMB No. 0704-0188	
The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing the burden, to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.					
1. REPORT DATE (DD-MM-YYYY) 21-06-2021		2. REPORT TYPE Final		3. DATES COVERED (From - To) 01 Sep 2017 - 31 Aug 2020	
4. TITLE AND SUBTITLE Damage Tolerance and Durability of Structural Power Composites				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER FA9550-17-1-0244	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) Dan Zenkert				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) KUNGLIGA TEKNISKA HOGSKOLAN 230 W 41ST STREET FL 7 NEW YORK, NY 10044 US				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) EOARD UNIT 4515 APO AE 09421-4515				10. SPONSOR/MONITOR'S ACRONYM(S) AFRL/AFOSR IOE	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S) AFRL-AFOSR-UK-TR-2021-0012	
12. DISTRIBUTION/AVAILABILITY STATEMENT A Distribution Unlimited: PB Public Release					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT Research objectives successfully met and deliverable received. Follow on grant already awarded.					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			DAVID GARNER
U	U	U	SAR	103	19b. TELEPHONE NUMBER (Include area code) 314-235-6420

Final Technical report

Damage Tolerance and Durability of Structural Power Composites, Award no.: FA9550-17-1-0244

This is a technical report on the work performed by KTH – Royal Institute of Technology (KTH), Stockholm, Sweden under the award no. FA9550-17-1-0244 during the time period 2017-09-01 to 2020-08-31. It is intentionally brief and only covers short descriptions of the work performed that has resulted in publications. The journal publications are appended to this report.

The work is focused on realizing carbon fibre based structural battery composites. It has several streams of research. Development of structural battery electrolytes which are ionically conductive and can transfer mechanical loads like the matrix material in a composite. Measurements of the fibre/matrix adhesion using these novel structural battery electrolytes. Modelling of systems level performance using structural batteries. Life cycle analysis (LCA) of structural batteries compared to using monofunctional systems of structural materials and batteries. Introducing a new multifunctional metric to better showcase the advantages of using structural batteries and multifunctional materials in general. We have written a review paper on the current state-of-the-art of structural batteries. We have then used the knowledge and materials developed to make a new type of shape morphing material, which is based on the same fundamental technologies used in a structural battery. Finally, we studied Potassium ion insertion in carbon fibres to investigate if this other ion chemistry is suitable to create multifunctional composites, particularly for energy storage, sensing and morphing. Some more in-depth descriptions of this work is presented below.

All-in-all the work has resulted in 8 journal papers and 5 conference papers completely or partly funded by this AFOSR/EOARD grant. It has also contributed to the completion of a Ph.D.-thesis. Some of the work has been done in collaboration with Chalmers University of Technology (Chalmers) with Prof. Leif Asp and his group (2 of the papers), and with Imperial College London (ICL) with Prof. Greenhalgh and his group (1 paper).

The Team

This project has been conducted as part of a larger portfolio of projects run by an interdisciplinary team at KTH headed by Profs. Johansson, Lindbergh and Zenkert. All together six Ph.D.-students has been involved (Figure 1).

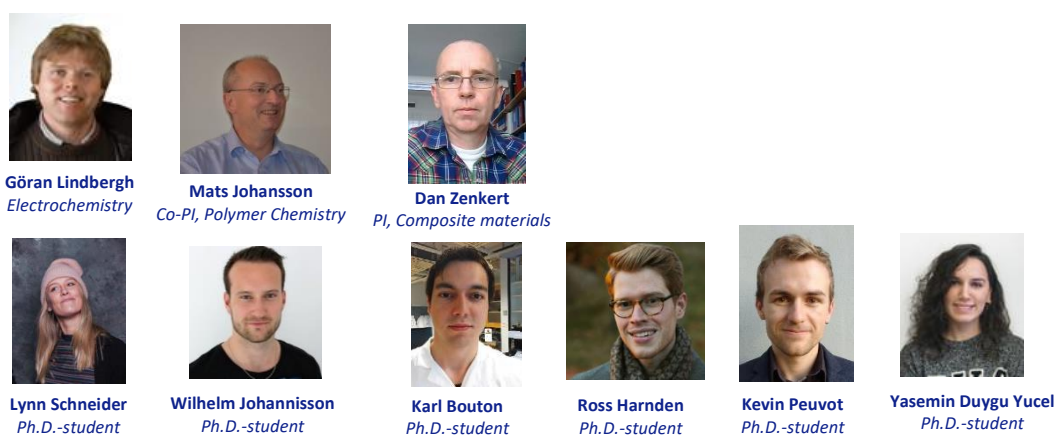


Figure 1: The structural battery research team at KTH in 2020

Short summary of accomplishments

- Improved structural battery electrolyte that can be used with thermal curing
- Measured and characterised interfacial strength between carbon fibres and the structural battery electrolyte
- Developed a parameter based models for predicting mass savings and performance envelopes using structural batteries compared to conventional materials and batteries
- Performed full life cycle analysis of structural batteries with promising results
- Conceived and developed a new metric for the evaluation of the performance of multifunctional materials, e.g. structural batteries and structural supercapacitors
- Combined all previous research work on structural batteries in a review paper
- Created, built, tested and verified a new approach for shape-morphing of stiff carbon fibre composite using electrochemical actuation
- Investigated alternative chemistries (Sodium and Potassium) for structural batteries and multifunctional carbon fibre composite materials

Impact in brief

- Taken several important steps towards realising structural batteries
- Shown that structural batteries can save mass on systems level and lead to reduced environmental impact
- Created a new route for shape-morphing of composites

Next major steps

- Continue to pursue realising full structural battery cells and characterise electrochemical and mechanical properties
- Further develop routes for carbon fibre based structural positive electrodes
- Characterise the multifunctional performance of structural battery full cells
- Further develop shape-morphing composite materials and also pursuing other functionalities such as sensing and energy harvesting

Papers published in peer-reviewed journals with EOARD/AFOSR funding

Schneider L, Ihrner N, Zenkert D, Johansson M., "Bicontinuous electrolytes via thermally initiated polymerization for structural lithium ion batteries", *ACS Applied Energy Materials*, Vol 2 (6), 2019, pp 4362-4369 (<https://doi.org/10.1021/acsaem.9b00563>), Open Access

This paper is a continuation of previous work on developing a new structural battery electrolyte (SBE). It is a two phase system with one solid polymer part (approx. 60% wt) and one liquid electrolyte part (approx. 40% wt). This is achieved by so called polymerization induced phase separation (PIPS) creating a bi-continuous network of a solid polymer and liquid electrolyte separated at the nano-scale. This method enables the creation of a solid polymer system that can transfer load between carbon fibres whereas the liquid network enables ion transfer, thus creating a truly multifunctional matrix system. What is new in this paper is that the polymerization is done by thermal curing, instead of previously by UV-curing, providing a necessary step towards

manufacturing of multiple layer structural batteries in an efficient process (Figure 2). Half cells with carbon fibres showed good electrochemical properties as well as good mechanical properties.

This work was conducted by KTH.

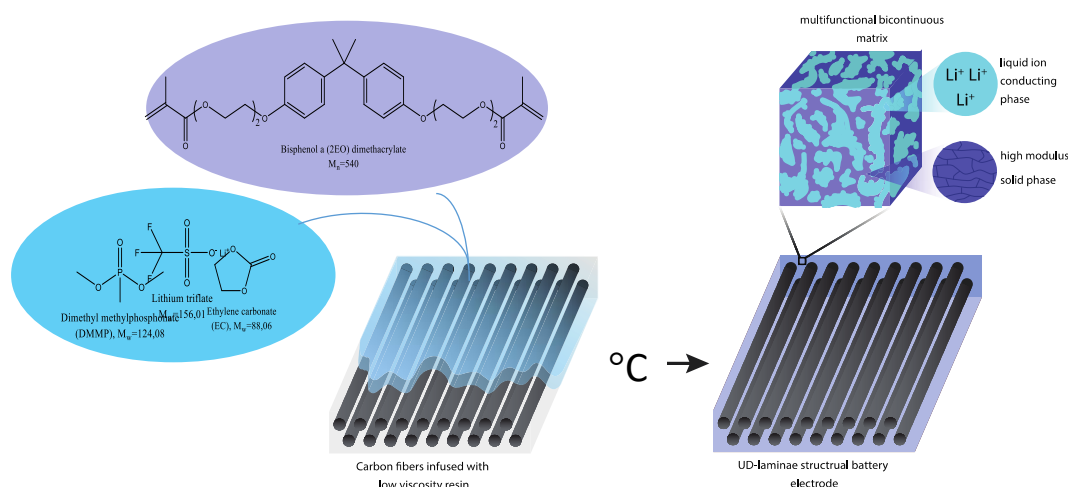


Figure 2: Manufacturing of carbon fibre half-cell using the SBE. The SBE is a mixture of monomer and electrolyte which is vacuum infused into a dry carbon fibre fabric. Heat is applied and polymerization starts creating a bicontinuous network of a solid polymer and the liquid electrolyte.

Xu J., Johannisson W., Johansen M., Liu F., Zenkert D., Asp L., Lindbergh G., "Characterisation of the adhesive properties between structural battery electrolytes and carbon fibres", *Composites Science and Technology*, Vol 188, 2020, 107962 (<https://doi.org/10.1016/j.compscitech.2019.107962>), to be made publicly available shortly

This paper is follow-on to the work on the SBE, however this time devoted to studying the interface between the SBE and the carbon fibres. This interface must be multifunctional: transfer mechanical loads and be ion conductive. This leads to a trade-off between the polymer contact creating adhesion and liquid contact creating ionic conductivity (Figure 3 left). We investigated the fibre-matrix adhesion between carbon fibres with different sizing and two different SBE systems, using micro droplet testing supported (Figure 3, right) by transverse tensile tests. The results show that the mechanical adhesion of the fibre-matrix interface is lower than that of a commercial non-ion conducting polymer matrix but sufficient for structural battery applications.

This work was a collaboration between KTH and Chalmers.

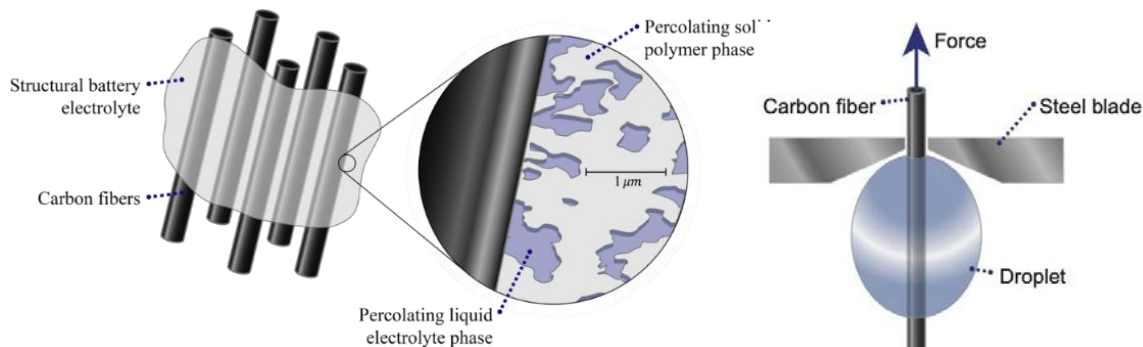


Figure 3: (left) Schematic of carbon fibers in a structural battery electrolyte. Within a structural battery, the carbon fibers are included in a structural battery electrolyte. This matrix material both transfer load between the reinforcing fibers using a percolating network of solid polymer, and conduct lithium ions through a network of liquid electrolyte. (right) The micro droplet test set-up.

Johannisson W., Zenkert D, Lindbergh G., "Model of a structural battery and its potential for system level mass savings", *Multifunctional Materials*, Vol 2, 2019, 035002 (<https://doi.org/10.1088/2399-7532/ab3bdd>), Open Access

There are many design parameters for a structural battery and in order to understand their impact and importance, this paper presents a model for multifunctional performance. The mechanical properties and electrical energy storage of the structural battery are matched to the mechanical behaviour of a conventional carbon fibre composite, and the electrical energy storage of a standard lithium ion battery (Figure 4). The latter are both monofunctional and have known performance and mass. In order to calculate the benefit of using structural batteries, the mass of the structural battery is compared to that of the two monofunctional systems. There is often an inverse relationship between the mechanical and electrochemical properties of multifunctional materials, in order to understand these relationships a sensitivity analysis is performed on variables for the structural battery. This gives new insight into the complex multifunctional design of structural batteries. The results show that it is possible to save mass compared to monofunctional systems but that it depends strongly on the structure it is compared with. With improvements to the design of the structural battery it would be possible to achieve mass saving compared to state-of-the-art composite laminates and lithium ion batteries. An example is shown below for a study on commercial aircraft interior panels (Figure 5).

This work was conducted by KTH.

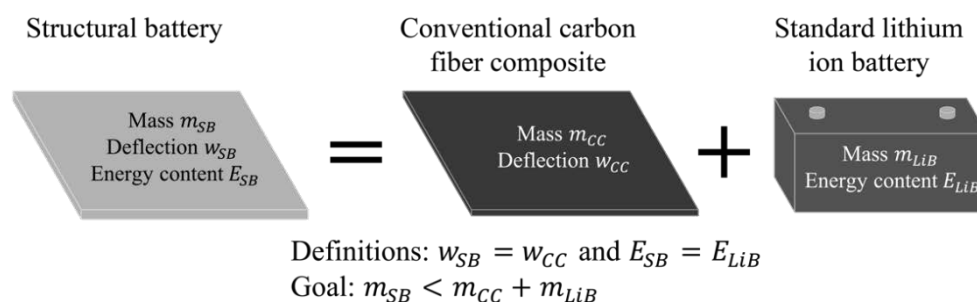


Figure 4: Schematic representation of the modelled systems.

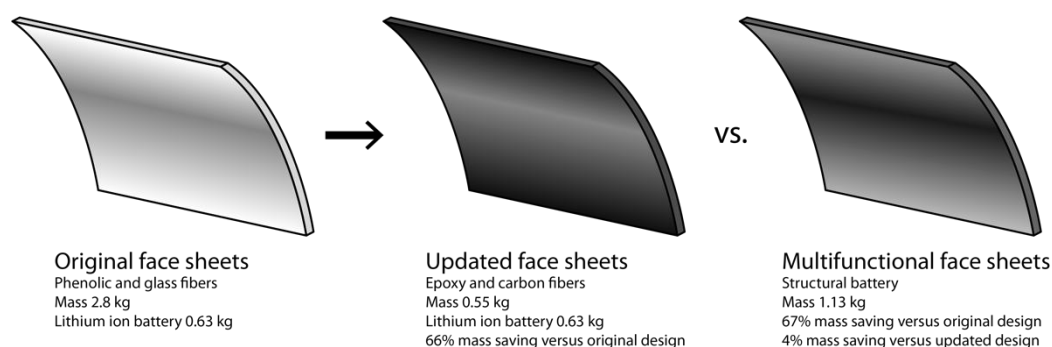


Figure 5: Modelling schematic and results from using structural batteries in interior panels in aircraft. Original face sheets of the panel contain glass fibre phenolic prepreg, those are improved with carbon fibre and epoxy face sheets. These updated face sheets and a corresponding lithium ion battery is compared to structural battery face sheets.

Zackrisson M., Jönsson C., Johansson W., Fransson K., Posner S., Zenkert D., Lindbergh G.,
 "Prospective life cycle assessment of a structural battery", *Sustainability*, Vol 11, 2019, 5679
<https://doi.org/10.3390/su11205679>, Open Access

This is in some way an extension of the above paper but now comparing the life cycle environmental footprint of using structural batteries compared to monofunctional systems, i.e. a separate structure and a separate battery pack. This paper is investigating a future structural battery that is incorporated in the roof of an electric vehicle. The structural battery is replacing the original steel roof of the vehicle, and part of the original traction battery. The environmental implications of this structural battery roof are investigated with a life cycle assessment, which shows that a structural battery roof can avoid climate impacts in substantive quantities. The main emissions for the structural battery stem from its production and efforts should be focused there to further improve the environmental benefits of the structural battery. Toxicity is investigated with a novel chemical risk assessment from a life cycle perspective, which shows that two chemicals should be targeted for substitution. Below is a result from the research showing the reduced net life cycle climate impact (in kg CO₂-eq.) when a roof of an electric vehicle and parts of its traction battery are replaced with a structural battery roof (Figure 6).

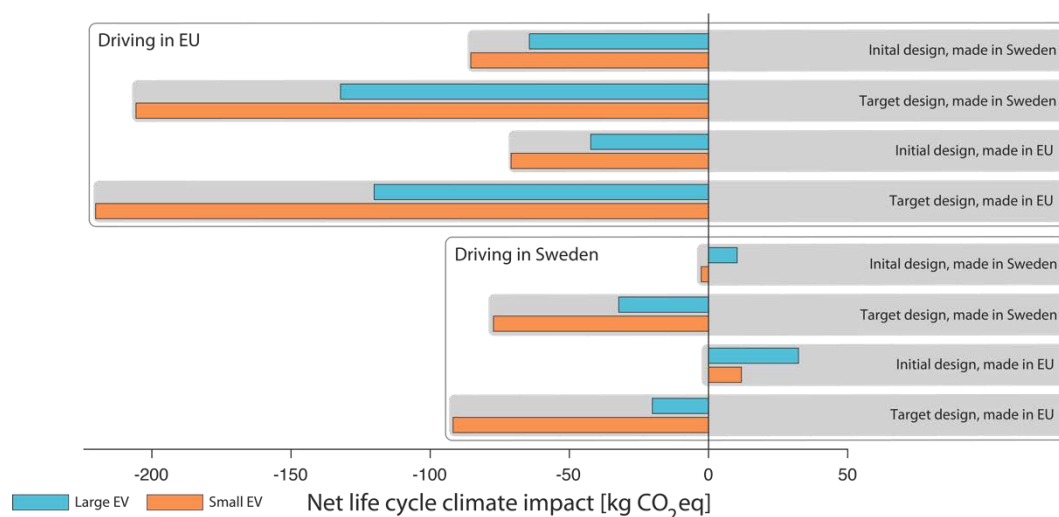


Figure 6: Net life cycle climate impacts of structural battery roof.

This work has been conducted by researchers at KTH in collaboration with LCA experts at the Research Institute of Sweden (RISE).

Asp L., Johansson M., Lindbergh G., Xu J., Zenkert., "Carbon Fibre Composite Structural Batteries: A Review", *Functional Composites and Structures*, Vol 1, 042001, 2019
<https://dx.doi.org/10.1088/2631-6331/ab5571>, Open Access

In this paper we provide an overview of research performed on structural battery composites to date. The conceptual idea is shown in Figure 7. Substantial work has been performed. However, significant work on the structural battery full cell and its manufacture and validation remains before structural battery composites offer a solution for mass-less energy storage in future electric road, air and sea transport applications. To date, no show-stoppers for the realisation of structural battery composites have been identified.

This work was a collaboration between KTH and Chalmers.

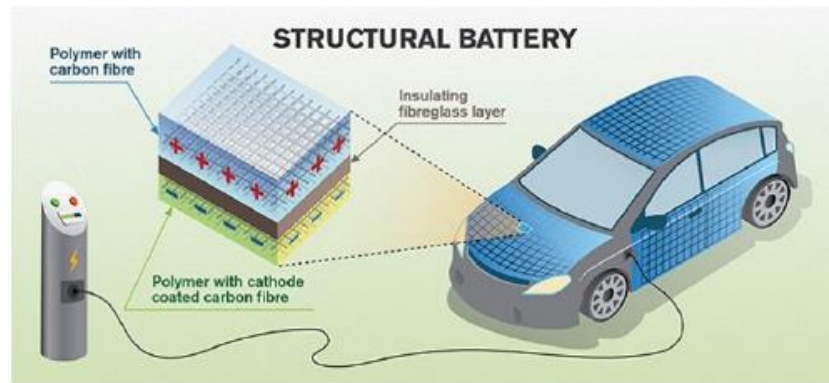


Figure 7: The concept of structural batteries, a material that carries loads and stores energy simultaneously.

Johannisson W., Nguyen S., Lindbergh G., Zenkert D., Greenhalgh E., Shaffer M., Kucernak A., "A residual performance methodology to evaluate multifunctional systems", *Multifunctional Materials*, Vol 3(2), 2020, 025002 (<https://doi.org/10.1088/2399-7532/ab8e95>), Open Access

Quantifying the advantages of a multifunctional solution over monofunctional systems can be challenging. One approach is to calculate a reduction in mass, volume or some other penalty function. Another approach is to use a multifunctional efficiency metric. However, either approach can lead to results that are unfamiliar or difficult to interpret and implement for an audience without a multifunctional materials background. In this paper we introduce a comparative metric for multifunctional materials that correlates with familiar design parameters for monofunctional materials. The methodology is schematically illustrated in Figure 8.

This metric allows the potential benefits of the multifunctional system to be understood easily without needing a holistic viewpoint. The analysis is applied to two different examples of multifunctional systems; a structural battery and a structural supercapacitor, demonstrating the methodology and its potential for state-of-the-art structural power materials to offer a weight saving over conventional systems. This metric offers a new way to communicate research on structural power which could help identify and prioritise future research.

This work was a collaboration between KTH and Imperial College London.

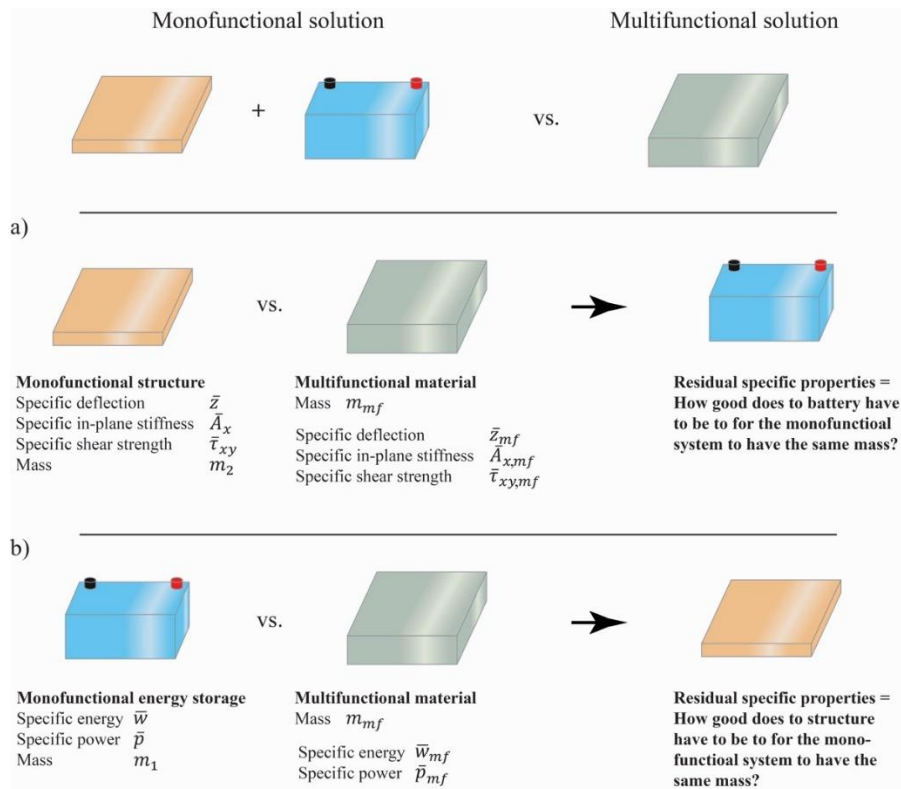


Figure 8: Diagram showing the comparison between two monofunctional systems versus a multifunctional system. One way to present the residual specific properties is by separating the comparisons into: (a) a monofunctional structure is compared to a multifunctional solution. The mass difference between the two is the residual mass for the monofunctional battery, and the residual specific properties are essentially how good the monofunctional battery has to be in order for the monofunctional solution to have the same properties as the multifunctional. (b) A monofunctional battery is compared to a multifunctional solution. The mass difference between the two is the residual mass for the monofunctional structure, and the residual specific properties are essentially how good the monofunctional structure has to be in order for the monofunctional solution to have the same properties as the multifunctional.

Johannisson W., Harnden R., Zenkert D., Lindbergh G., "Shape-morphing carbon fibre composite using electrochemical actuation", *Proceedings of the National Academy of Sciences*, Vol 117(14), 2020, pp 7658-7664 (<https://doi.org/10.1073/pnas.1921132117>), Open Access

This paper does not deal with structural batteries per se, but is an extension of that work. It demonstrates a proof-of-concept for a stiff, morphable solid-state composite material. It is made from commercial carbon fibres and a structural battery electrolyte (SBE). By combining these elements we show that it is possible to form a low-density material with a stiffness higher than that of aluminium, that is morphable at voltages up to 1.5 V, exhibits an inherent zero-power hold, and can produce large deformations and high gravimetric actuation energies. The morphing material is characterized mechanically, and its behaviour agrees well with modelling predictions.

The conceptual idea is based on work on carbon fibre structural batteries and combines the work on lithiated carbon fibres and the use of the new SBE. The morphing material presented is formed from two Li-activated carbon fibre layers, electrically insulated from one another by a commercial ceramic separator layer and embedded in the SBE to form a structural composite laminate (Figure 8 left). By applying an electrical current Li ions are transferred through the SBE from one carbon fibre layer to

the other, causing the discharging layer to contract, while the charging layer expands, morphing the entire laminate in a bending motion (Figure 9 right). The morphing mechanism is thus provided by the load-carrying material itself, forming a truly multifunctional material that adds little to no parasitic mass to a structure and is electrically controlled.

This work was conducted by KTH.

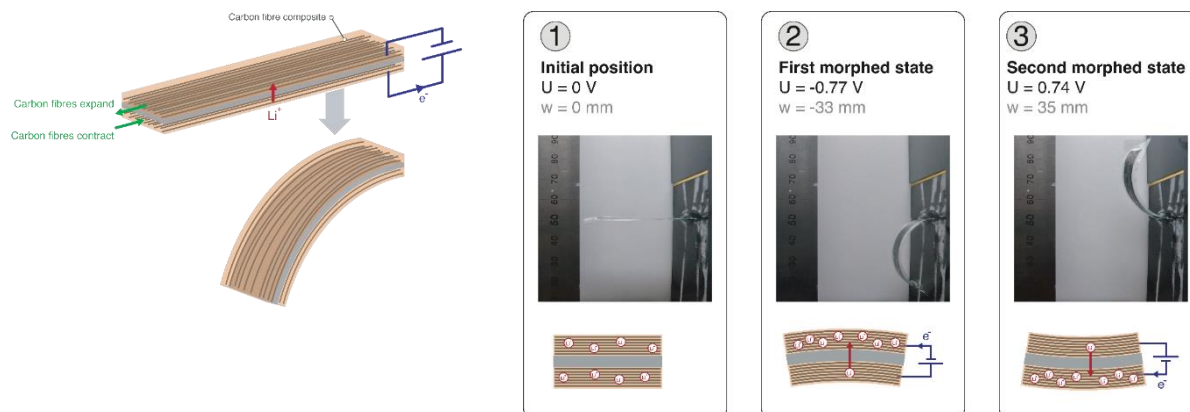


Figure 9: (left) Schematic of conceptual idea: Li ions are discharged from one carbon fibre layer to the other by application of a current, causing the discharging layer to contract in the fibre direction, and the charging layer to expand. This creates an overall bending deformation. (right) Experiment showing the morphing carbon fibre composite material in a cantilever setup. A current is applied between the carbon fibre layers with cut-off voltages of -1.5 and 1.5 V. This causes Li to transfer from one carbon fibre layer to the other. The charging carbon fibre expands in the fibre direction as it reaches a higher state of charge, while the carbon fibre layer that is discharging contracts, creating a bending deformation.

Harnden R., Zenkert D., Lindbergh G., "Potassium-insertion in PAN-based carbon fibres for multifunctional energy storage, morphing, and strain-sensing", *Carbon*, Vol 171, 2021, pp 671-680, <https://doi.org/10.1016/j.carbon.2020.09.042>, Open access

In this study we present the electrochemical functionalisation of intermediate modulus PAN-based CFs with potassium for application in multifunctional structural materials. This work focusses on the concepts of structural energy storage, morphing, and strain-sensing (Fig. 10); comparing potassium-functionalisation of the CFs with previous work carried out using lithium and sodium. The electrochemical cycling performance of the CF electrodes in potassium-ion half cells is characterised, and the effect of electrochemical cycling on mechanical performance is measured. The axial expansion of CFs during potassiation is analysed for different current densities, and an analytical model is used to show the resulting morphing performance. Finally, the voltage-strain coupling in the potassiated CFs is quantified. Potassium-insertion in commercial PAN-based CFs provides a way of augmenting the CFs with further functionality such as energy storage, morphing, and strain-sensing. Potassium-insertion appears slightly more promising than sodium-insertion for creating multifunctionality, although lithium insertion seems to be the more promising route for high performance structures so far.

This work was conducted by KTH. Note: all though the paper will be officially published in January 2021, it is already available online and the paper was submitted for publication in May 2020.

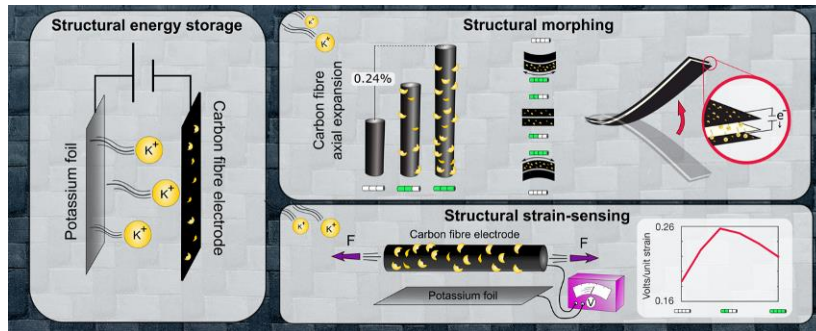


Figure 10: Potential multifunctional properties of carbon fibres using potassium insertion; structural energy storage, structural morphing and structural strain sensing.

Papers presented at international conferences with EOARD/AFOSR funding

Zenkert D., Lindbergh G. and Johansson M., "Carbon fibre composites as batteries, sensors, actuators and for energy harvesting", *Proc. ICCM22*, Melbourne, Australia, August 2019.

Johannisson W., Zackrisson M., Jönsson C., Zenkert D., and Lindbergh G., "Modelling and Design of structural batteries with life cycle assessment", *Proc. ICCM22*, Melbourne, Australia, August 2019.

Schneider L.M., Ihrner N., Zenkert D. and Johansson M., "Manufacturing techniques And mechanical Properties of Structural batteries after Prolonged Electrochemical Performance", *Proc. ICCM22*, Melbourne, Australia, August 2019.

Bouton K., Zenkert D. and Lindbergh G., "Structural positive electrodes for multifunctional composite materials", *Proc. ICCM22*, Melbourne, Australia, August 2019.

Johannisson W., Harnden R, Geiger K., Zenkert D., Lindbergh G., "Morphing carbon fibre composites using electrochemical actuation", *Proc. ICCM22*, Melbourne, Australia, August 2019.

Dissertations (partly EOARD/AFOSR funded)

Johannisson W., *Exploring structural carbon fiber composites for mass-less energy and actuation*, Ph.D.-thesis, KTH Royal Institute of Technology, June 2020, ISBN 978-91-7873-552-5

Thesis introduction can be found at:

<http://kth.diva-portal.org/smash/get/diva2:1429398/FULLTEXT01.pdf>



Characterization of the adhesive properties between structural battery electrolytes and carbon fibers

Johanna Xu^{a,c}, Wilhelm Johannisson^b, Marcus Johansen^c, Fang Liu^c, Dan Zenkert^b, Göran Lindbergh^d, Leif E. Asp^{c,*}

^a Department of Engineering Sciences and Mathematics, Material Science, Luleå University of Technology, SE-971 87, Luleå, Sweden

^b Department of Aeronautical and Vehicle Engineering, KTH Royal Institute of Technology, SE-100 44, Stockholm, Sweden

^c Department of Industrial and Materials Science, Chalmers University of Technology, SE-412 96, Gothenburg, Sweden

^d Department of Chemical Engineering, KTH Royal Institute of Technology, SE-100 44, Stockholm, Sweden

ARTICLE INFO

Keywords:

- A. Functional composites
- A. Carbon fibres
- B. Fibre/matrix bond
- B. Interfacial strength
- D. Scanning electron microscopy (SEM)

ABSTRACT

Structural batteries can simultaneously store electrical energy and carry mechanical load, being similar to both laminated carbon fiber composites and lithium ion batteries. The matrix in a structural battery must both conduct ions and transfer load between the fibers, made possible with a phase-separated combination of a solid polymer and a liquid electrolyte. This leads to a trade-off between the polymer contact creating adhesion and liquid contact creating ionic conductivity. Here we investigate the fiber-matrix adhesion between carbon fibres with different sizing and two different matrix systems, using microbond testing supported by transverse tensile tests. The results show that the mechanical adhesion of the fiber-matrix interface is lower than that of a commercial non-ion conducting polymer matrix but sufficient for structural battery applications.

1. Introduction

In the transport sector there is a growing demand for electrification decreasing the environmental footprint [1–4]. However, for electrical vehicles, there is a challenge in the specific energy of the batteries. In order for a vehicle to have sufficient range, it needs to carry a large and heavy battery pack, which further limits the range. A possible route to decrease the mass of electrical vehicles is to use structural batteries [5–11]. Structural batteries are multifunctional materials that simultaneously store electric energy as a lithium ion battery and carry mechanical loads as a composite laminate. Carbon fibers insert lithium in its microstructure similar to commercial graphitic electrodes [6]. Thus, one concept of a structural battery consists of one carbon fiber layer acting as the negative electrode, a glass fiber separator layer and a LiFePO₄-coated carbon fiber layer as positive electrode [11,12]. Similar to a composite laminate, the layers are held together with a matrix that both distributes the mechanical load and simultaneously conducts lithium ions between the carbon fiber layers. Such a multifunctional matrix material has recently been developed, called a structural battery electrolyte (SBE) [13]. It is made from a porous network of a polymer phase for mechanical integrity and a percolating liquid electrolyte phase

for ion conduction, see Fig. 1. These have been shown to have some mechanical integrity, while also being able to conduct lithium ions through electrochemical cycling [13–15]. This mechanical integrity seems to be unaffected by electrochemical cycling [14,15].

Development of the SBE is one of the biggest challenges for structural batteries, as the mechanical and electrical demands are conflicting [16]. Enhancement of mechanical performance typically results in a reduction in electrochemical performance, and vice-versa. The fiber/SBE interface presents the same conflicting challenge. The adhesion between the carbon fibers and the SBE is important for the overall mechanical properties of the material, just like the matrix to fiber adhesion for any high-performance fiber composite. Regarding electrochemical performance, the interface is the site at which the lithium ions must pass for the necessary electrochemical reactions to occur, requiring liquid electrolyte contact with the surface of the carbon fibers. This means that both the polymer phase and the liquid phase need physical contact with the fiber surface. Hence, the mechanically adhesive surface area is limited, and the mechanical adhesion is expected to be lower than for a conventional matrix system. Due to this very complex interface region, there is a significant need to further understand the adhesive properties between the SBE and the carbon fibers.

* Corresponding author.

E-mail address: leif.asp@chalmers.se (L.E. Asp).

<https://doi.org/10.1016/j.compscitech.2019.107962>

Received 23 September 2019; Received in revised form 9 December 2019; Accepted 18 December 2019

Available online 20 December 2019

0266-3538/© 2019 Elsevier Ltd. All rights reserved.

Herein, we investigate the interface adhesion between two different carbon fiber types and two different SBEs previously reported in literature [14,15]. The mechanical adhesion between the fiber and the SBE is characterized by using a microbond test. To complement the microbond tests, the apparent transverse UD lamina strength was measured, providing strength properties in a different stress state and length-scale. For reference a similar commercial vinyl ester resin was used that has no ion conducting capability. We found that the SBEs investigated here exhibit a good multifunctional fiber/SBE interface, with lower interfacial shear strength and apparent transverse strength than commercial vinyl ester resin, which shows promise for the realization of structural batteries.

2. Materials

Two different SBE systems are compared, and a commercial matrix is used as control. The two SBE systems are referred to as SBE1 and SBE2, with the formulations presented in Table S1, with about 61 wt% structural polymer phase and 39 wt% liquid electrolyte phase. SBE1 follows the formulation used by Johannisson et al. [14]. SBE2 is similar to that used by Schneider et al. [15], with the difference that *dimethyl methylphosphonate* in the electrolyte is exchanged with *propylene carbonate*. The main difference between SBE1 and SBE2 is that they contain different monomers; *bisphenol A dimethacrylate* and *bisphenol A ethoxylate dimethacrylate*, respectively. The latter results in a lower matrix elastic modulus due to a less densely crosslinked polymer network (and lower T_g), as well as a smaller pore size, both still in the sub-micron range [13]. However, these monomers are still rather similar in structure and both have been shown to work well electrochemically [13–15]. The monomers are also similar to those typically used in conventional vinyl ester matrices. Thus, Reichhold Dion 9102 [17], a common vinyl ester resin, was chosen as control.

Two carbon fiber types are used; T800H-6k-40 B [18] (referred to as T800H) purchased from Toray CMA Inc. and T800S-12 k-50C [19] (referred to as T800S) received from Oxeon AB. These carbon fibers have been chosen since they are known to work very well electrochemically. They are the same fibers but with different fiber count (6 k vs. 12 k), and most importantly they have different sizing. They thus have the same electrochemical performance but possibly different adhesion properties. 40 B is a sizing for “Epoxy, phenolic, BMI” [20] while 50C is a sizing referred to as “General purpose: Epoxy, phenolic, polyester, vinyl ester” [20]. Both have 1 wt% sizing applied to the fibers and are surface treated with oxidation to improve the adhesive properties [20]. The lack of specific knowledge on the chemical composition of the sizing is a concern for structural battery technology research since it affects both adhesion and electrochemical properties [6]. Yet it is preferable to

employ sized fibers over unsized. Not only because unsized fibers are not readily available, but mostly for handling purposes during manufacturing of structural batteries.

3. Experimental

3.1. Microbond testing

The adhesive properties of the interface between fiber and matrix, has been investigated using the microbond test, sometimes referred to as the micro droplet test, developed by Miller et al. [21]. The results from microbond testing should be interpreted as qualitative [22]. Nevertheless, the microbond test is preferred not only because of its simplicity, but also because the opacity of the SBE disqualifies other characterization tests, such as the single fiber fragmentation test. One disadvantage with the microbond test is the difficulty to monitor the failure mode of the specimens due to the small specimen size. This is overcome by post-test fractography in a scanning electron microscope (SEM).

The specimens for microbond tests were made by first extracting single filaments from the carbon fiber tow and attaching them to paper frames in order to contain, protect and facilitate the handling of the single carbon fibers. A single drop of the uncured matrix was then placed on each individual carbon fiber using a syringe. The drop was cured with its corresponding curing method; i) UV-curing for SBE1, ii) thermal curing at 90 °C for SBE2 and iii) thermal curing according to manufacturer specifications for the vinyl ester control. Prior to the microbond test, each matrix droplet was studied in an optical microscope in order to investigate its shape and measure the length (L_e) of the fiber embedded within the matrix droplet. The microbond tests are made by loading the droplets on single carbon fibers through two steel blades, see Fig. 2a. All tests were performed in an Instron 4411 universal test frame equipped with a 5 N load cell and pneumatic grips, using displacement control with the loading rate of 0.2 mm/min.

A microbond test load-displacement curve for carbon fiber/epoxy is considered to consist of three parts [23], schematically shown in Fig. 2b. In the first part, the curve is nearly linear, and the fiber-matrix interface remains intact. When the load reaches some critical value, often referred to as the debond force, F_d , the fiber begins to debond from the matrix, and the recorded force continues to increase. After a peak load, F_{max} is reached, the entire embedded length fully debonds, and the measured force drops dramatically. From this moment until complete pull-out, or end of test, the “tail” force is due to frictional interaction between the fiber and the matrix.

From these data, the interfacial shear stress τ , was calculated using the relationship [23]:

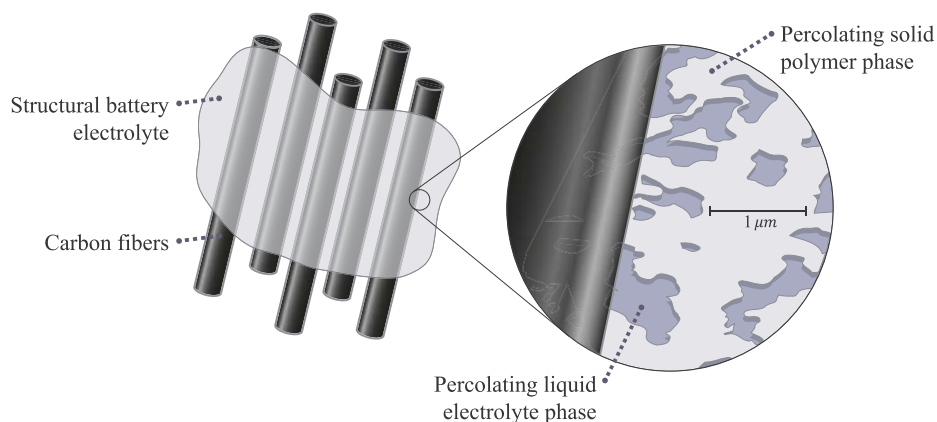


Fig. 1. Schematic of carbon fibers in a structural battery electrolyte. Within a structural battery, the carbon fibers are included in a structural battery electrolyte. This matrix material both transfer load between the reinforcing fibers using a percolating network of solid polymer, and conduct lithium ions through a network of liquid electrolyte.

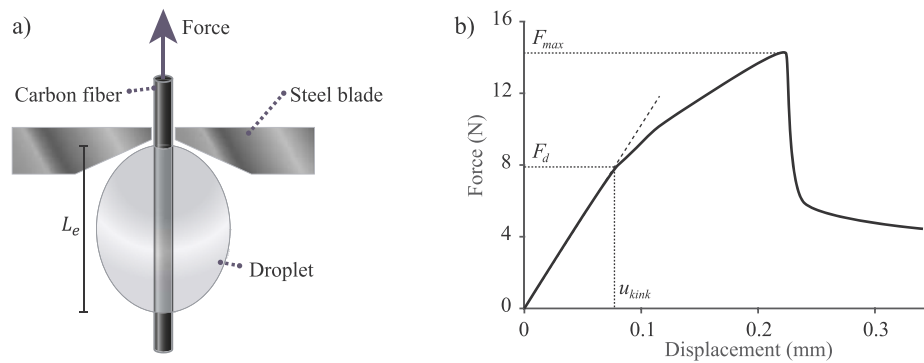


Fig. 2. Microdroplet testing. a) Schematic showing microdroplet testing. The droplet on the carbon fiber is loaded through two steel blades. b) An example of a common force-displacement curve for microdroplet tests showing a “kink” at debonding force F_d and peak force F_{max} , reproduced from Ref. [23].

$$\tau = F / (2r_f \pi \cdot L_e) \quad (1)$$

where F is the applied load, r_f is the radius of the fiber given from the manufacturer's data sheets [18,19] and L_e is the measured embedded length of the fiber. The apparent interfacial shear strength (IFSS) is given from $F = F_{max}$ and debond stress from $F = F_d$. The typical fiber breaking strain is about 1.9% strain according to the manufacturer data sheets. Therefore, for fiber/matrix debonding to occur without fiber breakage, the force can at most be 0.4 N, for a fiber with a 5 μm diameter and a modulus of 294 GPa [18,19]. This imposes a restriction on the embedded fiber length (L_e), depending on the interface quality, which is unknown in advance.

After testing, the fiber with a debonded resin droplet was mounted to specimen holder and palladium coated for subsequent examination in a JEOL JSM-7800 F Prime SEM, investigating the fracture surfaces.

3.2. Three-point bending test

The transverse tensile strength is of particular interest in this context since it is a matrix and interface-controlled property. For electrochemical properties the laminae must be thin, providing a challenge for transverse tensile testing. To measure an apparent transverse strength a three-point bending configuration was used where the laminae were oriented to bend in the transverse tensile direction, see Fig. 3.

The samples for three-point bending tests were prepared by making single unidirectional laminae from spread tow carbon fibers. The fiber tows were spread to produce thin laminae; T800H was spread in-house while T800S was spread by Oxeon AB. The laminae were manufactured using vacuum assisted resin infusion and cured according to the method for the corresponding matrix system, see section 3.1. The measured sample thicknesses and fiber volume fractions are given in Table S2.

The three-point bending tests were performed according to Johansson et al. [14] by measuring the bending stiffness of a substrate

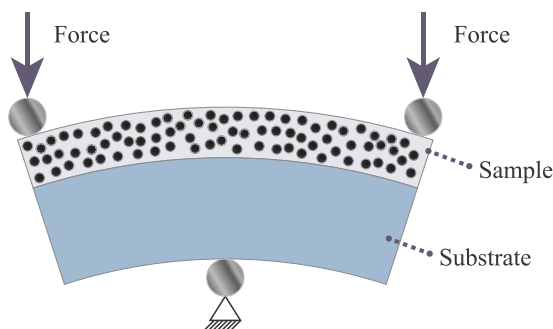


Fig. 3. Schematic representation of the three-point bend testing. Bending force is applied to a two-layer assembly consisting of a substrate with known bending stiffness and a sample with unknown elastic properties.

material (0.13 mm PET film) and subsequently measuring the bending stiffness of a two-layer assembly consisting of a sample adhered with Reichhold Dion 9102 [17] to the substrate material. Then, using laminate theory [24], it is possible to back-calculate the mechanical properties of the sample. The apparent transverse tensile strength was then defined from the load at first deviation from linearity in the load-displacement curves for the two-layer assembly.

4. Results

4.1. Fiber contact angle and embedded length

The formation of SBE droplets on both fiber types were quite similar in size, about 300 μm in diameter. The domain size of the matrix phase-separation is several orders of magnitude smaller than the droplet size (submicron to a few hundred microns) implying the even the small drop well represents bulk material properties. Optical microscopy examination shows a slight difference in contact angle between SBE1 (Fig. 4a and b) and SBE2 (Fig. 4c and d). SBE1 forms near-perfect spherical droplets with large contact angle, while SBE2 appears slightly more elongated and lower contact angle, indicating an improved wettability compared to SBE1 [25,26]. The difference in transparency of the two SBEs is pronounced, where SBE1 is opaque due to light scattering while SBE2 is semi-transparent, indicating that SBE2 has a smaller pore size than SBE1 [13].

4.2. Microbond testing

Representative interfacial shear stress-displacement graphs from microbond testing are shown in Fig. 5, for each of the fiber/matrix systems. Only T800H/SBE1 (dotted black line) shows a clear distinction of debond stress and IFSS. For all other material systems, the force increased linearly up to IFSS at which it suddenly dropped and debonding occurred.

The average IFSS values for the different material systems is shown in Fig. 6, including standard deviations. The difference in IFSS between the two SBEs is clear, where SBE2 with both T800H and T800S carbon fibers results in considerably higher IFSS than for SBE1. However, no clear difference in IFSS can be found between T800S and T800H carbon fibers, indicating that the fiber sizing has little influence on the adhesion.

4.3. Post-test fractography

The SBE1/T800H system showed matrix residue on the fiber after debonding, see Fig. 7a. Such cohesive failure is generally associated with strong mechanical adhesion [27]. However, it showed the lowest IFSS value (Fig. 6). The load-displacement curves also showed deviating behavior in comparison to the other material systems, with an onset of

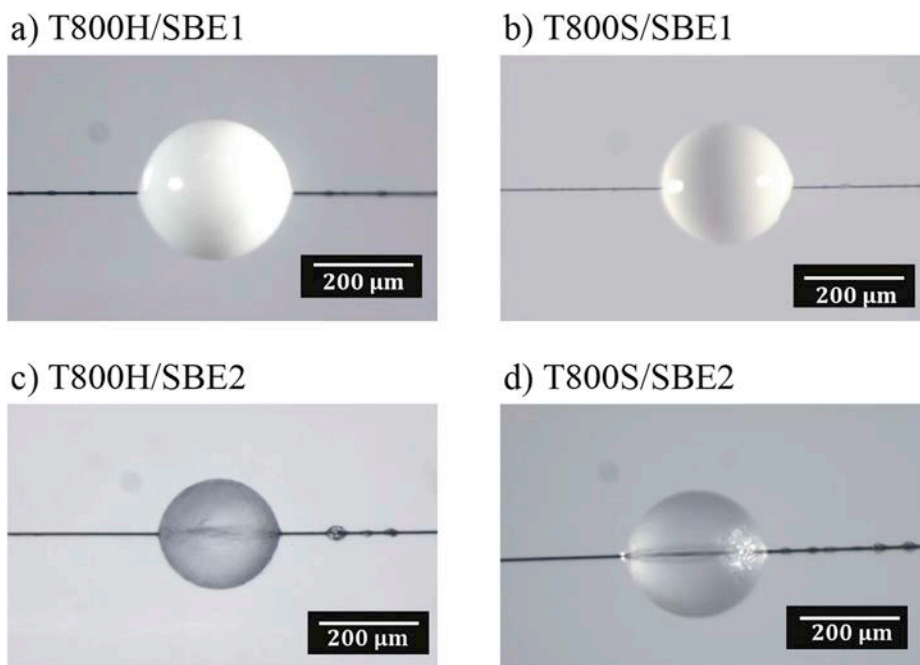


Fig. 4. Polymerized SBE droplets on carbon fiber prior to test. a) SBE1 droplet on T800H carbon fiber. b) SBE1 droplet on T800S carbon fiber. c) SBE2 on T800H carbon fiber and d) SBE2 droplet on T800S carbon fiber. SBE1 is opaque and droplets exhibit larger contact angles compared to corresponding semi-transparent SBE2 droplets.

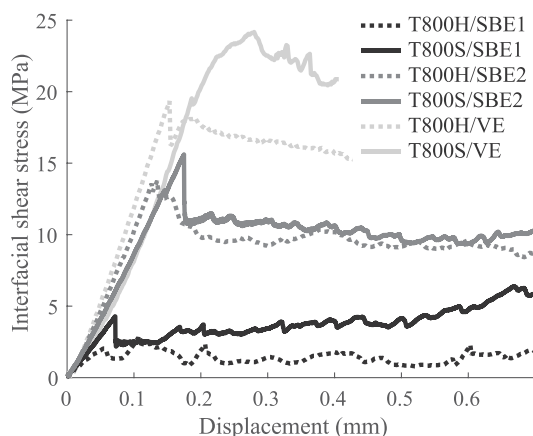


Fig. 5. Representative interfacial shear stress-displacement curves for the microbond testing. IFSS is defined at maximum stress, followed by a region with the droplet slipping along the fiber.

debonding at low loads (Fig. 5). One possible explanation is a formation of a thicker inhomogeneous region around the interface, and that failure is occurring outside this region and not at the fiber-to-matrix interface. For SBE1/T800S the failure occurred very close to the fiber interface, but still within the SBE, indicating a more cohesive failure mode, as shown in Fig. 7b. Fig. 7b also shows residues on the fiber surface demonstrating the phase separation at the interface.

For the SBE2/T800H system interfacial separation was the main failure mode. There is virtually no SBE residue on the fiber surface as seen in Fig. 8a, as the surface of the debonded fiber is consistent with the fiber surface of pristine fibers. See Fig. S1 for carbon fiber surface as received from manufacturer. Despite the clean surface, the SBE2/T800H IFSS is higher than that of SBE2/T800S, Fig. 8b, which shows the same cohesive failure mode as SBE1/T800S, Fig. 8b.

Fig. 9 shows SEM pictures of a droplet top (meniscus) remaining on T800S fibers after the pullout, indicating complete debonding [28]. No

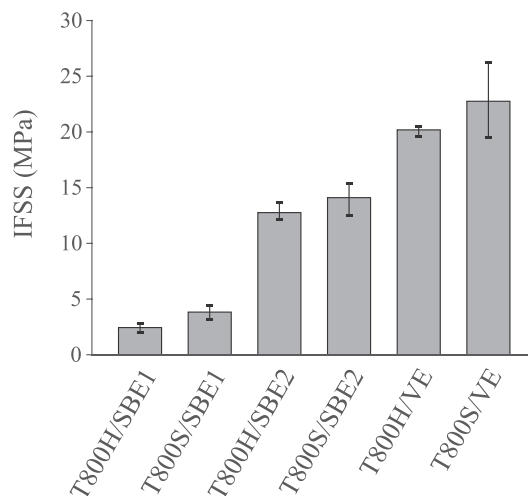


Fig. 6. Average interfacial shear strength values measured for the different fibers and SBE systems, including control samples made with vinyl ester (VE). Error bars represent measurement standard deviations with at least 3 samples per system.

matrix cracks nor damage from the blade on the droplet were found. This implies that the measured decrease in force cannot be attributed to matrix damage on the droplet. Consequently, the T800S fiber pullout was accomplished by debonding all of the interface for both SBE1 and SBE2. Although handling of these post-test microbond specimens with SBE droplets loosely attached to the brittle fiber was done with utmost care, many specimens were destroyed during sample preparation, and therefore no images of the droplet meniscus of SBEs on T800H are available. However, the similarity in load-displacement curves of T800H/SBE2 and T800S/SBE2 (Fig. 5), suggests similar behavior.

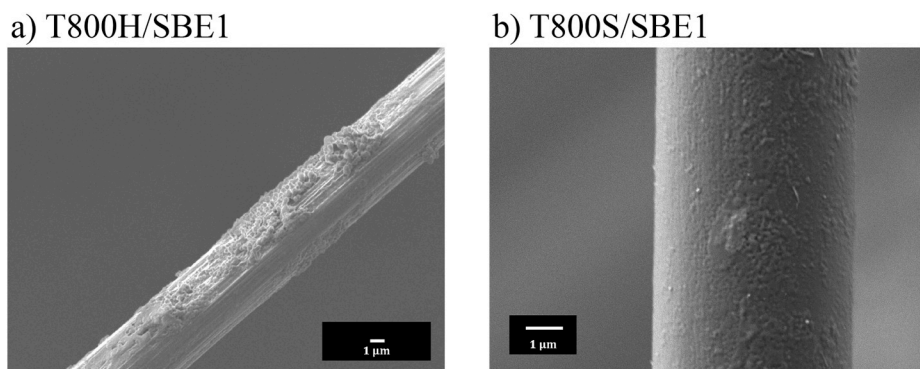


Fig. 7. SEM images of the debonded fiber surface of a) T800H/SBE1 (4 k magnification) with considerable amount of material attached to the fiber after debonding and b) T800S/SBE1 (10 k magnification).

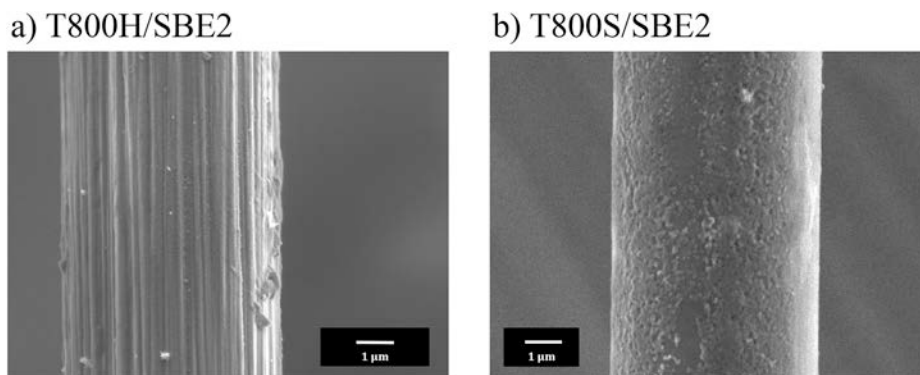


Fig. 8. SEM images of the debonded fiber surface with porous residues, for a) T800H/SBE2 (10 k magnification), with virtually no residual SBE on the fiber surface and b) T800S/SBE2 (10 k magnification).

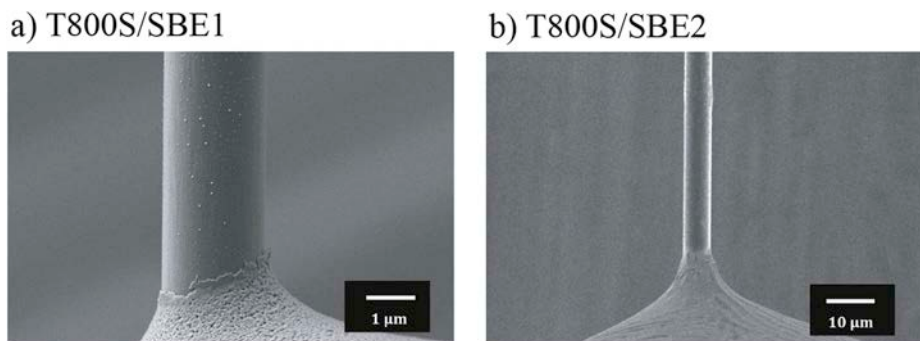


Fig. 9. SEM images showing droplet meniscus after the microbond test. a) T800S/SBE1 (4 k magnification). b) T800S/SBE2 (1 k magnification).

4.4. Three-point bending test

The average apparent transverse tensile Young's modulus and apparent transverse tensile strength from the three-point bending tests are shown in Fig. 10. Depending on the samples' constituents, the deviations which mark the ultimate loads are more or less pronounced, see Fig. S2 for representative load-displacement curves. Nevertheless, the tensile strength results show a similar but less pronounced trend as for the IFSS testing (Fig. 6). SBE1 has a slightly lower apparent transverse tensile strength than SBE2, which in turn is lower than the vinyl ester control samples. Furthermore, the results show no statistical difference between T800H and T800S carbon fibers.

5. Discussion and conclusions

In a structural battery it is necessary for the matrix to simultaneously transfer loads between fibers while also conducting lithium ions to and from the fibers. The interface between fiber and matrix is equally important and has the same requirements.

The structural battery electrolyte (SBE) matrices used herein are two-phase systems consisting of a polymer phase with an interpenetrating network of liquid electrolyte. Both SBEs studied herein have previously been shown to work well electrochemically and are capable of conducting lithium ions through the SBE and the carbon fiber-to-SBE interface [13–15]. This confirms that the liquid phase of the SBE is in contact with the carbon fibers. The SBE to fiber interface exhibits reasonable IFSS and apparent transverse strength confirming mechanical adhesion. Thus, it is a truly multifunctional interface.

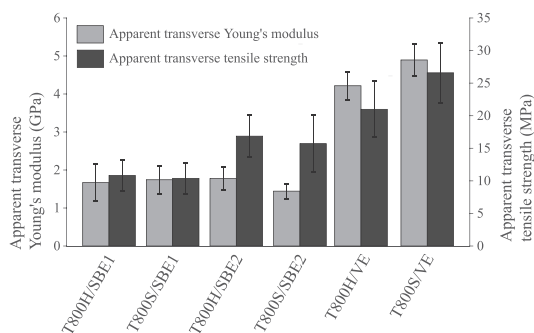


Fig. 10. Average apparent transverse Young's modulus and tensile strength results from three-point bending tests. Error bars represent measurement standard deviations with 6 samples per system.

Results show that both IFSS and apparent transverse tensile strength for SBE2 are higher than that of SBE1. As expected, both are lower than that of the vinyl ester control which has complete adhesive contact area to the fiber. The combination of mechanical and ion-conduction requirements of the SBE to fiber interface is especially crucial for structural battery development, since too large polymer phase contact will diminish energy storage and too small polymer phase contact impacts structural performance.

Fiber sizing appears to have little influence on the interfacial adhesion, at least for the systems studied herein. The difference in interfacial adhesion comparing SBE1 and SBE2 could thus be related to the different monomers. Also, UV-curing is known to have slightly lower degree of cure than thermal curing [13], which could also explain the difference in interfacial adhesion. Anyway, thermal curing is needed for upscaling manufacturing of structural batteries consisting of multiple carbon fiber layers.

The results are promising for further development of structural batteries, which may help decrease vehicle mass and green-house emissions. However, there is still room for improvement of the mechanical and electrochemical properties of the SBE and SBE to fiber interface. The long-term goal is to optimize SBE formulations in relation to ion conductivity, stiffness, strength, adhesion, etc. The methods presented in this paper are necessary to optimize multifunctional matrix systems for future structural batteries.

Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Declaration of competing interest

The authors declare no competing interests.

CRediT authorship contribution statement

Johanna Xu: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Validation, Visualization, Writing - review & editing. **Wilhelm Johannisson:** Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Validation, Visualization, Writing - review & editing. **Marcus Johansen:** Investigation. **Fang Liu:** Investigation. **Dan Zenkert:** Writing - original draft. **Göran Lindbergh:** Writing - original draft. **Leif E. Asp:** Funding acquisition, Supervision, Writing - review & editing.

Acknowledgements

This work was supported the Swedish Research Council [grand numbers 2017-03898, 621-2014-4577]; the Swedish Energy Agency

[grant number 46598-1]; the strategic innovation program LIGHTer (funding provided by Vinnova, the Swedish Energy Agency and Formas); H2020 Clean Sky II [grant number 738085]; and the Air Force Office of Scientific Research [grant number FA9550-17-1-0244]. Oxeon is acknowledged for providing T800SC-12 k-50C carbon fibers. The Swedish research group Kombatt-II is acknowledged for its synergism throughout this work.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.compscitech.2019.107962>.

References

- [1] OCDE/GD(96)136, Pollution Prevention and Control - Environmental Criteria for Sustainable Transport, Tech. Report, OECD, 1996.
- [2] EPOSS ERTRAC, The Electrification Approach to Urban Mobility and Transport, 2009.
- [3] European Commission, Energy, Transport and Environment Indicators, 2017, <https://doi.org/10.2785/889945>.
- [4] European Commission, Reducing CO2 emissions from passenger cars, Eur. Community (2019). https://ec.europa.eu/clima/policies/transport/vehicles/cars_en. (Accessed 28 February 2019).
- [5] J.F. Snyder, E.B. Gienger, E.D. Wetzel, Performance metrics for structural composites with electrochemical multifunctionality, *J. Compos. Mater.* 49 (2015) 1835–1848, <https://doi.org/10.1177/0021998314568167>.
- [6] M.H. Kjell, E. Jacques, D. Zenkert, M. Behm, G. Lindbergh, PAN-based carbon fiber negative electrodes for structural lithium-ion batteries, *J. Electrochem. Soc.* 158 (2011) A1455, <https://doi.org/10.1149/2.053112jes>.
- [7] E. Jacques, M.H. Kjell, D. Zenkert, G. Lindbergh, M. Behm, M. Willgert, Impact of electrochemical cycling on the tensile properties of carbon fibres for structural lithium-ion composite batteries, *Compos. Sci. Technol.* 72 (2012) 792–798, <https://doi.org/10.1016/j.compscitech.2012.02.006>.
- [8] E. Jacques, M.H. Kjell, D. Zenkert, G. Lindbergh, The effect of lithium-intercalation on the mechanical properties of carbon fibres, *Carbon N. Y.* 68 (2014) 725–733, <https://doi.org/10.1016/j.carbon.2013.11.056>.
- [9] Y. Yu, B. Zhang, M. Feng, G. Qi, F. Tian, Q. Feng, J. Yang, S. Wang, Multifunctional structural lithium ion batteries based on carbon fiber reinforced plastic composites, *Compos. Sci. Technol.* 147 (2017) 62–70, <https://doi.org/10.1016/j.compscitech.2017.04.031>.
- [10] S. Ekstedt, M. Wysocki, L.E. Asp, Structural batteries made from fibre reinforced composites, *Plast. Rubber Compos.* 39 (2010) 148–150, <https://doi.org/10.1179/174328910X12647080902259>.
- [11] W. Johannisson, D. Zenkert, G. Lindbergh, Model of a structural battery and its potential for system level mass savings, *Multifunct. Mater.* 2 (2019), 035002, <https://doi.org/10.1088/2399-7532/ab3bdd>.
- [12] J. Hagberg, H.A. Maples, K.S.P. Alvim, J. Xu, W. Johannisson, A. Bismarck, D. Zenkert, G. Lindbergh, Lithium iron phosphate coated carbon fiber electrodes for structural lithium ion batteries, *Compos. Sci. Technol.* 162 (2018), <https://doi.org/10.1016/j.compscitech.2018.04.041>.
- [13] N. Ihrner, W. Johannisson, F. Sieland, D. Zenkert, M. Johansson, Structural lithium ion battery electrolytes: via reaction induced phase-separation, *J. Mater. Chem. A* 5 (2017) 25652–25659, <https://doi.org/10.1039/c7ta04684g>.
- [14] W. Johannisson, N. Ihrner, D. Zenkert, M. Johansson, D. Carlstedt, L.E. Asp, F. Sieland, Multifunctional performance of a carbon fiber UD lamina electrode for structural batteries, *Compos. Sci. Technol.* 168 (2018), <https://doi.org/10.1016/j.compscitech.2018.08.044>.
- [15] L.M. Schneider, N. Ihrner, D. Zenkert, M. Johansson, Bicontinuous electrolytes via thermally initiated polymerization for structural lithium ion batteries, *ACS Appl. Energy Mater.* 2 (2019), <https://doi.org/10.1021/acsaelm.9b00563>.
- [16] L.E. Asp, E.S. Greenhalgh, Structural power composites, *Compos. Sci. Technol.* (2014), <https://doi.org/10.1016/j.compscitech.2014.06.020>.
- [17] Reichhold, DION 9102 Data sheet, 2012.
- [18] Toray Carbon Fibres America Inc., T800H Data Sheet, 2019.
- [19] Toray Carbon Fibres America Inc., T800S Data Sheet, 2019.
- [20] Toray Carbon Fibres America Inc., Explanation of Product Code, 2019. https://www.toraycma.com/file_viewer.php?id=4468.
- [21] B. Miller, P. Muri, L. Rebenfeld, A microbond method for determination of the shear strength of a fiber/resin interface, *Compos. Sci. Technol.* (1987), [https://doi.org/10.1016/0266-3538\(87\)90059-5](https://doi.org/10.1016/0266-3538(87)90059-5).
- [22] M.J. Pitkethly, J.P. Favre, U. Gaur, J. Jakubowski, S.F. Mudrich, D.L. Caldwell, L. T. Drzal, M. Nardin, H.D. Wagner, L. Di Landro, A. Hampe, J.P. Armistead, M. Desaege, I. Verpoest, A round-robin programme on interfacial test methods, *Compos. Sci. Technol.* (1993), [https://doi.org/10.1016/0266-3538\(93\)90138-7](https://doi.org/10.1016/0266-3538(93)90138-7).
- [23] S. Zhandarov, E. Mäder, Peak force as function of the embedded length in pull-out and microbond tests: effect of specimen geometry, *J. Adhes. Sci. Technol.* 19 (2005) 817–855, <https://doi.org/10.1163/1568561054929937>.
- [24] B.D. Agarwal, L.J. Broutman, Analysis and Performance of Fiber Composites, second ed., A Wiley-Interscience Publications, 1990.

- [25] J. Xie, D. Xin, H. Cao, C. Wang, Y. Zhao, L. Yao, F. Ji, Y. Qiu, Improving carbon fiber adhesion to polyimide with atmospheric pressure plasma treatment, *Surf. Coat. Technol.* 206 (2011) 191–201, <https://doi.org/10.1016/j.surfcoat.2011.04.016>.
- [26] Y. Luo, Y. Zhao, Y. Duan, S. Du, Surface and wettability property analysis of CCF300 carbon fibers with different sizing or without sizing, *Mater. Des.* 32 (2011) 941–946, <https://doi.org/10.1016/J.MATDES.2010.08.004>.
- [27] Delamination-dominated failures in polymer composites, in: E.S. Greenhalgh (Ed.), *Fail. Anal. Fractography Polym. Compos.*, Woodhead Publishing, 2009, pp. 164–237, <https://doi.org/10.1533/9781845696818.164>.
- [28] M. Nishikawa, T. Okabe, K. Hemmi, N. Takeda, Micromechanical modeling of the microbond test to quantify the interfacial properties of fiber-reinforced composites, *Int. J. Solids Struct.* (2008), <https://doi.org/10.1016/j.ijsolstr.2008.02.021>.

PAPER • OPEN ACCESS

Model of a structural battery and its potential for system level mass savings

To cite this article: Wilhelm Johannisson *et al* 2019 *Multifunct. Mater.* **2** 035002

View the [article online](#) for updates and enhancements.

Multifunctional Materials



PAPER

OPEN ACCESS

RECEIVED
29 April 2019

REVISED
20 June 2019

ACCEPTED FOR PUBLICATION
16 August 2019

PUBLISHED
10 September 2019

Original content from this work may be used under the terms of the [Creative Commons Attribution 3.0 licence](#).

Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI.



Model of a structural battery and its potential for system level mass savings

Wilhelm Johannisson¹ , Dan Zenkert¹ and Göran Lindbergh²

¹ Department of Aeronautical and Vehicle Engineering, KTH Royal Institute of Technology, SE-100 44 Stockholm, Sweden

² Department of Chemical Engineering, KTH Royal Institute of Technology, SE-100 44 Stockholm, Sweden

E-mail: wjoh@kth.se

Keywords: multifunctional material, modelling, multifunctional efficiency, weight saving

Supplementary material for this article is available [online](#)

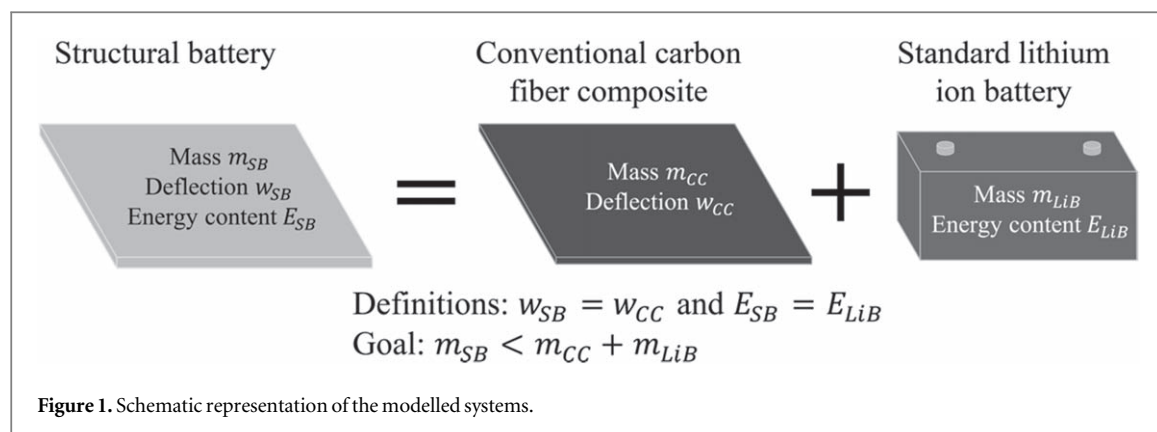
Abstract

Structural batteries are materials that can carry mechanical load while storing electrical energy. This is achieved by combining the properties of carbon fiber composites and lithium ion batteries. There are many design parameters for a structural battery and in order to understand their impact and importance, this paper presents a model for multifunctional performance. The mechanical behavior and electrical energy storage of the structural battery are matched to the mechanical behavior of a conventional carbon fiber composite, and the electrical energy storage of a standard lithium ion battery. The latter are both monofunctional and have known performance and mass. In order to calculate the benefit of using structural batteries, the mass of the structural battery is compared to that of the two monofunctional systems. There is often an inverse relationship between the mechanical and electrochemical properties of multifunctional materials, in order to understand these relationships a sensitivity analysis is performed on variables for the structural battery. This gives new insight into the complex multifunctional design of structural batteries. The results show that it is possible to save mass compared to monofunctional systems but that it depends strongly on the structure it is compared with. With improvements to the design of the structural battery it would be possible to achieve mass saving compared to state-of-the-art composite laminates and lithium ion batteries.

Introduction

There is a growing trend within the transport sector for electric mobility [1–4]. In the automotive industry this is mostly driven by the requirement to reduce vehicles' tail pipe emissions drastically by 2021 [5]. The aviation industry has similar aims and are investigating fully electric flight, for which some studies have been presented [6, 7]. For electric mobility, the main challenge is the specific energy of the batteries, which means that a large amount of batteries is required to reach sufficient range. These batteries are heavy, which further hinders the vehicle range and increases energy consumption. So, a good strategy is then to decrease the mass elsewhere, for instance by incorporating lightweight materials. Another way to decrease mass is to incorporate different functions into the same unit, making them multifunctional, or in other words, making parts or structures perform multiple tasks.

A multifunctional material is a material that intrinsically can perform two or more functions at the same time. The objective for this multifunctional material is to have a beneficial impact on a system level compared to separate monofunctional constituents, e.g. by decreasing total system mass. A structural battery is a multifunctional material that is designed to simultaneously store electrical energy and carry mechanical load. Its combined energy storage and mechanical properties diminish the need for conventional batteries and construction materials, and by doing so, decreases the total mass or volume of the system. Significant research has been done on structural battery electrodes, electrolytes, and separators, as well as structural battery



construction [8–23]. However, a fully integrated structural battery with sufficient mechanical and energy storage properties has yet to be experimentally demonstrated.

The most common technology to envision a structural battery is the combination of lithium ion battery (LiB) technology and a carbon fiber composite laminate. Carbon fibers are an excellent reinforcement material and at the same time function well as a negative electrode in an LiB [20, 22, 23]. LiBs are usually made by stacking alternate layers of electrodes and separators, in a similar way to laminated carbon fibers composites. However, LiBs use liquid or gel electrolytes to enable ion transport between the electrodes. In contrast, in order for carbon fibers to have any mechanical performance, the fibers need to be incorporated into a solid matrix material that distributes the mechanical load. The ion conduction and mechanical stability are usually competing properties and a trade-off has to be made. A recent electrolyte material has been developed that facilitates this, known as a structural battery electrolyte (SBE) [11]. This SBE is, on the sub-micron scale, a phase-separated percolating network consisting of a polymer structural backbone and a lithium ion conductive liquid electrolyte. Similar systems can be found in other research [12, 15, 24]. Recent work used this SBE to make a carbon fiber composite lamina that functions as a negative electrode within a lithium ion cell [12, 14, 15] and presents composite material engineering constants for a carbon fiber composite lamina, as well electrochemical properties. In order to make a complete structural battery cell, the negative electrode needs to be combined with a positive electrode. Generally positive electrodes are made from LiFePO_4 or similar lithium-based ceramics. Within a standard LiB, this material is adhered to an aluminum foil with polyvinylidene fluoride (PVDF) binder and carbon black (CB) to enable electric conduction from the LiFePO_4 particles to the aluminum foil [25]. Research has been done that instead incorporates LiFePO_4 -coatings on carbon fibers in order to make positive electrodes for structural batteries [13]. It is shown that the coating can transfer mechanical load and that it has good electrochemical capacity.

This research presents a model for a structural battery; however, the actual structural battery has not yet been realized. This model is intended to shed light on the design of structural batteries, with focus on their potential to outperform monofunctional components. All modelling is made analytically with a bottom-up-approach, both the electrochemical and solid mechanics fields use well-known expressions. The model links and combines these completely separate fields into the same analysis, which, to the best of our knowledge, has never been done before.

The work presented by Snyder *et al* [26] and O'Brien *et al* [27] highlights a performance metric for structural power composites. The work is focused on structural super capacitors but can also be applied to structural batteries. Their metric is used to validate multifunctional performance and is applied at manufactured structural capacitors. These does not present a parametric model for predicting such supercapacitors. In the research presented in this report, we have chosen to use a different evaluation compared to Snyder *et al* and O'Brien *et al*, since our focus is on direct mass saving. The mass of the structural battery (m_{SB}) is calculated, and directly compared to the combined mass of a conventional carbon fiber composite plate (m_{CC}) and a standard LiB (m_{LiB}). The model is built such that the structural battery has the same mechanical stiffness for a given load case as the conventional carbon fiber composite plate. While at the same time, the structural battery and the standard LiB store the same amount of electrical energy. This means that for the structural battery to outperform the monofunctional plate and battery, the relationship $m_{SB} < m_{CC} + m_{LiB}$ is desired, see figure 1.

The structural battery is designed as a layered stack of alternating positive and negative electrodes, with separators. The negative electrodes are modelled as unidirectional (UD) carbon fiber layer, with electrochemical and mechanical data as presented by Johansson *et al* [14]. The model of the positive electrodes is based on the same UD carbon fiber layer, but this time also coated with a positive electrode material [13]. The separator is modelled as a layer of randomly oriented glass fiber. The angle of each layer can be altered, and a stacking

sequence is chosen to be a quasi-isotropic layup of 0° , 90° , -45° , and $+45^\circ$ layers. The same layup is used for the conventional carbon fiber composite plate. This means that the mechanical properties of this stack can be calculated using lamination theory, and electrochemical energy can also be calculated for each internal cell made from negative and positive electrodes. All internal design parameters, such as volume fractions, thicknesses, and material properties are variables. Electrochemical energy is dependent on the charge and discharge time of the cell. In this study the electrochemical energy is measured at a constant charge and discharging time of 10 h. This charge time is used based on the availability of data in literature. Power output of the structural battery is not investigated due to lack of available data.

The model starts off with an initial design, with variables corresponding to what would be possible to achieve today if manufacturing the structural battery and which are taken from the open literature. Variables are then varied, within physical boundaries, in order to understand the system's behavior. The desire of this variable variation is to find out how a structural battery should be designed in order to increase its performance. These adjustments are then made to the design and referred to as a target design, since it indicates what is theoretically achievable for the structural battery. The model is also used to investigate more applied case-studies of the structural battery, where the model is adapted to investigate the use of structural batteries in the interior panel of an aircraft, the roof of an electric vehicle, the hull of an electric ferry, and the chassis of a laptop computer.

The model highlights how to design a structural battery in order to increase its ability to outperform the monofunctional plate and battery. It shows that the structural battery has a potential to outperform the monofunctional constituents with a potential mass saving of 26%. The model further shows that the structural battery is favorable to use in all analyzed case-studies. This means that the structural battery is a promising concept to decrease mass within electric mobility and electronics.

Models in literature

Modelling is used to facilitate understanding of a system's behavior and it is extensively used to predict performance. Within the electrochemical field it is, among other things, used to study LiBs, especially the prediction and understanding of the general properties, aging, life cycle, and applications [28–35]. Models also exist for analyzing and predicting the thermal behavior [36–42] and mechanical properties [43–47] of LiBs. Particularly, work has been focused on the mechanical properties of electrodes and separators [48–51], pouch cells [52–56] and the commercial 18650-cell [57–63]. Note that none of these are multifunctional, the focus in these studies is mainly regarding short circuit and failure mechanisms. Also, all of these models focus on LiBs that already exists and they are, in most cases, verified with testing. In the same way, in the field of solid mechanics and fibrous composites, modelling is used to predict structural properties of materials.

Multiphysics models has been done on the behavior of carbon fibers in structural batteries. In particular, it is known that carbon fibers expand longitudinally and radially when they are intercalated with lithium ions [64]. This behavior has been investigated with regards to internal stresses and dimension changes for single fiber batteries [65, 66]. This phenomenon has also been investigated for a layered composite with the intention to minimize external deformations [67], or maximize them which is necessary for electrochemical actuators. Furthermore, Carlstedt *et al* [68] has shown that the state of charge of a single fiber battery has an impact on the overall stiffness of the structural battery. It has also been shown that the thermal and diffusion induced stresses in a single fiber battery are important to take into account in its design [69]. An early approach towards predicting both electrochemical and mechanical properties of a laminated structural battery has been shown by Carlstedt *et al* [70], which investigates a structural battery in a single cell setup that is patch-wise laminated in a reinforcement casing. This paper presents three fixed configurations of structural batteries but does not investigate if the proposed structural batteries outperform monofunctional materials and batteries. No further references on modelling or prediction of combined electrochemical and mechanical properties, with regards to multifunctional performance, can be found.

Limitations and uncertainties

The type of modelling presented in this research intrinsically comes with uncertainties and assumptions, especially since a physical structural battery has not been demonstrated yet and thus no experimental validation can be done. Some data has been found on testing of similar materials in open literature. For instance, the electrode capacities are based on data for the materials in liquid electrolyte and commercial separators. This data is then adapted to the structural battery system containing an SBE. Thus, more testing and development is needed to have more reference data to compare with and possibly update the model.

The design of the structural battery is also an early approach. For instance, the casing of the structural battery will require additional testing to ensure encapsulation against humidity. Furthermore, this casing is only modelled on the top and bottom of the structural battery layup, not on the sides. In addition, the structural battery would likely need further casing against physical damage and impact. However, this is the same for the

standard LiB which herein are modelled with only a pouch bag as protection, which is not appropriate protection from the environment or impact loads.

Strength of a structural material is an important fundamental property for design and construction. In the field of fiber composites material failure is a completely separate research topic, mostly due to the complex nature of failure in laminated fiber composites. Tensile failure in fiber composites is characterized by microcracking, fiber failure, interfacial failure, matrix failure and/or debonding, all with their own strength definitions. For compressive failure, kink-bands are common, requiring significant research to characterize, model and predict. And, the laminated nature of the composite material give rise to interlaminar failure modes too. What is central in all strength prediction in composites is the requirement for a lot of measurement data. Initial but limited studies and measurements regarding the strength of structural battery laminas have been made [13–15]. However, a lot of measurement data is still missing in order to produce trustworthy models of the failure characteristics of a complete structural battery laminate. Thus, in this research we have chosen not to investigate structural battery strength.

Cost is a central factor within design and manufacturing and may become crucial for future implementation of structural batteries. However, a complete analysis and cost model for a structural battery would require further assumptions of manufacturing methods, processing, manufacturing times, energy requirements, automation etc. These are speculative, especially since the material does not yet exist, and may have a significantly larger impact on the total material cost than the actual bill of materials in this model. Therefore, we have chosen not to investigate cost in the context of this paper.

Electrochemical modelling is also challenging, and simplifications and assumptions have been made with regards to the energy properties of the structural battery. The dependence on volume fraction of fibers in the electrodes is simplified in such way that mass transport of lithium ions in the SBE is not considered. The limitations in mass transport would result in a restraint on the maximum volume fraction of fibers simply due to the carbon fibers being too packed, thus limiting the movement of lithium ions in the surrounding SBE. This mass transport is a significant limitation for the power output of the structural battery.

Power is also not investigated in this research in order to avoid drawing premature conclusions. Modelling battery power is a complex topic for this geometry, requiring non-analytical models with significant knowledge on limitations from lithium ion transport, conductivity and electrode overpotentials. This data does not yet exist for the structural battery and it would be very questionable extrapolating data from standard lithium ion batteries due to the interpenetrating structural and liquid nature of the SBE. Usually within battery research, a new battery is designed and built first with high energy density and then, as research and knowledge progresses, the battery is further optimized for power output. It is likely that this trend is going to be present for structural battery research in the future.

Method

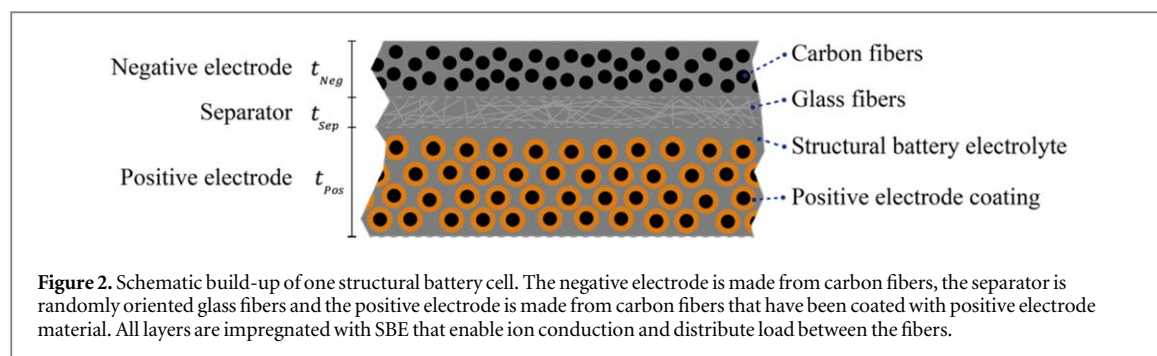
Below follow sections explaining the different parts of the structural battery and how these are treated in the model. Similar explanations are given for the conventional carbon fiber composite and standard lithium ion battery. Following this are details regarding the load cases, boundary conditions, the mass saving and variable sensitivity. A complete list of nomenclature can be found in appendix table A1 and all constants for the calculations are presented in appendix table A2.

Structural battery

A schematic of a representative structural battery cell that consists of a negative electrode, a positive electrode and a separator is shown in figure 2. Current collectors are generally needed in lithium batteries but for the structural battery the carbon fibers are utilized as current collectors since carbon fibers are good electrical conductors.

Negative electrode lamina

The carbon fibers used in this analysis come in tows of 6000 filaments (T800HB-6k-40B from Toray). In order to make thin laminas of the carbon fibers, the fiber tow is spread to a uniform band in order to make a thin sheet of unidirectional carbon fibers. This sheet will then have an areal density of carbon fibers ρ_A . With a spread width of 10 mm, this areal density is 22.8 g m^{-2} . Thus, the mass of carbon fibers in the negative electrode is calculated by $m_{\text{CF,Neg}} = \rho_A \cdot w \cdot L$, where w and L are the dimensions of the plate ($1 \text{ m} \times 1 \text{ m}$). In order to make a composite lamina the negative electrode is impregnated with SBE, to achieve a volume fraction of fibers $v_{f,\text{Neg}}$. The lamina will then be a negative electrode unidirectional composite. The thickness of the negative electrode can be calculated by the volume fractions of SBE and carbon fibers, as well as the plate dimensions. Carbon fibers also have a gravimetric electrochemical capacity c_{CF} , and with a known mass of carbon fibers in the negative



electrode $m_{CF,Neg}$. The total electrochemical capacity of the negative electrode can then be found through $C_{Neg} = c_{CF} \cdot m_{CF,Neg}$.

Positive electrode lamina

The positive electrode is modelled to have the same amount of carbon fibers as the negative electrode and the carbon fiber tow is spread in the same way. Additionally, the carbon fibers are coated with a layer of active material ($LiFePO_4$) to constitute a positive electrode. In order for the active material to stick to the carbon fiber, PVDF is used as binder material and carbon black (CB) for additional electrical conductivity of the active material. The mass ratio of the coating materials is chosen as 89:6:5 ($LiFePO_4$:CB:PVDF) as given in [13]. The amount of $LiFePO_4$ is given from balancing the amount of active material in the negative and positive electrodes, so that the electrodes have the same electrochemical capacity. Thus, the mass of active material ($LiFePO_4$) in the positive electrode is given from $m_{LiFePO_4} = \frac{C_{Neg}}{c_{LiFePO_4}}$. The coated carbon fibers in the positive electrode are impregnated with SBE to make a composite lamina. The thickness of the positive electrode is defined based on the amount of $LiFePO_4$ particles needed to balance the cell, as well as the volume fraction of fibers.

Separator

The separator is modelled as a composite lamina made from randomly oriented E-glass fibers (72 GPa elastic modulus), and the matrix is the same SBE as in the rest of the structural battery. The SBE's elastic modulus is in the initial case given from Johansson *et al* [14] but treated as a variable in the variable sensitivity analysis. The separator has a volume fraction of fibers $v_{F,sep}$ and a separator thickness t_{sep} .

Electrode capacity

The gravimetric electrochemical capacity of all LiB electrodes depends on the charge and discharge time of the battery. This is also the case for the carbon fibers and $LiFePO_4$ in the structural battery. For simplification, the structural battery is investigated at a 10 h charge and 10 h discharge cycle. Kjell *et al* [71] has reported approximately 240 mAh g⁻¹ for carbon fibers at 10 h charge time and Hagberg *et al* [13] has reported approximately 110 mAh g⁻¹ for $LiFePO_4$ coated carbon fibers at 10 h charge time.

This data from Kjell *et al* and Hagberg *et al* are for the electrode materials in liquid electrolyte and 250 μ m Whatman glass microfiber filter separator. This is not the case in the structural battery. No such measurement data exists for a structural battery yet, instead this data is adapted to estimate possible material properties for carbon fiber and $LiFePO_4$ in a structural battery. Using the ion conductivity of liquid electrolyte (called LP40) (8 mS cm⁻¹ [72]) and the Whatman separator thickness (250 μ m), the electrochemical capacity can be adjusted to values relevant for the conductivity of the SBE and the thickness of the structural battery separator. This gives a gravimetric electrochemical capacity for the structural battery, at a 10 h charge and discharge, of 100 mAh g⁻¹ for the carbon fibers and 109 mAh g⁻¹ for the $LiFePO_4$.

Structural battery energy

The electrical energy ϵ_{LiB} in one electrochemical cell (1 layer of negative electrode, 1 layer of separator and 1 layer of positive electrode) is calculated by $\epsilon_{LiB} = C \cdot U_{eff}$ where C is the minimum electrode capacity $C = \min(C_{Pos}, C_{Neg})$. Herein, the electrode capacity is modelled to be the same in order to have an electrochemically balanced battery. The effective electrical cell potential U_{eff} is given by $U_{eff} = U - U_{drop}$, where U_{drop} is the potential drop over the separator layer, calculated by

$$U_{drop} = \frac{1}{K} \cdot \frac{t_{eff}}{A} \cdot I, \quad (1)$$

where K is the ion conductivity in the separator, t_{eff} is the effective distance between the electrodes taken as the distance between middle planes of the two electrodes $t_{eff} = t_{sep} + 0.5t_{Neg} + 0.5t_{Pos}$, A is the separator area

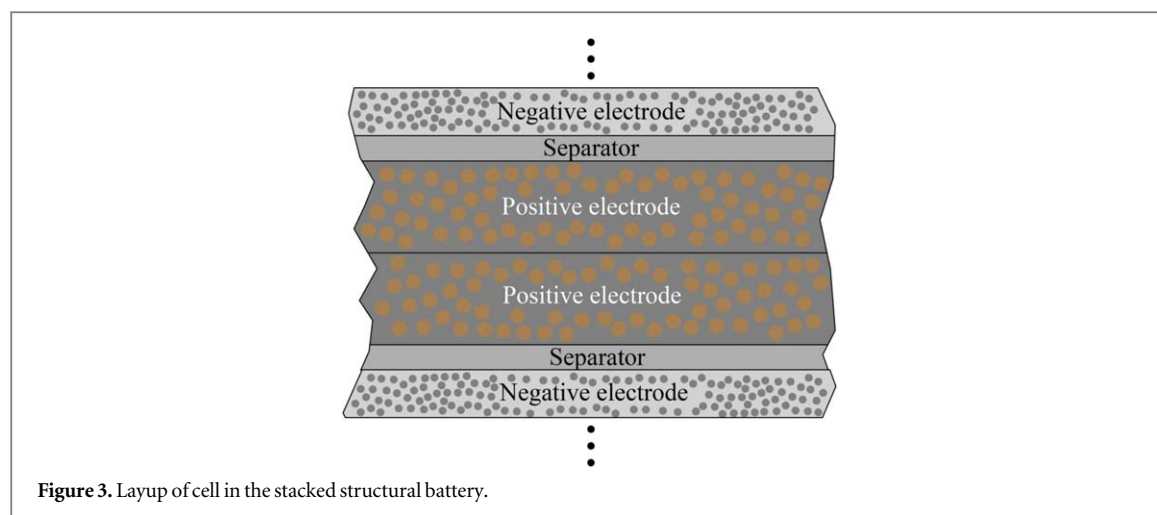


Figure 3. Layout of cell in the stacked structural battery.

($A = w \cdot L$), and I is the charge current, given by $I = C/T$, where T is the charge time. This is a simplified approach, not taking account of the full complexity of calculating the potential drop in the electrodes.

The conductivity in the separator depends on the conductivity of the SBE and the volume fraction of glass fibers in the separator, according to equation (2). The power 3 is added in order to account for the added tortuosity caused by the glass fibers in the separator

$$K = K_{\text{SBE}} \cdot (1 - v_{f,\text{Sep}})^3. \quad (2)$$

These relationships naturally include some basic assumptions; first is that the system is considered isothermal, meaning that heat generation in the structural battery is not included. Thus, effects of temperature on conductivity, transport limitations and reaction rates are neglected. All of these are important for future research on structural batteries but given the long charging and discharging time in this model, the effect of these are limited. Furthermore, any first-cycle effects, such as trapped lithium or solid-electrolyte interphase-layer formation, are not considered.

Cell stacking and layup sequence

The stacking of the structural battery is made by alternating mirrored cells of negative, separator and positive electrodes as shown in figure 3.

The stacking sequence can be made arbitrary as with classical lamination theory. In this case we, for simplicity, study a quasi-isotropic laminate with the layup: $[0_{\text{GFweave}}, 0_-, 0_{\text{Sep}}, 0_+, 90_+, 0_{\text{Sep}}, 90_-, -45_-, 0_{\text{Sep}}, -45_+, 45_+, 0_{\text{Sep}}, 45_-]_S$. Note that the separator layer is independent of lamina direction since it is a thin randomly oriented glass fiber composite lamina. The outermost layer is modelled by a glass fiber weave (0/90) with epoxy, with the data presented in table A2 in appendix. This layer is used as a protective casing-layer for the structural battery and has a thickness t_{Case} . It provides structural capacity but no electrochemical capacity.

Standard LiB

A standard LiB is modelled by a known energy density W_{LiB} , chosen to match a state-of-the-art LiB. The total energy of the standard LiB should then be the same as the structural battery, thus giving the mass of the standard LiB, denoted m_{LiB} . The energy density depends on the charge time of the battery. Data for this dependence is found in previous research [73, 74], which leads to an energy density of 177.3 Wh kg^{-1} at a 10 h charge and discharge rate. This represents a state-of-the-art energy optimized commercial LiB.

Conventional carbon fiber composite

For mechanical comparison, a standard carbon fiber composite laminate is modelled the same way as the structural battery. Also, the composite has a similar fiber layup $[0, 90, -45, 45]_S$ consisting of unidirectional carbon fiber/epoxy pre-preg laminas, as in state-of-the-art high-performance carbon fiber laminates used in aerospace applications. The thickness of each lamina is the same and found through an optimization procedure in order for this laminate to have the same stiffness as the structural battery for a given load case. The mass of the standard composite laminate is also calculated, and denoted m_{CC} .

Calculating material stiffness properties

The lamina's longitudinal, transverse and shear stiffnesses are governed by rule of mixtures (Voigt and extended-Reuss material models), and lamination theory links the lamina properties and layup to structural

properties [75]. The same method is used for all the structural battery layers (negative electrode, positive electrode, separator and casing). This means that all stiffnesses of the system are fully parametric and based on the volume fractions, matrix and fiber stiffnesses in the corresponding laminas. These rules, including lamination theory does naturally come with a set of assumptions regarding the system, most importantly that the matrix and fibers are homogenous, linearly elastic and isotropic. The SBE is not homogenous in this research, but it has been shown that it still behaves as a homogenous structural material at the macro scale [14]. Furthermore, rule of mixtures and lamination theory assume complete bonding between fibers and matrix, another unclear property of the SBE. This most likely has the largest effect on the strength of the laminas, which is another reason strength is not considered in this model; the uncertainty is too large.

The structural battery negative electrode has measured properties given from [14], giving the SBE's elastic modulus in the initial case, however this metric is treated as a variable in the variable sensitivity analysis. Stiffness measurements do not exist for the separator or positive electrode. As stated, the separator is treated as a randomly oriented short-fiber lamina, and the mechanical properties of this lamina are calculated using empirical relationships for randomly oriented short fibers [75]. However, in the positive electrode, the fibers are coated with a positive electrode coating. The properties of this coating have been analyzed by Hagberg *et al* [13] which shows that the coating does adhere sufficiently to transfer mechanical load. Also, the stiffness of the coating is higher than that of the SBE. Thus, treating the positive electrode the same way as the negative electrode will produce a lower bound on the lamina stiffness.

Load case and boundary conditions

The stiffness of the mechanical structure, the plate, depends on the load case and can broadly be divided into the stretch dominated structures and bending dominated structures. In the former case the stiffness is given by the extensional stiffness matrix A and the latter by the bending stiffness matrix D . Other load cases could also be investigated, such as buckling, shear or free vibration but are not further explored here.

Bending dominated structures

Since a composite plate generally is orthotropic, we have chosen an approach to compare different materials and configurations based on one single metric. The bending stiffness of a plate can be investigated analytically if the applied load is a distributed pressure and the plate has simply supported edges. This is done by lamination theory and the theory of anisotropic plates [76], and using the midpoint deflection as a single stiffness metric. Herein, a transverse pressure is used (1 N m^{-2}) since the purpose is to match the bending stiffness of the structural battery plate to the bending stiffness of any other material and plate configuration with the same dimensions and the same applied load.

Stretch dominated structures

An in-plane loading can be modelled by instead matching A_{11} -terms in the extensional stiffness matrix of the laminate [75]. The in-plane stiffness is also the most important factor for the bending stiffness of a sandwich plate, which is used in this analysis to investigate the usage of structural batteries as face sheets in a sandwich construction.

Mass-saving calculations

Mass is calculated for all the different components; structural battery, conventional carbon fiber composite, and a standard LiB. The mass saving with a multifunctional structural battery (in percent), compared to monofunctional carbon fiber composite and LiB is then calculated by:

$$MS = \frac{m_{CC} + m_{LiB} - m_{SB}}{m_{CC} + m_{LiB}}. \quad (3)$$

This equation is analogous to that presented by Snyder *et al* [26] (left side of equation (10)), from which their multifunctional efficiency is derived. The same method and metric can be applied in this research, but we have chosen to focus our results on the mass saving. Nevertheless, the resulting multifunctional efficiency, according to Snyder *et al* of the modelled structural batteries are still presented.

Sensitivity analysis

In order to investigate the consequence of altering the design of the structural battery, input values are varied in order to find their relationship to the mass saving potential. The analyzed input values are given in table 1, when one variable is varied at a time while all the other variables are kept constant at their initial value. The initial values are chosen such that they could be achievable today [11, 13, 14]. The range over which the variables are analyzed is chosen by what is assumed to be theoretically and physically possible.

Table 1. Variables for calculating the properties of a full cell laminated composite battery.

Property	Identity	Initial value	Unit
Volume fraction of fibers in the negative electrode	$vf_{F,Neg}$	0.18	—
Volume fraction of fibers in the positive electrode	$vf_{F,Pos}$	0.2	—
Volume fraction of glass fibers in the separator	$vf_{F,Sep}$	0.1	—
Thickness of the separator	t_{Sep}	20	μm
Carbon fiber area density	ρ_A	22.8	g m^{-2}
SBE ion conductivity	K	$1.5 \cdot 10^{-4}$	S cm^{-1}

The sensitivity analysis is performed in order to find where and how improvements can be made in the design of the structural battery. In a second iteration, these improvements are made on all variables, which provide a reference for what is the best theoretically possible structural battery. The mass saving and mechanical/electrochemical properties of this design are also investigated.

Results and discussion

Mass saving with initial design

The model estimates the individual masses and potential mass savings, the applied load case is a distributed pressure with simply supported boundary conditions, i.e. assuming a bending dominated structure. The initial design of the structural battery results in a negative potential mass saving of -5.5% , see table 2 for complete results. Thus, it is not possible to save mass compared to a conventional carbon fiber composite plate and standard LiB by incorporating the initial design of the structural battery. However, this is with current structural battery technology, which is expected to be improved with further research. Note also that this comparison is made against state-of-the-art high performance pre-preg type carbon fiber laminates used in aerospace applications, and a with state-of-the-art LiB.

The structural battery has an energy density of about 25 Wh kg^{-1} . Scholz *et al* [7] have presented 51.8 Wh kg^{-1} as the required minimum specific energy for a structural battery to make contributions in electric flight, for small all electric aircraft. This initial design of a structural battery has not yet reached those levels.

Variable sensitivity

The initial values of the variables are used as a baseline on a bending dominated structure. Each variable is then varied individually, and the others are kept constant at their initial values, giving the results shown in figure 4. For clarity, each of the variables are individually discussed in the following sections.

Volume fraction of fibers in the negative electrode

A higher volume fraction of fibers in the negative electrode ($vf_{F,Neg}$) results in a larger potential mass saving as seen in figure 4(a). This is due to a larger percentage of fibers in the electrode increasing the elastic moduli of the lamina. The volume fraction of fibers in the negative electrode is thus an important variable to improve for the mass saving potential of the structural battery.

Volume fraction of fibers in the positive electrode

Varying the volume fraction of fibers in the positive electrode ($vf_{F,Pos}$) has the same effect as varying $vf_{F,Neg}$. A higher $vf_{F,Pos}$ results in larger mass saving, as seen in figure 4(b). This is due to increased volume fraction of fibers resulting in increased mechanical properties, but also shorter internal distances in the battery which improves electrochemical properties. The volume fraction of fibers in the positive electrode has a large impact on the mass saving potential of the structural battery and is important to improve when manufacturing structural batteries.

Volume fraction of fibers in the separator

The relationship for volume fraction of glass fibers in the separator ($vf_{F,Sep}$) is the opposite of the two other volume fractions ($vf_{F,Neg}$ and $vf_{F,Pos}$). Figure 4(c) shows that a higher $vf_{F,Sep}$ results in decreased mass saving. This is due to the added mass of glass fibers in the separator not contributing enough to the overall stiffness of the structural battery compared to its mass increase. Also, more glass fibers in the separator decrease the ion conductivity. Nevertheless, the influence of $vf_{F,Sep}$ is not as significant as the volume fractions of the other two layers.

Table 2. Results for the initial design of the structural battery, when compared to a conventional carbon fiber composite and a standard lithium ion battery.

Property	Value	Unit
Mass saving	−5.5	%
Multifunctional efficiency [26]	0.4	—
Structural battery thickness	1.4	mm
Structural battery mass	2	kg
Structural battery energy density	25	Wh kg ^{−1}
Conventional carbon fiber composite thickness	1	mm
Conventional carbon fiber composite mass	1.6	kg
Standard lithium ion battery mass	0.3	kg
Structural battery in-plane elastic modulus	19.1	GPa
Structural battery in-plane shear modulus	6.5	GPa
Conventional carbon fiber composite in-plane elastic modulus	54.6	GPa
Conventional carbon fiber composite in-plane shear modulus	20.6	GPa
Negative electrode lamina stiffness properties		
Longitudinal modulus	53	GPa
Transverse modulus	1.5	GPa
Shear modulus	1.3	GPa
Positive electrode lamina stiffness properties		
Longitudinal modulus	58	GPa
Transverse modulus	1.4	GPa
Shear modulus	1.3	GPa
Separator lamina stiffness properties		
In-plane modulus	4.6	GPa
Shear modulus	1.6	GPa

Thickness of the separator

The mass saving decreases with a larger thickness of the separator (t_{sep}), as seen in figure 4(d). Not only has the separator a low elastic modulus which makes it unfavorable mechanically—meaning that a thinner separator will decrease the mass of the structural battery—but also, a shorter distance between the electrodes will increase the energy storage of the structural battery. The thickness of the separator is a very important design variable for the structural battery and should be made as thin as possible.

Carbon fiber areal density

An increased carbon fiber areal density (ρ_A) increases the mass saving of the structural battery, as shown in figure 4(e). Note that an increased ρ_A increases the thickness of both the negative and positive electrodes. This increase of mass saving is linked to the electrodes becoming thicker in relation to the separator. Thus, the laminate gains mechanical rigidity.

Ionic conductivity of SBE

The dependence on ion conductivity of the SBE (K) is shown in figure 4(f), which displays a large mass saving if the ion conductivity of the SBE is increased. The ion conductivity is important for the mass saving of the structural battery and large improvements can be made with an increased ion conductivity up to about $1 \cdot 10^{-3} \text{ S cm}^{-1}$ after which the mass saving potential levels off as it approaches the conductivity of liquid electrolytes.

Elastic modulus of the SBE

The elastic modulus of the SBE (E_{SBE}) is also investigated but not shown with a figure since it is small and has a linear relationship with the mass saving of the structural battery. Increasing the modulus from 600 to 1000 MPa the mass saving increases from −5.5% to −4.1%. This increase is directly linked to an increased stiffness of the structural battery and thus a higher mass saving. However, the increase is not substantial in comparison to some of the other variables since it mainly increases matrix-dominated properties like E_2 and G_{12} .

Mass saving with target design

To find the largest theoretically possible mass saving with a structural battery, each of the variables are adjusted to maximize the mass saving. Each of the values are chosen to be theoretically achievable with further improvements of the structural battery material constituents and improved manufacturing methods. These values are referred to as target values and are presented in table 3. Note that the volume fraction of glass fibers in

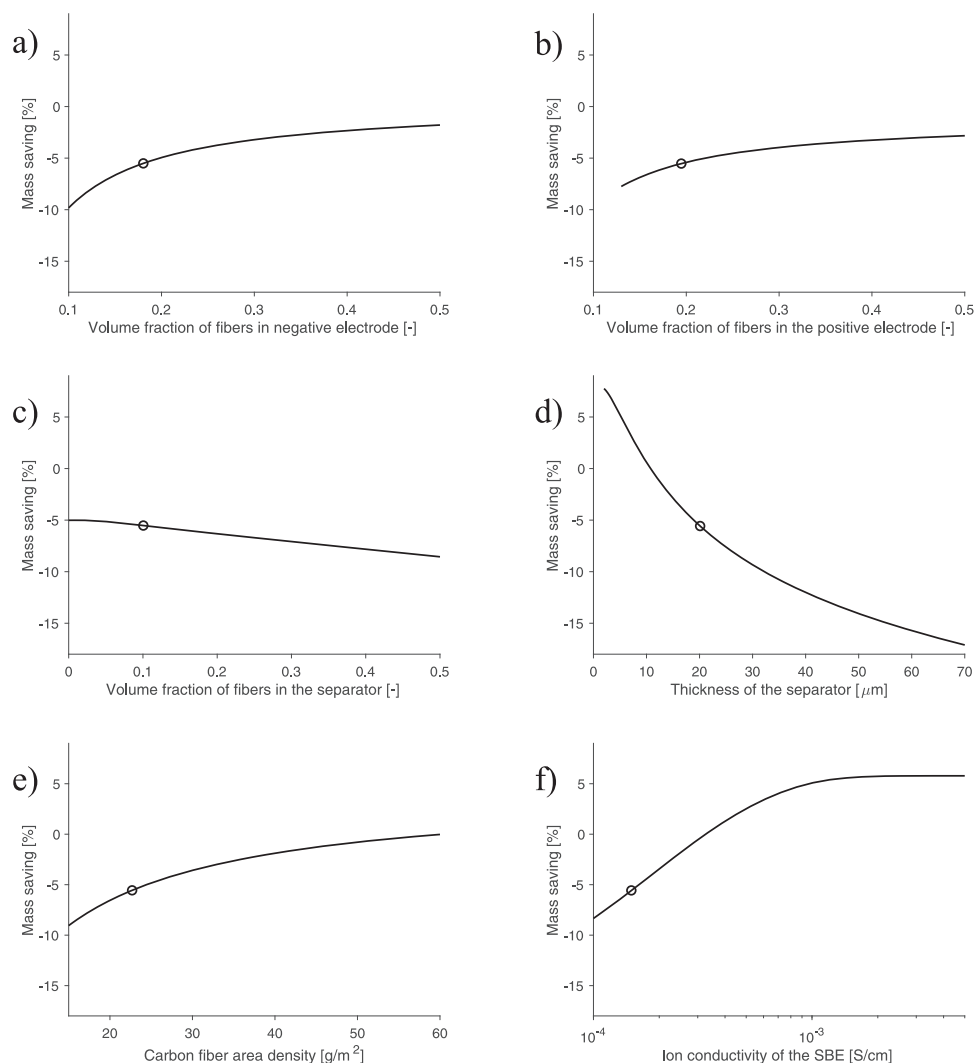


Figure 4. Results obtained from individually varying variables for a structural battery, the potential mass saving is stated versus a conventional carbon fiber composite plate with the same mechanical response and a standard LiB with the same energy content. Initial design parameters are marked with a circle. (a) Varying volume fraction of fibers in the negative electrode. (b) Varying volume fraction of fibers in the positive electrode. (c) Varying volume fraction of fibers in the separator. (d) Varying separator thickness. (e) Varying the areal density of carbon fibers in the electrodes. (f) Varying the ion conductivity of the electrolyte.

the separator is decreased to zero. Resin-rich areas in composites can lead to challenges with regards to strength, which could also be the case in the separator layer. This could be overcome with an additional high porosity separator inlay for physical separation, given the thin separator. It is also assumed that an elastic modulus of 1000 MPa for the SBE is within reach in the future [11]. The improvement on ionic conductivity is challenging, as it is reaching the conductivity of pure liquid electrolytes. The ionic conductivity is chosen at $1.5 \cdot 10^{-3}$ S cm^{-1} as a reasonable goal for future research.

For the target design values of the structural battery the model shows a potential mass saving of 26%, see table 4 for complete results. Thus, making it possible to save considerable mass compared to a conventional carbon fiber composite plate and standard LiB. Note that the mass of the structural battery is higher for the target design than the initial design. This is due to the fact that the target design has a higher density but lower thickness than the initial design thanks to higher mechanical properties. However, the thickness is decreased less than the density is increased since the stiffness of the plate has a cubic dependence on its thickness (bending dominated).

The energy density of the structural battery is about 110 Wh kg^{-1} . Compared to the required 51.8 Wh kg^{-1} to make contributions in electric flight for small all-electric aircraft [7]. This target design has well surpassed that limit, which further emphasizes the ability of the structural battery to outperform the monofunctional carbon fiber composite plate and standard LiB.

Future improvements

In order to improve the model, more measurement data would be needed. For instance, different separator thicknesses and charge and discharge times. These inputs on electrochemical performance would not only mean

Table 3. Target values for maximizing the mass saving from using a structural battery.

Property	Identity	Target value	Unit
Volume fraction of fibers in the negative electrode	$v_{F,Neg}^f$	0.5	—
Volume fraction of fibers in the positive electrode	$v_{F,Pos}^f$	0.27	—
Volume fraction of glass fibers in the separator	$v_{F,Sep}^f$	0	—
Thickness of the separator	t_{Sep}	10	μm
Carbon fiber areal density	ρ_A	45.6	g m^{-2}
SBE ion conductivity	K	$1.5 \cdot 10^{-3}$	S cm^{-1}

Table 4. Results for the target design of the structural battery, when compared to a conventional carbon fiber composite and a standard lithium ion battery.

Property	Value	Unit
Mass saving	26	%
Multifunctional efficiency [26]	1.07	—
Structural battery thickness	1.4	mm
Structural battery mass	2.6	kg
Structural battery energy density	110	Wh kg^{-1}
Conventional carbon fiber composite thickness	1.2	mm
Conventional carbon fiber composite mass	1.9	kg
Standard lithium ion battery mass	1.7	kg
Structural battery in-plane elastic modulus	33	GPa
Structural battery in-plane shear modulus	12	GPa
Conventional carbon fiber composite in-plane elastic modulus	55	GPa
Conventional carbon fiber composite in-plane shear modulus	21	GPa
Negative electrode lamina stiffness properties		
Longitudinal modulus	147	GPa
Transverse modulus	1.8	GPa
Shear modulus	1.8	GPa
Positive electrode lamina stiffness properties		
Longitudinal modulus	81	GPa
Transverse modulus	2.0	GPa
Shear modulus	1.3	GPa
Separator lamina stiffness properties		
In-plane modulus	1	GPa
Shear modulus	0.4	GPa

that the model is further refined but would enable modelling of the rate dependencies for the structural battery. This would also allow for predictions on power output of the structural battery.

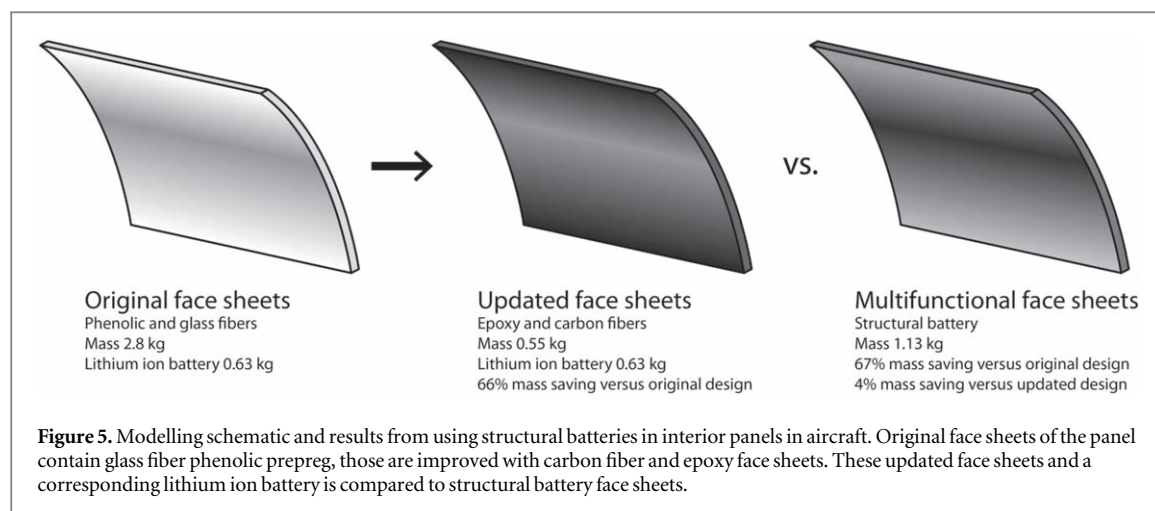
The mass transport of lithium ions in the SBE is a significant limitation for power output of this structural battery, and the mass transport has not been investigated in detail in this study. For instance, the mass transport of ions will be significantly hindered if the volume fraction of fibers in any electrode is too high, since fibers that are too tight to each other will obstruct the transport of ions further into the tow.

One large improvement to the properties of the structural battery would be to use a different positive electrode material. The LiFePO_4 used in this model has together with carbon fiber negative electrode a nominal cell potential of about 2.8 V, while for instance an NMC type of electrode material has about 3.2 V nominal cell potential [77]. This increase in cell potential would further increase the mass saving of the structural battery. It is not yet known if NMC type electrode materials work within a structural battery, so further investigations are needed in order to ensure their function.

The model incorporates an early approach for a casing material around the structural battery, this casing has not been validated for use with the structural battery. For instance, it is not known that it can enclose the battery cells sufficiently to withstand moisture leakage for a long time, or what type of protection it provides against impacts to the structural battery.

Cost has not been investigated at all within this analysis, mostly because it is too early in the development process to have useful insight into manufacturing methods and material costs. Further analysis is needed on the cost of the structural battery in order to aid its realization.

Strength is a central property for structural materials, which has not been investigated at all within this research. Predicting strength of fiber composites is complicated and requires additional material testing in order



to be validated and trustworthy. Since this information doesn't exist yet for the structural batteries in this research it is best left for future studies.

Case-studies

In order to further explore the usefulness of structural batteries, several case-studies have been made. Each case-study models an original system, some have a different construction material (glass fiber composite, steel or aluminum) than the carbon fiber composite in this research. It is known that just incorporating carbon fiber composites does save mass compared to these materials. In order to make a fair comparison to the structural battery, these systems are first replaced with the monofunctional carbon fiber composite as presented in this research. Next, the implications of replacing that with a structural battery are investigated. These case-studies include an interior panel of an aircraft, the roof of an electric vehicle, a hull panel in an electric ferry and a laptop computer chassis. The specific design and construction of these cases are further explained below.

Interior panel in aircraft

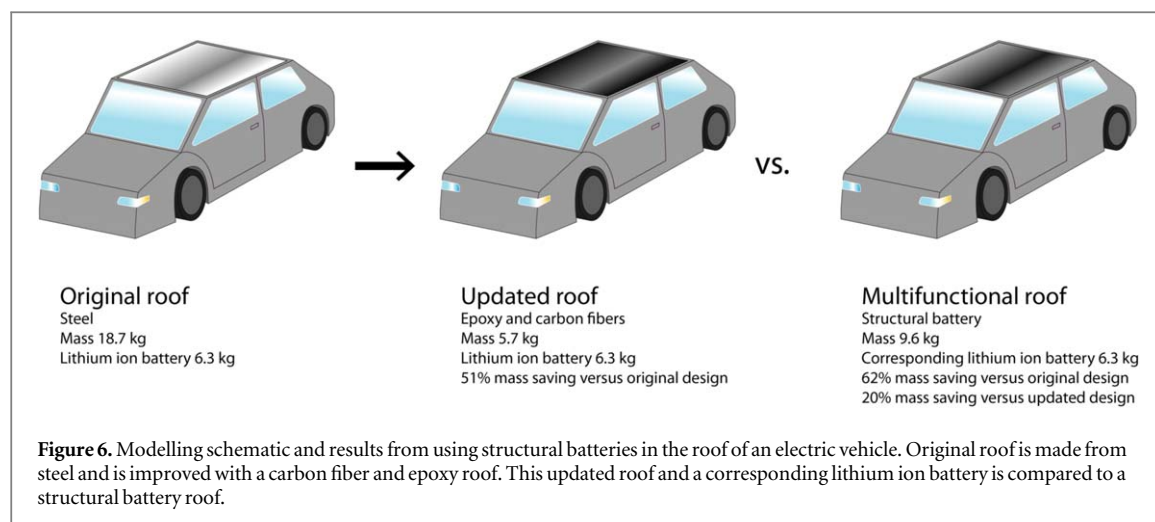
The interior wall panels in a commercial aircraft are commonly made with two windows per panel and are curved to match the fuselage of the aircraft, they are about 2 m high and 1.5 m wide. Such interior panels are typically constructed with two layers of biaxial glass fiber phenolic prepreg plies on each side of a 6 mm foam core material. Each ply has a fabric areal mass of 296 g m^{-2} and approximately 50% fraction of fibers by volume with a density of 2.085 g cm^{-3} and a ply thickness of 0.240 mm. One original face sheet has an approximate mass of 2.8 kg. The panels are mainly designed for stiffness against a pressure load from a person onto the panel.

In order to simplify the modelling of such panel the windows and any fasteners are not considered. Since the panel is a sandwich construction, the stiffness of the panel is mainly given from the in-plane stiffness (A_{11}) of the face sheets, i.e. a stretch dominated structure. The original glass fiber phenolic-based face sheets are first updated with equivalent carbon fiber and epoxy (with regards to stiffness). The carbon fiber epoxy has the same properties as in the presented model. Then, these updated face sheets are compared to that of a structural battery using the target design and the layup $[0_{\text{GFweave}}, 0_-, 0_{\text{Sep}}, 90_+]$, with a casing thickness of 0.05 mm. This results in a potential mass saving of 4%, see figure 5 for schematics and further results.

Electric vehicle roof

Another possible application for a structural battery is the roof of an electric vehicle. The roof of an electric vehicle can be simplified as a flat sheet of steel ($E_{\text{steel}} = 200 \text{ GPa}$, $\nu_{\text{steel}} = 0.25$ and $\rho_{\text{steel}} = 7800 \frac{\text{kg}}{\text{m}^3}$), with a length of 2 m and width of 1.5 m with a thickness of 0.8 mm. This original roof has a mass of approximately 18.7 kg.

The roof of a vehicle is not designed to have any significant load carrying capability with respect to the stiffness and strength of the chassis, but rather should be stiff enough to not deform permanently due to pressure on the surface. The roof is here modelled as a bend dominated structure and fasteners are not considered. The original steel roof is first improved with a carbon fiber and epoxy composite roof with the same material properties as the presented model (as well as having the same global stiffness), and this roof is then compared to the roof made from a structural battery. The structural battery, utilizing the target design could have the layup:



$$[0_{\text{GFweave}}, 90_+, 0_{\text{Sep}}, 90_-, 0_-, 0_{\text{Sep}}, 0_+, 90_+, 0_{\text{Sep}}, 90_-, -45_-, 0_{\text{Sep}}, -45_+, 45_+, 0_{\text{Sep}}, 45_-]_S.$$

Resulting in a mass saving of 22%, further results and schematics are shown in figure 6.

Hull of electric ferry

An electric ferry can be constructed from carbon fiber reinforced epoxy on either side of a sandwich core material. The material properties of these face-sheets are assumed to be the same as those in the presented model. Since the ferry is made with a sandwich construction, the stiffness of the panel is mainly given from the in-plane stiffness (A_{11}) of the face sheets, i.e. the analysis of these face sheets is made with a stretch dominated design. Any fasteners, bulkheads or other stiffeners are not considered. A structural battery using the target design could use the layout:

$$\left[\begin{array}{c} 0_{\text{GFweave}}, 90_+, 0_{\text{Sep}}, 90_-, 0_-, 0_{\text{Sep}}, 0_+, 90_+, 0_{\text{Sep}}, 90_-, -45_-, 0_{\text{Sep}}, \\ -45_+, 45_+, 0_{\text{Sep}}, 45_-, 0_-, 0_{\text{Sep}}, 0_+, 90_+, 0_{\text{Sep}}, 90_-, -45_-, 0_{\text{Sep}}, -45_+, 45_+, 0_{\text{Sep}}, 45_- \end{array} \right]_S. \text{ Which results in}$$

a mass saving for the structural battery face sheets of 12%, see figure 7 for schematic and further results.

Laptop computer chassis

A laptop computer requires a battery pack for portable energy and a chassis in order to protect its sensitive internal components. One idea is to build the flat parts of the chassis out of structural batteries. A laptop chassis can be made from 0.75 mm thick aluminum with the material properties $E_{\text{alu}} = 70$ GPa, $\nu_{\text{alu}} = 0.33$ and $\rho_{\text{alu}} = 2700 \frac{\text{kg}}{\text{m}^3}$. The laptop has the dimensions 0.225 and 0.325 m, which means that one sheet has 0.15 kg mass. A disassembled laptop is shown in figure 8. The laptop battery has a total capacity of 34 Wh and a mass of 0.188 kg.

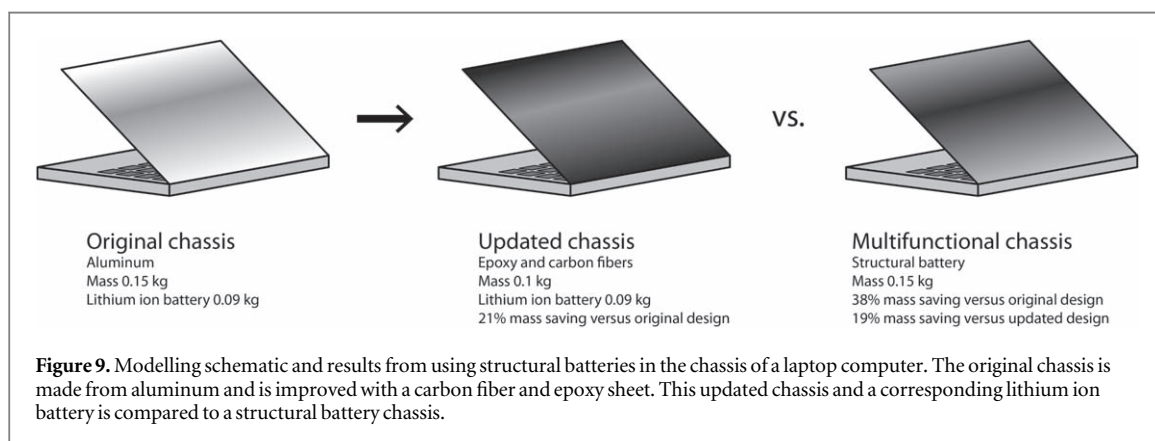
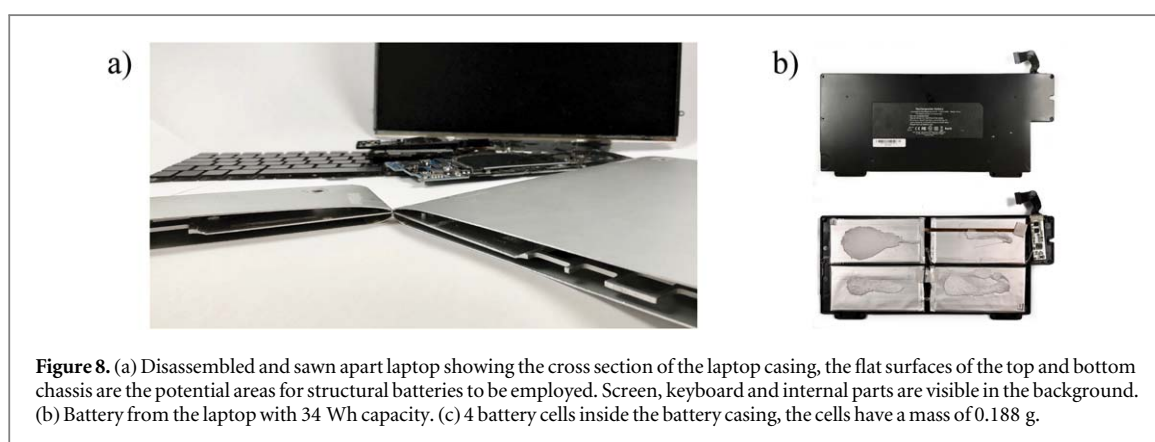
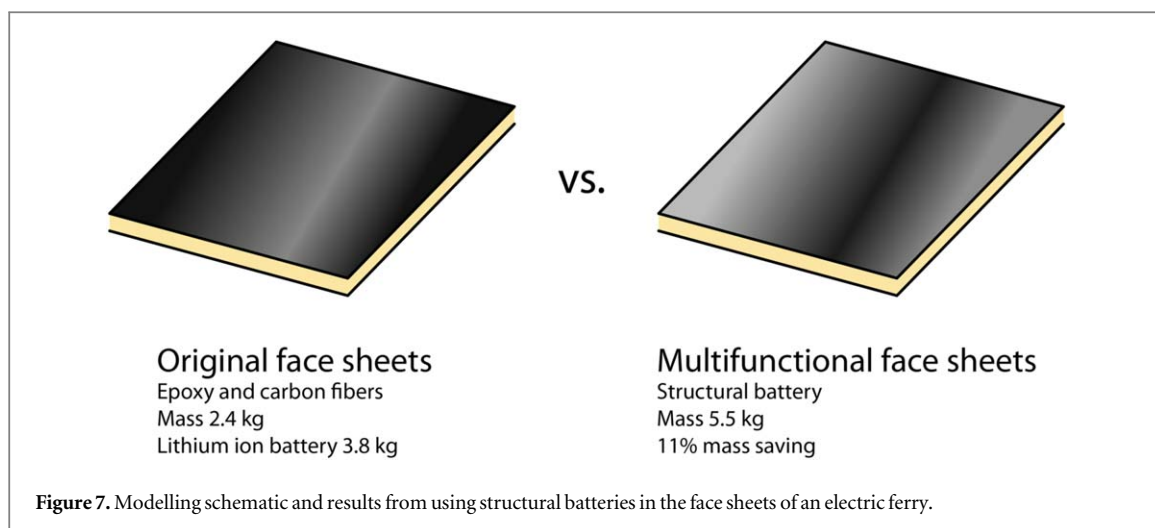
It is assumed that the laptop chassis is mostly designed for handling and impact resistance and thus the larger flat parts are mostly subjected to pressure loads. In this analysis they are investigated with a bending stiffness dominated design. Any fasteners or other stiffeners are not considered. First, the original aluminum plate is updated with a carbon fiber and epoxy plate, its material properties are the same as in the presented model, and the final plate has the same global stiffness as the original aluminum one. A structural battery is then compared to this, using the target design, it could use the layout:

$$[0_{\text{GFweave}}, 0_-, 0_{\text{Sep}}, 0_+, 90_+, 0_{\text{Sep}}, 90_-, -45_-, 0_{\text{Sep}}, 45_+]_S.$$

The potential mass saving is about 20%, this and more results can be seen in figure 9, as well as a schematic of the model. It is worth noting that a laptop has two possible positions for this structural battery sheet, a top cover for the screen and one on the bottom of the laptop. Replacing those two sheets would almost fulfill the original energy content of the laptop of 34 Wh and possibly eliminate the need to have any other internal battery.

Conclusions

The modelling presented herein investigates the design of structural batteries that can simultaneously carry mechanical load and store electrical energy. This research was conducted by analytically investigating a flat structural battery; calculating the mechanical properties and electrochemical energy storage potential. The



mechanical properties are then compared to a plate made of a conventional carbon fiber composite, while the energy storage is related to a standard LiB.

The analysis of such multifunctional materials is complex, especially since they often have opposing and competing properties, e.g. improved conductivity often decreases mechanical stiffness. In order to understand these impacts, a variable sensitivity analysis has provided vital insights for further research and design of structural batteries. It shows that the most crucial improvements to the structural battery would be to increase the volume fraction of carbon fibers in the positive and negative electrodes and decrease the separator thickness. The volume fraction of glass fibers in the separator has a smaller impact on the mass saving, where less glass fibers are more favorable. Furthermore, increasing the ionic conductivity and elastic modulus of the SBE also has

a large positive impact on the properties of the structural battery, however these improvements are more challenging.

The initial design of the structural battery may not provide enough mass saving in order to be a viable option to replace state-of-the-art high performance monofunctional systems. However, with insights from the variable sensitivity it is possible to make predictions for future improvements in the design of structural batteries. These improvements show that structural batteries can be an advantageous construction material with significant mass saving compared to monofunctional systems consisting of state-of-the-art carbon fiber composite laminates and LiBs. Additionally, case-studies are used to investigate the usage of structural batteries in an aircraft interior, an electric car, an electric ferry, and a laptop computer. All of these applications show potential to incorporate structural batteries with potential mass savings, also showing that the gain using structural batteries depends on the system it is compared with.

The modelling presented in this paper is an important tool to understand aspects of designing a structural battery and provides valuable insights for future research in the field. Additionally, it shows that structural batteries have the potential to save significant mass for electric mobility and electronics.

Acknowledgments

This work was supported the Swedish Research Council, projects 2017–03898 and 621–2014–4577, the strategic innovation program LIGHTer (funding provided by Vinnova, the Swedish Energy Agency and Formas), H2020 Clean Sky II project no. 738085 and by the Air Force Office of Scientific Research under award number FA9550–17–1–0244. The Swedish research group Kombatt is acknowledged for its synergism throughout this work.

Appendix A

The nomenclature is given in table A1 and constant input values in table A2.

Table A1. Nomenclature.

Property	Identity	Unit
Mass of the structural battery	m_{SB}	m
Mass of the conventional carbon fiber composite	m_{CC}	m
Mass of the standard LiB	m_{LiB}	m
Mass saving of structural battery	$MS_{\%}$	%
Multifunctional efficiency	η_{mf}	—
Volume fraction of fibers in the negative electrode	$v_{F,Neg}^f$	—
Volume fraction of fibers in the positive electrode	$v_{F,Pos}^f$	—
Volume fraction of glass fibers in the separator	$v_{F,Sep}^f$	—
Plate length	L	m
Plate width	w	m
Thickness of the separator	t_{Sep}	μm
Carbon fiber areal density	ρ_A	$g\ m^{-2}$
Charge time of the battery	T	h
Ion conductivity of the SBE	K_{SBE}	$S\ cm^{-1}$
SBE elastic modulus	E_{SBE}	MPa
Mass of carbon fibers in the negative electrode	$m_{CF,Neg}$	m
Volume of the carbon fibers in the negative electrode	$V_{CF,Neg}$	m^3
Volume of SBE in the negative electrode	$V_{SBE,Neg}$	m^3
Thickness of the negative electrode	t_{Neg}	m
Carbon fiber gravimetric electrochemical capacity	c_{CF}	$Ah\ kg^{-1}$
LiFePO ₄ gravimetric electrochemical capacity	c_{LiFePO_4}	$Ah\ kg^{-1}$
Electrochemical capacity of the negative electrode	C_{Neg}	Ah
Electrochemical capacity of the positive electrode	C_{Pos}	Ah
Mass of LiFePO ₄ in the positive electrode	m_{LiFePO_4}	m
Volume of carbon fibers in the positive electrode	$V_{CF,Pos}$	m^3

Table A1. (Continued.)

Property	Identity	Unit
Volume of coating in the positive electrode	V_{coating}	m^3
Volume of SBE in the positive electrode	$V_{\text{SBE,Pos}}$	m^3
Thickness of the positive electrode	t_{pos}	m
Ion conductivity of LP40	K_{LP40}	S cm^{-1}
Thickness of Whatman filter separator	t_{Whatman}	m
Reference thickness of the SBE-based separator	t_{SBE}	m
Electrochemical energy in the structural battery	ϵ_{SB}	Wh
Effective cell potential	U_{eff}	V
Nominal cell potential	U	V
IR-based voltage drop	U_{drop}	V
Electrochemical capacity	C	Ah
Ion conductivity	K	S cm^{-1}
Effective distance between electrodes	t_{eff}	m
Electrode area	A	m^2
Charging current	I	A
Structural efficiency	n_s	—
Energy efficiency	n_e	—
Structural battery midpoint deflection	z_{SB}	m
Conventional carbon fiber composite midpoint deflection	z_{CC}	m
Electrochemical energy in the standard LiB	ϵ_{LiB}	Wh

Table A2. Input values for calculating the properties of a full cell laminated composite battery.

Property	Identity	Value	Unit
SBE density	ρ_{SBE}	1123	kg/m^3
Charging and discharging time	T	10	h
Structural battery carbon fiber density [78]	ρ_{CF}	1810	kg/m^3
LiFePO ₄ density [79]	ρ_{LiFePO_4}	3600	kg/m^3
Polyvinylidene fluoride density [80]	ρ_{PVDF}	1780	kg/m^3
Carbon black density [81]	ρ_{CB}	2000	kg/m^3
Cell potential (LiFePO ₄ to carbon fibers)	U	2.8	V
Structural battery carbon fiber elastic modulus [78]	E_{CF}	294000	MPa
Structural battery carbon fiber Poisson's ratio	ν_{CF}	0.3	—
Carbon fiber/SBE lamina Poisson's ratio	ν_{SB}	0.36	—
T800HB-6000-40B carbon fiber tow linear density [78]	ρ_{Tow}	$2.23 \cdot 10^{-4}$	g/mm
Energy density of a standard LiB [73,74]	W_{LiB}	177.3	Wh/kg
Conventional UD carbon fiber composite longitudinal elastic modulus*	$E_{1,\text{CC}}$	147000	MPa
Conventional UD carbon fiber composite transverse elastic modulus*	$E_{2,\text{CC}}$	9000	MPa
Conventional UD carbon fiber composite shear modulus*	$G_{12,\text{CC}}$	3300	MPa
Conventional UD carbon fiber composite Poisson's ratio*	ν_{CC}	0.31	—
Conventional UD carbon fiber composite density*	ρ_{CC}	1600	kg/m^3
Glass fiber composite casing longitudinal elastic modulus [83]	$E_{1,\text{Case}}$	25000	MPa
Glass fiber composite casing transverse elastic modulus [83]	$E_{2,\text{Case}}$	25000	MPa
Glass fiber composite casing shear modulus [83]	$G_{12,\text{Case}}$	4000	MPa
Glass fiber composite casing Poisson's ratio [83]	ν_{Case}	0.2	—
Glass fiber composite casing thickness	t_{Case}	0.1	mm
Glass fiber composite casing density [83]	ρ_{Case}	1900	kg/m^3
Separator E-Glass fiber elastic modulus	E_{GF}	72000	MPa
Separator Poisson's ratio	ν_{Sep}	0.36	—
Steel elastic modulus	E_{steel}	200000	MPa
Steel Poisson's ratio	ν_{steel}	0.25	—
Steel density	ρ_{steel}	7800	kg/m^3
Aluminum elastic modulus	E_{alu}	70000	MPa
Aluminum Poisson's ratio	ν_{alu}	0.33	—
Aluminum density	ρ_{alu}	2700	kg/m^3
Current ion conductivity of the SBE [14]	K_{SBE}	$1.5 \cdot 10^{-4}$	S/cm
Current elastic modulus of the SBE [14]	E_{SBE}	600	MPa

* Typical properties for a UD carbon fiber and epoxy lamina [82].

ORCID iDs

Wilhelm Johannisson  <https://orcid.org/0000-0002-1194-9479>

Dan Zenkert  <https://orcid.org/0000-0002-9744-4550>

Göran Lindbergh  <https://orcid.org/0000-0001-9203-9313>

References

- [1] EPoS ERTRAC 2009 The electrification approach to urban mobility and transport, 2019
- [2] Schauer J J 2011 Human behavior research and the design of sustainable transport systems *Environ. Res. Lett.* **6** 034010
- [3] European Commission 2017 Energy, transport and environment indicators (doi:10.1088/2399-7532/ab3bdd)
- [4] Organisation for Economic Co-operation and Development 1996 Pollution prevention and control—environmental criteria for sustainable transport, 1996 OCDE/GD(96)136
- [5] European Commission 2019 Reducing CO₂ emissions from passenger cars *Eur. Commun.* (https://ec.europa.eu/clima/policies/transport/vehicles/cars_en) (Accessed: 28 February, 2019)
- [6] Schäfer A W, Barrett S R H, Doyme K, Dray L M, Gnadt A R, Self R, O'Sullivan A, Synodinos A P and Gnadt A R 2018 Technological, economic and environmental prospects of all-electric aircraft *Nat. Energy* **4** 160–6
- [7] Scholz A E, Hermanutz A and Hornung M 2018 Feasibility analysis and comparative assessment of structural power technology in all-electric composite aircraft *MSc Thesis*, Dtsch. Luft- Und Raumfahrtkongress (doi:10.25967/480065)
- [8] South J T, Carter R H, Snyder J F, Hilton C D, O'Brien D J and Wetzel E D 2005 Multifunctional power-generating and energy-storing structural composites for US army applications *Mater. Res. Soc.* NN4.6. 1–12
- [9] Snyder J F, Carter R H, Wong E L, Nguyen P A, Xu K, Ngo E H and Wetzel E D 2007 Multifunctional structural composite batteries *Repr. from Proc. Soc. Adv. Mater. Process Eng.* 2006 ARL-RP-192
- [10] Asp L E and Greenhalgh E S 2014 Structural power composites *Compos. Sci. Technol.* **101** 41–61
- [11] Ihrner N, Johannisson W, Sieland F, Zenkert D and Johansson M 2017 Structural lithium ion battery electrolytes: via reaction induced phase-separation *J. Mater. Chem. A* **5** 25652–9
- [12] Yu Y, Zhang B, Feng M, Qi G, Tian F, Feng Q, Yang J and Wang S 2017 Multifunctional structural lithium ion batteries based on carbon fiber reinforced plastic composites *Compos. Sci. Technol.* **147** 62–70
- [13] Hagberg J, Maples H A, Alvim K S P, Xu J, Johannisson W, Bismarck A, Zenkert D and Lindbergh G 2018 Lithium iron phosphate coated carbon fiber electrodes for structural lithium ion batteries *Compos. Sci. Technol.* **162** 235–43
- [14] Johannisson W, Ihrner N, Zenkert D, Johansson M, Carlstedt D, Asp L E and Sieland F 2018 Multifunctional performance of a carbon fiber UD lamina electrode for structural batteries *Compos. Sci. Technol.* **168** 81–7
- [15] Javaid A and Ali M Z 2018 Multifunctional structural lithium ion batteries for electrical energy storage applications *Mater. Res. Express* **5** 055701
- [16] Snyder J F, Carter R H and Wetzel E D 2007 Electrochemical and mechanical behavior in mechanically robust solid polymer electrolytes for use in multifunctional structural batteries *Chem. Mater.* **19** 3793–801
- [17] Snyder J F, Carter R H, Xu K, Wong E I, Nguyen P A, Hgo E H and Wetzel E D 2006 Multifunctional structural composite capacitors for US army applications *Proc. 25th Army Sci. Conf.*
- [18] Wong E, Baechle D, Xu K, Carter R H, Snyder J F and Wetzel E D 2007 Design and processing of structural composite batteries *Proc. Soc. Adv. Mater. Process Eng.*
- [19] Snyder J F, Wetzel E D and Watson C M 2009 Improving multifunctional behavior in structural electrolytes through copolymerization of structure- and conductivity-promoting monomers *Polymer* **50** 4906–16
- [20] Hellqvist Kjell M, Jacques E, Zenkert D, Behm M and Lindbergh G 2011 PAN-Based carbon fiber Negative electrodes for structural lithium-ion batteries *J. Electrochem. Soc.* **158** A1455
- [21] Willgert M, Hellqvist Kjell M, Jacques E, Behm M, Lindbergh G and Johansson M 2011 Photoinduced free radical polymerization of thermoset lithium battery electrolytes *Eur. Polym. J.* **47** 2372–8
- [22] Jacques E, Hellqvist Kjell M, Zenkert D, Lindbergh G, Behm M and Willgert M 2012 Impact of electrochemical cycling on the tensile properties of carbon fibres for structural lithium-ion composite batteries *Compos. Sci. Technol.* **72** 792–8
- [23] Jacques E, Hellqvist Kjell M, Zenkert D and Lindbergh G 2014 The effect of lithium-intercalation on the mechanical properties of carbon fibres *Carbon* **68** 725–33
- [24] Feng Q, Yang J, Yu Y, Tian F, Zhang B, Feng M and Wang S 2017 The ionic conductivity, mechanical performance and morphology of two-phase structural electrolytes based on polyethylene glycol, epoxy resin and nano-silica *Mater. Sci. Eng. B* **219** 37–44
- [25] Van Schalkwijk W A and Scrosati B 2002 *Advances in Lithium-Ion Batteries* (Boston, MA: Springer)
- [26] Snyder J F, Gienger E and Wetzel E D 2015 Performance metrics for structural composites with electrochemical multifunctionality *J. Compos. Mater.* **49** 1835–48
- [27] O'Brien D J, Baechle D M and Wetzel E D 2011 Design and performance of multifunctional structural composite capacitors *J. Compos. Mater.* **45** 2797–809
- [28] Ning G and Popov B N 2004 Cycle life modeling of lithium-ion batteries *J. Electrochem. Soc.* **151** A1584
- [29] Newman J, Thomas K E, Hafezi H and Wheeler D R 2003 Modeling of lithium-ion batteries *J. Power Sources* **119–121** 838–43
- [30] Czerepicki A and Koniak M 2017 A method of computer modelling the lithium-ion batteries aging process based on the experimental characteristics *IOP Conf. Ser.: Mater. Sci. Eng.* **211** 012006
- [31] Torchio M, Magni L, Gopaluni R B, Raimondo D M and Braatz R D 2016 LIONSIMBA: a MATLAB framework based on a finite volume model suitable for li-ion battery design, simulation, and control *J. Electrochem. Soc.* **163** A1192–205
- [32] Galushkin N, Yazvinskaya N and Galushkin D 2014 Nonlinear structural model of the battery *Int. J. Electrochem. Sci.* **9** 6305–27
- [33] Ramadesigan V, Northrop P W C, De S, Santhanagopalan S, Braatz R D and Subramanian V R 2012 Modeling and simulation of lithium-ion batteries from a systems engineering perspective *J. Electrochem. Soc.* **159** R31–R45
- [34] García R E, Limthongkul P, Chiang Y-M, Bishop C M, García R E and Carter W C 2004 Microstructural modeling and design of rechargeable lithium-ion batteries *J. Electrochem. Soc.* **152** A255–63
- [35] Millner A 2010 Modeling lithium ion battery degradation in electric vehicles *2010 IEEE Conf. Innov. Technol. an Effic. Reliab. Electr. Supply* pp 349–56 CITRES 2010

- [36] Al Hallaj S, Maleki H, Hong J S and Selman J R 1999 Thermal modeling and design considerations of lithium-ion batteries *J. Power Sources* **83** 1–8
- [37] Forgez C, Do D V, Friedrich G, Morcrette M and Delacourt C 2010 Thermal modeling of a cylindrical LiFePO₄/graphite lithium-ion battery *J. Power Sources* **195** 2961–8
- [38] Damay N, Forgez C, Bichat M P and Friedrich G 2015 Thermal modeling of large prismatic LiFePO₄/graphite battery. Coupled thermal and heat generation models for characterization and simulation *J. Power Sources* **283** 37–45
- [39] Baba N, Yoshida H, Nagaoka M, Okuda C and Kawauchi S 2014 Numerical simulation of thermal behavior of lithium-ion secondary batteries using the enhanced single particle model *J. Power Sources* **252** 214–28
- [40] Chacko S and Chung Y M 2012 Thermal modelling of Li-ion polymer battery for electric vehicle drive cycles *J. Power Sources* **213** 296–303
- [41] Panchal S, Dincer I, Agelin-Chaab M, Fraser R and Fowler M 2015 Thermal modeling and validation of temperature distributions in a prismatic lithium-ion battery at different discharge rates and varying boundary conditions *Appl. Therm. Eng.* **96** 190–9
- [42] Wu B, Yufit V, Marinescu M, Offer G J, Martinez-Botas R F and Brandon N P 2013 Coupled thermal-electrochemical modelling of uneven heat generation in lithium-ion battery packs *J. Power Sources* **243** 544–54
- [43] Zhu J, Wierzbicki T and Li W 2018 A review of safety-focused mechanical modeling of commercial lithium-ion batteries *J. Power Sources* **378** 153–68
- [44] Kermani G and Sahraei E 2017 Review: characterization and modeling of the mechanical properties of lithium-ion batteries *Energies* **10** 1730
- [45] Xu J, Liu B, Wang L and Shang S 2015 Dynamic mechanical integrity of cylindrical lithium-ion battery cell upon crushing *Eng. Fail. Anal.* **53** 97–110
- [46] Sahraei E, Bosco E, Dixon B and Lai B 2016 Microscale failure mechanisms leading to internal short circuit in Li-ion batteries under complex loading scenarios *J. Power Sources* **319** 56–65
- [47] Kim S, Wee J, Peters K and Huang H Y S 2018 Multiphysics coupling in lithium-ion batteries with reconstructed porous microstructures *J. Phys. Chem. C* **122** 5280–90
- [48] Zhang C, Xu J, Cao L, Wu Z and Santhanagopalan S 2017 Constitutive behavior and progressive mechanical failure of electrodes in lithium-ion batteries *J. Power Sources* **357** 126–37
- [49] Giorgetti M, Mignani A, Aquilanti G, Conti P, Fehse M and Stievano L 2016 Structural and electronic studies of metal hexacyanoferrates based cathodes for Li rechargeable batteries *J. Phys.: Conf. Ser.* **712**
- [50] Zhang X, Sahraei E and Wang K 2016 Deformation and failure characteristics of four types of lithium-ion battery separators *J. Power Sources* **327** 693–701
- [51] Yan S, Huang X and Xiao X 2018 Measurement of the through thickness compression of a battery separator *J. Power Sources* **382** 13–21
- [52] Sahraei E, Hill R and Wierzbicki T 2012 Calibration and finite element simulation of pouch lithium-ion batteries for mechanical integrity *J. Power Sources* **201** 307–21
- [53] Sahraei E, Meier J and Wierzbicki T 2014 Characterizing and modeling mechanical properties and onset of short circuit for three types of lithium-ion pouch cells *J. Power Sources* **247** 503–16
- [54] Kisters T, Sahraei E and Wierzbicki T 2017 Dynamic impact tests on lithium-ion cells *Int. J. Impact Eng.* **108** 205–16
- [55] Shi X, Shi F, Chen G, Xia Y and Zhou Q 2017 Failure behaviours of 100% SOC lithium-ion battery modules under different impact loading conditions *Eng. Fail. Anal.* **82** 149–60
- [56] Hao W, Xie J and Wang F 2018 The indentation analysis triggering internal short circuit of lithium-ion pouch battery based on shape function theory *Int. J. Energy Res.* **42** 3696–703
- [57] Zhu J, Zhang X, Sahraei E and Wierzbicki T 2016 Deformation and failure mechanisms of 18650 battery cells under axial compression *J. Power Sources* **336** 332–40
- [58] Sahraei E, Campbell J and Wierzbicki T 2012 Modeling and short circuit detection of 18650 Li-ion cells under mechanical abuse conditions *J. Power Sources* **220** 360–72
- [59] Liu B, Zhao H, Yu H, Li J and Xu J 2017 Multiphysics computational framework for cylindrical lithium-ion batteries under mechanical abusive loading *Electrochim. Acta* **256** 172–84
- [60] Sheikh M, Elmarakbi A and Elkady M 2017 Thermal runaway detection of cylindrical 18650 lithium-ion battery under quasi-static loading conditions *J. Power Sources* **370** 61–70
- [61] Wang L, Yin S, Yu Z, Wang Y, Yu T X, Zhao J, Xie Z, Li Y and Xu J 2018 Unlocking the significant role of shell material for lithium-ion battery safety *Mater. Des.* **160** 601–10
- [62] Nguyen T N, Siegmund T, Tsutsui W, Liao H and Chen W 2016 Bi-objective optimal design of a damage-tolerant multifunctional battery system *Mater. Des.* **105** 51–65
- [63] Zhang C, Santhanagopalan S, Sprague M A and Pesaran A A 2015 Coupled mechanical-electrical-thermal modeling for short-circuit prediction in a lithium-ion cell under mechanical abuse *J. Power Sources* **290** 102–13
- [64] Jacques E, Hellqvist Kjell M, Zenkert D, Lindbergh G and Behm M 2013 Expansion of carbon fibres induced by lithium intercalation for structural electrode applications *Carbon* **59** 246–54
- [65] Xu J, Lindbergh G and Varna J 2018 Carbon fiber composites with battery function: Stresses and dimensional changes due to Li-ion diffusion *J. Compos. Mater.* **52** 2729–42
- [66] Xu J, Lindbergh G and Varna J 2018 Multiphysics modeling of mechanical and electrochemical phenomena in structural composites for energy storage: single carbon fiber micro-battery *J. Reinf. Plast. Compos.* **37** 701–15
- [67] Dionisi F, Harnden R and Zenkert D 2017 A model to analyse deformations and stresses in structural batteries due to electrode expansions *Compos. Struct.* **179** 580–9
- [68] Carlstedt D, Marklund E and Asp L E 2019 Effects of state of charge on elastic properties of 3D structural battery composites *Compos. Sci. Technol.* **169** 26–33
- [69] Carlstedt D and Asp L E 2019 Thermal and diffusion induced stresses in a structural battery under galvanostatic cycling *Compos. Sci. Technol.* **179** 69–78
- [70] Carlstedt D, Johansson W, Zenkert D, Linde P and Asp L E 2018 Conceptual design framework for laminated structural battery composites *Proc. 18th Eur. Conf. Compos. Mater.* pp 24–8
- [71] Kjell M H, Jacques E, Zenkert D, Behm M and Lindbergh G 2011 PAN-Based carbon fiber negative electrodes for structural lithium-ion batteries *J. Electrochem. Soc.* **158** A1455
- [72] Xiang H F, Jin Q Y, Chen C H, Ge X W, Guo S and Sun J H 2007 Dimethyl methylphosphonate-based nonflammable electrolyte and high safety lithium-ion batteries *J. Power Sources* **174** 335–41

- [73] Lu Z, Yu X, Zhang L, Meng X, Wei L and Jin L 2017 Experimental investigation on the charge-discharge performance of the commercial lithium-ion batteries *Energy Proc.* **143** 21–6
- [74] An F, Chen L, Huang J, Zhang J and Li P 2016 Rate dependence of cell-to-cell variations of lithium-ion cells *Sci. Rep.* **6** 4–10
- [75] Agarwal B D and Broutman L J 1990 *Analysis and Performance of Fiber Composites* 2nd ed (New York: Wiley-Interscience)
- [76] Whitney J M 1987 *Structural Analysis of Laminated Anisotropic Plates* (Lancaster, PA: Technomic Publishing Company, Inc.)
- [77] Reddy T 2010 *Linden's Handbook of Batteries* 4th ed (New York, NY: McGraw-Hill Education)
- [78] Technical data sheet No. CFA-007, T800H Data sheet, Toray carbon fibers America, Inc. 2019
- [79] Wu B, Ren Y and Li N 2011 LiFePO₄ cathode material *Electr. Veh. Benefits Barriers* (Rijeka: InTech) (doi:10.5772/18995)
- [80] The Quadrant group of companies, Symalit 1000 PVDF Technical Data Sheet, 2011
- [81] Institute for Occupational Safety and Health of the German Social Accident Insurance, GESTIS Substance Database, Carbon Black 2019 ([http://gestis-en.itrust.de/nxt/gateway.dll/gestis_en/091940.xml?f=templates\\$fn=default.htm\\$3.0](http://gestis-en.itrust.de/nxt/gateway.dll/gestis_en/091940.xml?f=templates$fn=default.htm$3.0))
- [82] Daniel I M and Ishai O 1994 *Engineering Mechanics of Composite Materials* (New York, NY: Oxford University Press, Inc.)
- [83] Performance Composites Ltd, Mechanical Properties of Carbon Fibre Composite Materials, Fibre/Epoxy resin (120 °C Cure) (2017) (http://performance-composites.com/carbonfibre/mechanicalproperties_2.asp)

Article

Prospective Life Cycle Assessment of a Structural Battery

Mats Zackrisson ^{1,*} , Christina Jönsson ¹ , Wilhelm Johannisson ², Kristin Fransson ³, Stefan Posner ⁴, Dan Zenkert ²  and Göran Lindbergh ⁵ 

¹ RISE IVF AB, SE-100 44 Stockholm, Sweden; christina.jonsson@ri.se

² Department of Aeronautical and Vehicle Engineering, KTH Royal Institute of Technology, SE-100 44 Stockholm, Sweden; wjoh@kth.se (W.J.); danz@kth.se (D.Z.)

³ Engelsons Postorder AB, SE-311 39 Falkenberg, Sweden; kristin.fransson@engelsons.se

⁴ Stefan Posner AB, SE-439 55 Åsa, Sweden; stefan.posnerab@gmail.com

⁵ Department of Chemical Engineering, KTH Royal Institute of Technology, SE-100 44 Stockholm, Sweden; gnli@kth.se

* Correspondence: mats.zackrisson@ri.se; Tel.: +46-(0)7-0780-6226

Received: 6 September 2019; Accepted: 8 October 2019; Published: 14 October 2019



Abstract: With increasing interest in reducing fossil fuel emissions, more and more development is focused on electric mobility. For electric vehicles, the main challenge is the mass of the batteries, which significantly increase the mass of the vehicles and limits their range. One possible concept to solve this is incorporating structural batteries; a structural material that both stores electrical energy and carries mechanical load. The concept envisions constructing the body of an electric vehicle with this material and thus reducing the need for further energy storage. This research is investigating a future structural battery that is incorporated in the roof of an electric vehicle. The structural battery is replacing the original steel roof of the vehicle, and part of the original traction battery. The environmental implications of this structural battery roof are investigated with a life cycle assessment, which shows that a structural battery roof can avoid climate impacts in substantive quantities. The main emissions for the structural battery stem from its production and efforts should be focused there to further improve the environmental benefits of the structural battery. Toxicity is investigated with a novel chemical risk assessment from a life cycle perspective, which shows that two chemicals should be targeted for substitution.

Keywords: LCA; chemical risk assessment; multifunctional material; environmental engineering; lightweight; prospective

1. Introduction

Electrification is seen as the main answer to the challenges of climate impact in the transport sector. Provided that the electricity can be generated from reasonably carbon lean energy sources, considerable reductions of carbon dioxide equivalents (CO₂-eq) emissions from the transport sector are possible [1–3]. However, cost and range are still difficult challenges for electric vehicles. One way to increase the vehicle range is by decreasing its mass by incorporating many functions in the same material. A multifunctional material that can carry both mechanical load and store electrical energy is generally referred to as a structural battery. A lot of research has gone into the design and construction of such structural batteries [4–7], but the actual concept has not yet been demonstrated or validated in an industrial setting.

Life cycle assessment (LCA) and chemical risk assessment (CRA) are well known tools to evaluate cradle-to-grave environmental impacts. Such evaluations are especially fruitful early in

the product development in order to help steer the design of both materials and processes [8–11]. It is understandable that such evaluations then are prospective in nature, since any final material compositions or processes may be different from those investigated. This is technically the purpose of the evaluations in the first place, to predict environmental hotspots in order to modify the design with less environmentally damaging alternatives.

This paper investigates a structural battery with LCA and CRA in order to explore the environmental impact and find such hotspots. The study is based on data from previous research which modelled structural batteries and calculated the potential mass saving of utilizing a structural battery in an electric vehicle [12]. It will be shown that a structural battery roof can avoid climate impacts in substantive quantities and even more so if the amount of energy used in its production can be reduced. The CRA targets two chemicals for substitution.

2. Materials and Methods

2.1. Structural Battery Design

The considered design of a structural battery has similarities to both lithium ion batteries and carbon fibre composites, and are made from alternating layers of negative electrodes, separators, and positive electrodes. Dispersed throughout all layers is a structural battery electrolyte (SBE) to both conduct lithium ions and distribute mechanical load between the carbon fibre electrodes, see Figure 1. The SBE is partly liquid to allow ion conduction, and partly solid to transfer mechanical load [4,6].

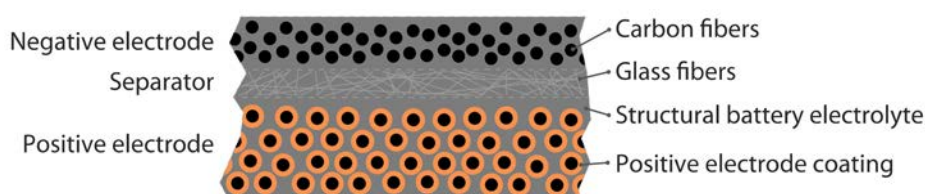


Figure 1. Build-up of a structural battery cell.

The negative electrodes are made from layers of carbon fibres, since carbon fibres are excellent reinforcement materials and it has been proven that they function well as negative electrodes in lithium ion battery cells [7,13,14]. Next, the separators are layers of randomly oriented glass fibres which are used to electrically insulate the two electrodes. The positive electrodes are considered to be based on carbon fibres, which in this case act as reinforcement and current collectors. The carbon fibres in the positive electrode are coated with lithium iron phosphate (LiFePO_4) [15], providing electrochemical storage, as well as a binder and carbon black for electrical contact.

Johannisson et al. created an analytical model of a structural battery in order to predict possible mechanical and electrical properties of the material [12]. This study also presented a design case where a roof was made from structural batteries to save mass compared to a separate steel roof and lithium ion traction battery in an electric vehicle. The results were divided into the current state of structural battery research (referred to as initial design), and what can be theoretically reachable with continuous improvements to its manufacturing and design (referred to as target design). The bill of materials (BOM) of these structural batteries are given in Table S1. The structural battery roofs weigh 7.8 kg and 9.2 kg for the initial and target designs and have energy densities of 41 Wh/kg and 121 Wh/kg, respectively. Given a steel roof weighing 18.6 kg, the initial design can save 10.8 kg of mass in the vehicle and the target design can save 9.4 kg. But they can also save between 2.2 and 12.9 kg of traction battery mass, making the total mass savings even greater (see Table S3).

2.2. Life Cycle Assessment

The function of a structural battery car roof is twofold; it needs to function as a car roof and as an electrical energy storage unit for the lifetime of the vehicle. Thus, the reference flow in the

study was one structural battery car roof, i.e., most results were measured against this reference flow, see Figure 2. Note, however, that this reference flow comes in two versions, depicting the current development status version and the targeted realistic future development. Results are mainly given as vehicle life cycle environmental impacts. End of life recycling was included, and it was assumed that recycled materials could replace virgin material input. If a quality deterioration of the recycled material compared to the virgin material was evident, this was considered in the model.

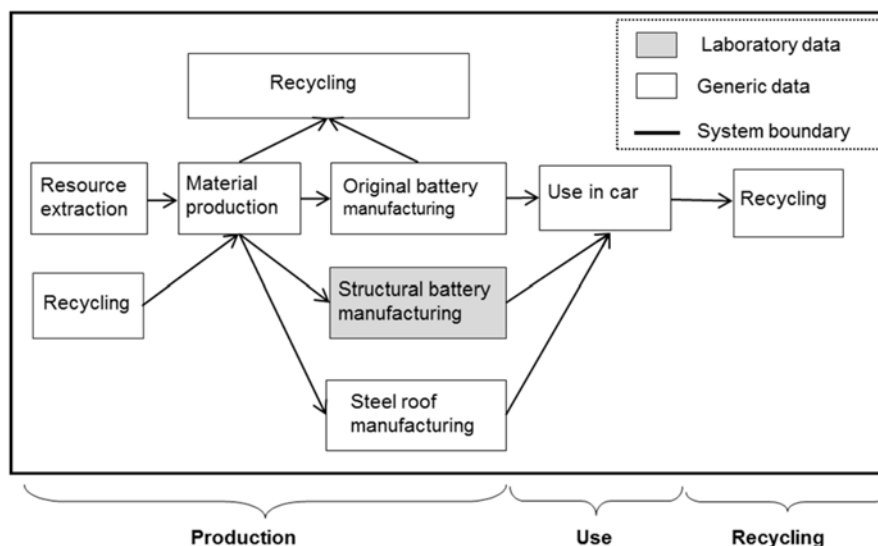


Figure 2. Life cycle assessment (LCA) system boundary when replacing a steel roof and traction battery with a structural battery in an electric vehicle.

To cover a whole life cycle, the production of the batteries (the structural as well as the original), the use of the batteries in the car and the recycling stages must be included. The production phase models were based on respective BOMs. The use of the structural battery in the car was modelled by considering the electricity needed to carry the mass of the structural battery in relation to the mass of the replaced original battery and steel roof.

The system boundary for the study was such that the vehicle itself was not present in the system, only the original roof, the structural battery roof, and the original battery (see Figure 2). In essence, the study will calculate the change in environmental impact when replacing a steel roof and an equivalent part of the original traction battery with a structural battery roof in a vehicle. Material production and manufacturing of the original battery cells, the structural battery roof, and the steel roof were included, as well as the benefits of the mass reduction during the use phase and the implications for recycling. The life cycle impacts for the alternative systems (structural battery roof system and steel roof system) will thus be compared.

The environmental impact categories climate impact (kilogram CO₂-eq), photochemical ozone formation (kilogram nitrogen oxide equivalents, NO_x-eq), and resource depletion (gram antimony equivalents, Sb-eq) were used as they are able to assess trade-offs between environmental impacts in different life cycle stages of vehicles. Toxicity has not been evaluated quantitatively with LCA. Instead a qualitative assessment has been made, see the section on CRA methodology. The reason for not including toxicity in the LCA was that earlier studies have shown that current methods for toxicity evaluation have considerable inadequacies related to metals and lithium in particular. There is a lack of data concerning lithium emissions and other battery related chemicals during the life cycle, and a lack of characterisation factors to translate such emissions into toxic impacts [16].

2.2.1. Electricity

In the base case, average Western European electricity was used for the use phase as well as the production phase. For sensitivity analysis Swedish average electricity was used for both use and/or production phases. Note that the Western European mix is considered as the present world average concerning climate footprint (414–428 g CO₂-eq/kWh). The lower value was associated with high voltage used for production, while the higher value was applied for the battery use phase. The Swedish mix (at 42–48 g CO₂-eq/kWh) can be used as an indication to evaluate the effect of future European energy targets [17]. The data sets used in the calculations are given in Table S2.

2.2.2. Production of Original Traction Battery and Steel Roof

Modelling of the batteries to be replaced by the structural battery was based on a model of a 24 kWh Lithium Nickel Manganese Cobalt oxide (NMC) batteries for a Nissan LEAF and on a model of an 85 kWh Lithium Nickel Cobalt Aluminium oxide (NCA) battery used in a Tesla model S. The characteristics of these batteries and the respective BOMs are shown in Tables S3, S4 and S5. The reason for examining two battery types with different sizes was to study the sensitivity of the result of these parameters and thereby increase the possibility to draw robust conclusions. Steel roof production was based on Ecoinvent data for unalloyed steel and hot-rolling along with data from an automobile parts manufacturer using 1.3 kWh electricity per kg for forming.

2.2.3. Production of the Structural Battery

The structural battery was modelled as battery cells with an external glass fibre casing. It will eventually need some battery management system (BMS) and some additional casing/packaging. Any extra devices for cooling a structural battery will not be required. Since there was no BMS for the structural battery, no BMS of the NMC and NCA batteries was considered replaced. The BMS was therefore removed from the NMC and NCA battery models. The weights of the resulting batteries without BMS are given in Table S3. Also, the structural battery has a casing included and natural cooling, it was therefore assumed that it could replace the modified batteries in proportion to its capacity. For an example of the resulting mass savings, see Table S3.

The negative electrode consisted of carbon fibres impregnated with SBE. The separator consisted of glass fibre impregnated with SBE. The upstream production of carbon and glass fibre was modelled with data from Das [18] and from Ecoinvent 3.5 [19] respectively. No losses were assumed.

The positive electrode was made of carbon fibres coated with LiFePO₄, Polyvinylidenefluoride (PVDF) binder, and carbon black. The coating process was an electrophoretic deposition (EPD) as presented by Hagberg et al. [15] and used a bath of acetone, iodine, and a surfactant, Triton X-100. The EPD process, including ultrasonication, needed 1 kJ electricity per gram of coated fibre. The bath of acetone, iodine, and a surfactant was assumed to be reused in the same way as other solvents are reused in cell production. According to Dunn et al. [20], about 99.5% of the solvent is recovered and can be reused; the rest is lost during production and combusted and must be replaced. LiFePO₄ was made from synthesising LiCO₃, Fe₂O₃, and (NH₄)₂HPO₄. Quantities were decided by molar calculation and the ingredients found in the Ecoinvent 3.5 database. In addition, the process needed 3 kJ electric energy per gram of LiFePO₄ for two temperature increases [21].

Production of the chemicals in the SBE was modelled in the LCA with data from Ecoinvent 3.5 [19]. The toxicity of each of the chemicals has also been investigated in a chemical risk assessment. LCA datasets for the main SBE constituents, bisphenol A dimethacrylate, and ethylene carbonate, making up 78% of the SBE, were found in the Ecoinvent database. The remaining SBE ingredients were modelled as average organic or inorganic chemicals, see Table S6.

In general, energy requirements for lithium cell manufacturing and battery assembly can vary largely, mainly depending on (1) which share of the manufacturing/assembly steps require dry room/clean room conditions and (2) plant throughput. Estimations and measurements vary between

1 MJ/kg battery to 400 MJ/kg battery of primary energy [22]. Kim et al. [1] reported 120 MJ/kg of primary energy for the production of the Ford Focus BEV battery. As the analysis required energy carriers, this study assumes 11.7 kWh electricity and 8.8 kWh gas per kg structural battery (corresponding to 150 MJ primary energy according to Kim et al. [1]), earlier reported by Zackrisson et al. [21] and also used for modelling the NMC and NCA batteries in this study. Real life energy requirements for manufacturing structural batteries will eventually depend on how much of the production will have to be done under clean room conditions.

2.2.4. Use Phase

The use phase of an EV battery model normally includes electricity losses and losses related to carrying the mass of the battery. This way of modelling the use phase of a car battery has been used in other LCAs [23]. The electricity losses were not quantified since they are the same in both cases.

The influence of the battery mass was modelled using an energy reduction value (ERV) of 0.69 kWh/(100 kg × 100 km) for the worldwide harmonised light-duty vehicles test procedure (WLTC) [24] as base case. The WLTC, in general, gives higher energy use and therefore also higher energy reductions for savings in mass compared to the new European driving cycle (NEDC), though both test procedures have been criticised as showing lower energy requirements and thus reductions than real life conditions. The NEDC's ERV value was 0.65 kWh/(100 kg × 100 km). The 18.6 kg steel roof was the reference from which the energy savings were calculated. In addition, the transport of the battery from the car manufacturer to the user was included in the use phase. For all considerations regarding transports, see Section 2.2.4 in the Supplementary material.

2.2.5. Recycling

A 300 km recycling transport was assumed for all parts: structural battery, steel roof, and the original traction battery. This represents a transport between the car scrap yard and fragmentation/recycling plants [25].

For the steel roof, 95% of the raw material was assumed to be recycled in accordance with the end-of-life vehicle directive [26] and replacing input steel quality, resulting in a net life cycle climate impact of 1.9 kg CO₂-eq per kg of steel roof.

For the structural battery, only the fibres will sustain the assumed pyrolysis recycling process. Furthermore, the recycled reinforcement fibres are believed to have significantly poorer properties than virgin fibres. The recycled carbon fibre was assumed to avoid 50% of the burdens of virgin carbon fibre [27] because it sells at 50% of virgin carbon fibre's price [28]. The same assumption was made for glass fibres. The 95% recycling rate from the end-of-life vehicle directive was assumed to apply also to the structural battery.

The recycling of the original batteries was modelled using default data from the Product Environmental Footprint Category Rules for High Specific Energy Rechargeable Batteries [29] for the cell constituents, combined with data from Ellingsen et al. [30] for the rest of the battery pack. Aluminium and steel give considerable climate avoidance contributions (from the rest-of-pack), however, while it entails 15 kg CO₂-eq to manufacture 1 kg NMC battery, the recycling avoids 1.2 kg CO₂-eq per kg NMC battery. The corresponding figures for the steel roof were 3 kg CO₂-eq/kg for the manufacturing of which 1.1 kg CO₂-eq/kg was avoided by its recycling, and for the structural battery roof at target level 19 kg CO₂-eq/kg for the manufacturing of which 4 kg CO₂-eq/kg was avoided by its recycling. See Figure S1 in the Supplementary material.

2.3. Chemical Risk Assessment from a Life Cycle Perspective

The CRA has been inspired by different assessment methods and tools in the open literature [31–34] and herein adapted to a life cycle perspective. Chemicals and process materials have been evaluated for hazards in the different life cycle phases. Hazards have also been associated with risk for exposure so the chemical risk for the user/worker can be assessed. Physical-chemical properties have thus been

used as well as hazard statements according to the Classification, Labelling, and Packaging (CLP) directive [35].

A four step CRA procedure was followed to qualitatively assess chemical hazards and legal risks:

1. Collection of safety data sheets (SDS), retrieved from the chemical suppliers.
2. Identification of hazard statements of the chemical mixture as well as the individual components from the SDS, according to CLP. In addition, the chemical abstract service (CAS) registry number for classified individual components are listed.
3. In order to identify any legal requirements, restrictions, or unharmonized classifications, the CAS numbers are investigated through the European Chemical Agency (ECHA) database [36].
4. Evaluation of risk in each life cycle phase according to criteria in Table S7.

Initially, work exposure limits and safety measures were included in the risk assessment matrix. The carcinogenic, mutagenic, and reproduction toxic (CMR), persistent, bio-accumulative, and toxic (PBT), and very persistent and very bio-accumulative (vPvB) properties are related to properties of high concern in existing European chemical legislation, i.e., registration, evaluation, and authorisation of chemicals (REACH) [37], and persistent organic pollutants (POP) regulation [38]. In the evaluation, other properties of lower concern have also been included, such as skin sensitising, respiratory and oral toxicity (see Table S8 for an example of data collected for the CRA).

The assessment was made in the different life cycle phases as well as an overall assessment. Assessment results were condensed and presented as low, medium, and high risk, visualised with green, yellow, and red. Properties that have been evaluated are the chemicals' intrinsic properties according to the hazard statement. See Table S7 for the evaluation criteria of risk and compliance that have been used for the assessment.

From a life cycle perspective, the risk relates to intrinsic properties (hazards) and exposure in three different life cycle phases of the battery (production, use, and end of life). The assessment of risks relates to the physical-chemical state and potential transformation. Thus, chemical transformations as a result of chemical reactions during production have been considered. In one life cycle phase, the chemicals may have one exposure potential and hazard, but in another phase the particular chemical is virtually non-existent due to the chemical transformation. For instance, the monomer Bisphenol A dimethacrylate which is present in the manufacturing phase but is then polymerised and not present in the following phases.

3. Results and Discussion

3.1. Life Cycle Assessment

Results are presented as the net difference in life cycle environmental impacts when replacing a steel roof and an equivalent part of the original battery with a structural battery roof. To obtain the net difference, the environmental impact of the reference steel roof life cycle is subtracted from the structural battery roof life cycle. If the resulting measure is negative, it means an avoided impact due to the structural battery roof. See Figure S1 for a graphical description of the net life cycle impacts.

The reason for examining two battery types with different sizes, two very different electricity mixes, and two different levels of technology development is to study the sensitivity of the result to these parameters and thereby increase the possibility of drawing robust conclusions. This follows the recommendations of Arvidsson et al. [8] for prospective LCAs to model emerging technologies using predictive scenarios.

It should be noted that assembly energy is very environmentally dominant for production of normal lithium ion batteries [1] and that the energy to produce carbon fibre is very environmentally dominant in production of normal carbon fibre reinforced plastic [18].

The net life cycle climate impacts are shown in Figure 3 for all the different cases of structural battery design, electricity mixes, and vehicle size. For all the cases with European electricity, the structural

battery roof avoided climate impact. As expected, the climate avoidance was larger at the target level of structural battery development. The climate avoidance was also larger in the small EV compared to the large EV. This is mainly due to that the NMC battery in the small vehicle has a lower energy density (81 Wh/kg) than the NCA battery in the large vehicle (138 Wh/kg). Only at the initial level of structural battery development in combination with Swedish electricity for propulsion did the structural battery lead to increased climate impact. This is mainly because the use phase savings are much smaller in Sweden.

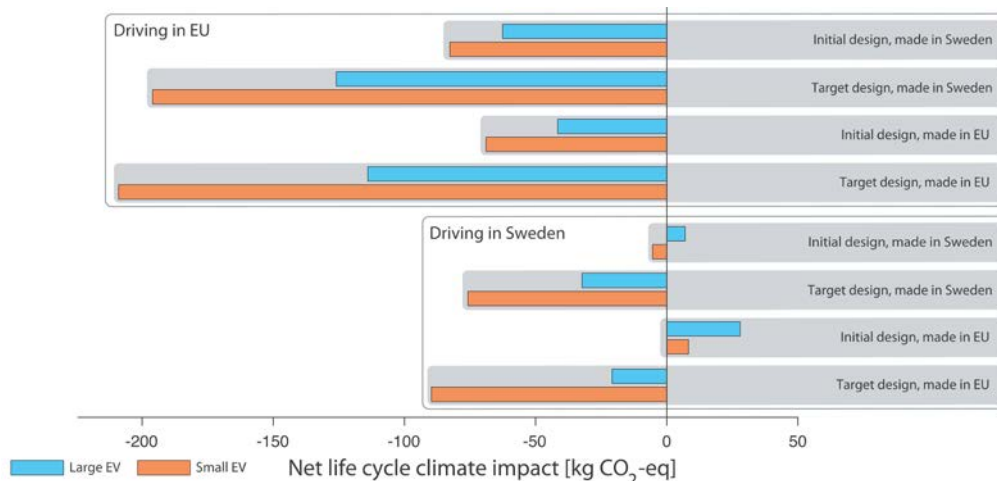


Figure 3. Net life cycle climate impacts of structural battery roof, all cases.

The net life cycle ozone formation impacts are shown in Figure 4, where it can be seen that using a structural battery roof avoids ozone formation in all examined cases. However, photochemical ozone formation impacts show a different pattern compared to climate impacts in that the largest savings from using a structural battery roof are for the large EV. The reason is not the size of the EV but the production of the NCA cathode which has relatively large NO_x-eq emissions [39].

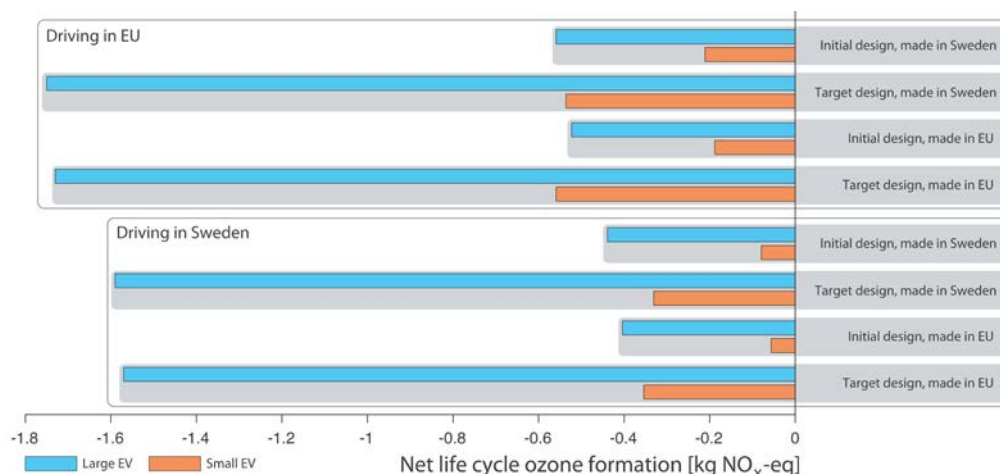


Figure 4. Net life cycle ozone formation of structural battery roof, all cases.

The results for abiotic depletion are shown in Figure 5. It can be seen that using a structural battery roof avoids abiotic depletion in all examined cases. Abiotic depletion showed the largest savings for the small EV, as for climate impact, but it is the replaced battery that dominated savings, similar to ozone formation. The scientific base for calculating abiotic resource depletion is not very solid [16]. There is a lack of universal consensus on methodology [40,41]. Resource depletion was included in the study for reasons of completeness but not further discussed here. It should be pointed out that,

as measured, a structural battery solution resulted in less resource depletion in all the 16 cases included in the sensitivity calculations (see Figure 5).

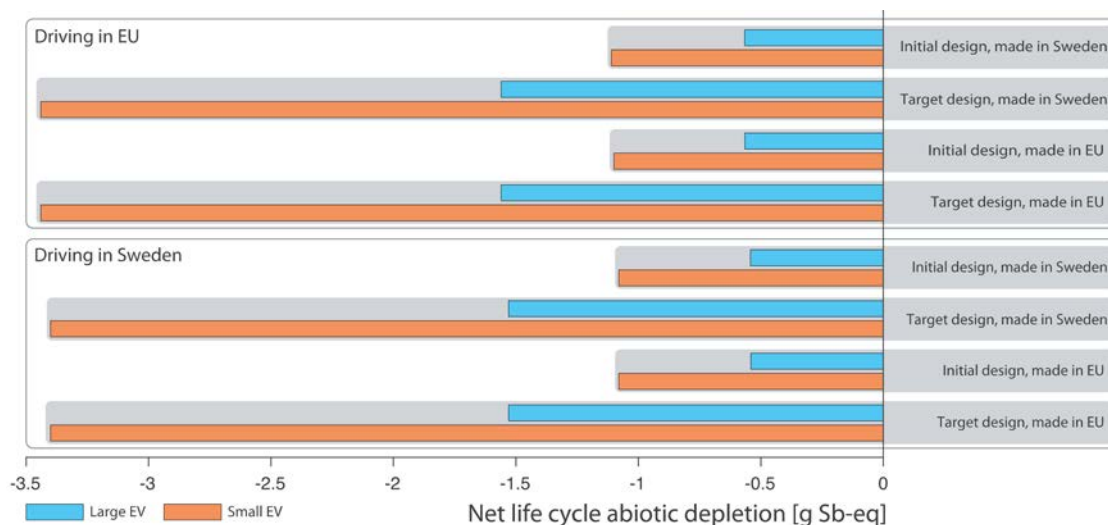


Figure 5. Net life cycle abiotic depletion of structural battery roof, all cases.

In summary, the structural battery in the small EV gave larger climate and abiotic depletion reductions than in the larger EV, while the structural battery in the large EV gave larger ozone formation reductions. However, the difference was more due to different battery chemistries and energy efficiency in the large EV (NCA, 138 Wh/kg) and the small EV (NMC, 81 Wh/kg) than the size of the vehicles. In all cases above, the structural battery outperformed the steel roof when European average electricity was used for manufacturing and during use of the battery, i.e., base case conditions. Since European average electricity is considered close to global average electricity and the electricity mix is the largest cause of results variability [3], it is concluded that from a global perspective, a structural battery roof applied in a small or a large EV gives less climate impact, ozone formation, and abiotic depletion than a steel roof. Furthermore, a structural battery at the target level gives more environmental impact avoidance than a structural battery at the initial level.

Environmental Impact of Structural Battery Production

Figure 6 shows the most environmentally dominant processes/materials for producing a structural battery.

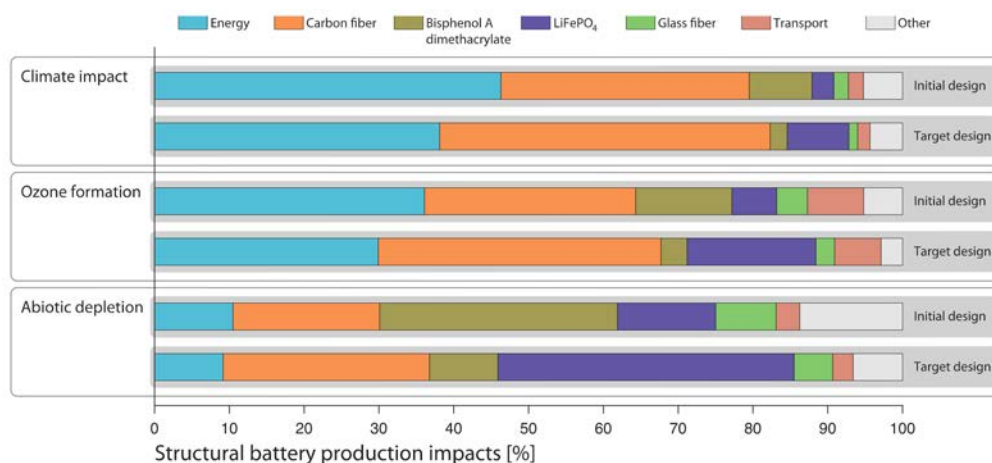


Figure 6. Source of environmental impacts for production of structural battery. European average electricity for production.

Climate impact for production of a structural battery roof at the initial level and target level is dominated by the assembly energy, the carbon fibre (most of which is manufacturing energy), and Bisphenol A dimethacrylate in the SBE and LiFePO_4 (see Figure 6). Since there are many more lithium coated carbon fibres and much less electrolyte in the target level structural battery roof, the relative climate impact changes for these constituents, i.e., carbon fibre and LiFePO_4 , increase at the expense of Bisphenol A dimethacrylate in the SBE. While the amount of assembly energy actually is larger at the target than initial level, its relative share of the climate impact decreases at target level due to the increase of lithium coated carbon fibres.

The ozone formation stems mainly from assembly energy, carbon fibre, Bisphenol A dimethacrylate in the SBE, LiFePO_4 , transports from raw material producers to cell manufacturing, and glass fibre, i.e., more or less the same dominance pattern as for the climate impact (see Figure 6). Carbon fibre and LiFePO_4 increase at the expense of Bisphenol A dimethacrylate in the SBE and the relative share of energy when moving from the initial to target level, just as for climate impacts.

Abiotic depletion at the initial level stems mainly from Bisphenol A dimethacrylate in the SBE, the carbon fibre, LiFePO_4 , assembly energy, and glass fibre (see Figure 6). Just as for climate impacts and ozone formation, carbon fibre and LiFePO_4 increase at the target level and Bisphenol A dimethacrylate in the SBE decreases.

3.2. LCA Results in Perspective

Is saving 209 kg CO_2 -eq when replacing a steel roof with a structural battery roof in a small EV, or 114 kg for the same replacement in a large EV (see Figure 3), a lot or hardly anything? To put these numbers in perspective, they can be distributed on a 200,000 km service life and compared with, for example, the indirect propulsion emissions of small and large vehicles respectively. Saving 209 kg CO_2 -eq in a small EV life cycle is equal to saving 1.3% of propulsion impacts when the vehicle is driven with West European electricity mix.

Another way of understanding the effects of a structural battery is to calculate how much extra range a structural battery car roof could supply assuming the same traction battery. With knowledge of vehicle electricity consumption, battery size, depth of discharge, weight saving, and energy reduction value, the extra range for the small vehicle is calculated to 5 km or 5% extra range (see Supplementary material Section 3.2 for further description). This 5% extra range is probably worth quite a lot more than about 1% less indirect climate impact. However, gaining range means keeping the original battery intact, so the climate impact avoidance would be less than 1% for the target structural battery design. But it would not be zero, since the battery roof is less heavy than the steel roof. Exchanging ten times more steel components with structural batteries would give ten times more range, i.e., exchanging 92 kg in the small EV would give 50 km, or 50%, more range. For the large EV with the NCA battery, the numbers are 4.5 km extra range, equivalent to 1.6% extra range for the 9.2 kg substitution.

3.3. Chemical Risk Assessment from a Life Cycle Perspective

Chemical risk has been evaluated with a novel CRA methodology to properly consider input chemicals for compliance and hazard. Previous tools for CRA address hazard and risk, but seldom consider life cycle phases. Another novel characteristic is the assessment for future legal risks and chemical legal compliance. For easy to perceive decision support, colour coding has been used. The chemicals included in the BOM have been evaluated and the results are summarised in Figure 7. Green marks indicate no/low risk, yellow indicates medium risk, and red indicates high risk which is recommended for substitution.

Chemical	Production	Use	End of life	Overall
Bisphenol A dimethacrylate	Skin and eye			
Lithium trifluoromethane-sulfonate	Skin, eye and inhalation		Skin, eye and inhalation	
Ethylene carbonate	Skin and oral		Skin and oral	Chemical management important
Dimethyl methylphosphonate	Skin	Skin	Skin	Suspected CMR, legal risk
2,2'-(Ethylenedioxy) diethanethiol	Suspected PBT			Legal
Tris(N-hydroxy-N-nitrosophenylamino-O,O')aluminium	Suspected carcinogenic			Suspected carcinogenic
2,2'-Azobis(2-methylpropionitrile)	Reactive, inhalation			
Carbon fibers				
Carbon black	Carcinogenic		Carcinogenic	Legal risk
Acetone	Flammable			
Iodine	Organ			Organ, legal risk
Triton X-100	Aquatic tox, skin and eye			
PVDF				
LiFePO ₄				
Propylene carbonate (possible substitute for Dimethyl methylphosphonate)	Eye		Eye	

Figure 7. Results of chemical risk assessment of the structural battery. For a green risk level, the chemicals have no hazard statements of high concern or low exposure of chemicals with properties of low concern such as skin irritants. At a yellow risk level, chemicals with hazard statements of lower concern but with higher exposure are included. A red risk level includes chemicals with properties of high concern such as carcinogenic, mutagenic, and reproduction toxic (CMR), persistent, bio-accumulative, and toxic (PBT), and/or very persistent and very bio-accumulative (vPvB). A red level also includes legal risks, both according to existing chemical regulations and possible coming regulations. For more details, see Figure S2.

The chemical risk assessment method suggested in this study has been iteratively developed, thus some initial aspects were excluded from the final version: protective measures, exposure routes, and work exposure limits were originally included but excluded in the final assessment since these aspects are covered by other included parameters (see Tables S9 and S10). Since the scope does not include upstream processes, possible production routes that include risk chemicals are omitted. This may be the case for production of PVDF that can include hazardous perfluoroalkyl substances (PFAS) and other similar risks connected to precursors and reactants.

Most chemicals used in the production of structural batteries are evaluated as low risk for production, use, and end of life-handling, thus resulting in low overall risk related to compliance and hazard. The main result is that dimethyl methylphosphonate and possibly ethylene carbonate

should be investigated for substitution. Propylene carbonate is suggested as a substitute for dimethyl methylphosphonate. This chemical has been assessed with the same method and is also presented in Figure 7.

4. Conclusions

Making an LCA and CRA early in the product development is especially fruitful to help steer the design of both materials and processes. Naturally, such assessments are prospective in nature, since any final material compositions or processes may be different from those investigated. Which is also the desired outcome of the LCA and CRA—to find environmental hotspots in order to modify the design with more environmentally friendly alternatives.

The LCA results show that, with global average conditions/electricity, replacing a steel part and lithium ion traction battery in an electric vehicle with a structural battery can avoid climate impact, ozone formation, and abiotic depletion in substantive quantities. The major climate impact for the production of a structural battery roof at the initial level stems from the assembly energy (45%), carbon fibre (32%), Bisphenol A dimethacrylate in the SBE (10%), and LiFePO_4 (3%). Ozone formation and abiotic depletion impacts for production of a structural battery roof show more or less the same pattern. Thus, improvement efforts should be focused on saving energy and/or improving the electricity mix for both cell production and carbon fibre production, and possibly finding alternatives to Bisphenol A dimethacrylate. The CRA suggests that substitution of dimethyl methylphosphonate should be considered due to suspected CMR properties and possible future legal risks. Also, ethylene carbonate is suggested as a candidate for substitution since it is toxic for dermal and oral contact and good safety measures are needed. Propylene carbonate has already been suggested as a substitute for dimethyl methylphosphonate and the assessment shows that it is a good substitute, significantly lowering the risk.

A natural expansion of the LCA presented in this research would be to involve substitution of more automotive parts in other materials, e.g., aluminium and plastic composites. Also, further analysis on the recycling of the structural battery material would be useful, both for more understanding of its impact and possible modification of the design and production to facilitate recycling and the reuse of materials with less quality loss.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2071-1050/11/20/5679/s1>, Table S1: Bill of materials for structural battery cells at initial and target levels, Table S2: Electricity mixes used in the study and their climate impact, Table S3: 24 kWh NMC battery and 85 kWh NCA battery, Table S4: BOM-list for 33 Ah LEAF original NMC cell (from AESC), Table S5: BOM-list for 3.1 Ah Tesla original NCA cell (NCR18650A from Panasonic), Table S6: Life cycle model for structural battery electrolyte, Table S7: Risk evaluation matrix including assessment criteria for evaluation of risk based on hazard and exposure, and suggested actions for the different identified risks, Table S8: Example of data collected for the chemical risk assessment, including name, CAS-RN, hazard statement and selected physical-chemical properties, Table S9: The information sources that have been used for assessing the chemical risks, Table S10: Information sources and aspects which were originally included in the chemical risk assessment but were excluded from the final assessment, Table S11: Physical hazard codes according to CLP, Table S12: Health hazard codes according to CLP, Table S13: Environmental hazard codes according to CLP, Figure S1: Net life cycle climate impacts of structural battery roof at target level in a small EV compared to steel roof, European electricity for production and propulsion. Processes contributing less than 15% not shown, Figure S2: Chemical risk assessment for chemicals in the structural battery. The table includes hazard information and assessment results for the different life cycle phases.

Author Contributions: Conceptualization, M.Z., C.J., W.J. and D.Z.; Data curation, C.J., W.J. and K.F.; Formal analysis, M.Z., C.J. and K.F.; Funding acquisition, C.J., K.F. and D.Z.; Investigation, M.Z., C.J., W.J. and K.F.; Methodology, M.Z., C.J., W.J. and K.F.; Project administration, C.J. and D.Z.; Resources, M.Z., C.J., W.J. and K.F.; Supervision, C.J. and D.Z.; Visualization, W.J.; Writing – original draft, M.Z.; Writing – review & editing, M.Z., C.J., W.J., K.F., S.P., D.Z. and G.L.

Funding: This research was funded by the XPRES initiative, the Swedish Research Council, projects 2017-03898 and 621-2014-4577, the strategic innovation program LIGHTer (funding provided by Vinnova, the Swedish Energy Agency and Formas), H2020 Clean Sky II project no. 738085 and by the Air Force Office of Scientific Research under award number FA9550-17-1-0244.

Acknowledgments: The LCA and CRA have been carried out by RISE IVF in close cooperation with the structural battery research group (Kombatt) at the Department of Aeronautical and Vehicle Engineering and Department of Chemical Engineering, KTH Royal Institute of Technology. The results of the LCA and CRA was communicated to the structural battery research group in an idea generation workshop in order to make the most possible use of the LCA results. It resulted in 35 ideas aiming at improving the environmental performance of a structural battery.

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

References

- Kim, H.C.; Wallington, T.J.; Arsenault, R.; Bae, C.; Ahn, S.; Lee, J. Cradle-to-Gate Emissions from a Commercial Electric Vehicle Li-Ion Battery: A Comparative Analysis. *Environ. Sci. Technol.* **2016**, *50*, 7715–7722. [CrossRef] [PubMed]
- Ellingsen, L.A.; Singh, B.; Strømman, A.H. The size and range effect: lifecycle greenhouse gas emissions of electric vehicles. *Environ. Res. Lett.* **2016**, *11*, 054010. [CrossRef]
- Cox, B.; Mutel, C.L.; Bauer, C.; Beltran, A.M.; Van Vuuren, D.P. Uncertain Environmental Footprint of Current and Future Battery Electric Vehicles. *Environ. Sci. Technol.* **2018**, *52*, 4989–4995. [CrossRef] [PubMed]
- South, J.T.; Carter, R.H.; Snyder, J.F.; Hilton, C.D.; O'Brien, D.J.; Wetzel, E.D. Multifunctional Power-Generating and Energy-Storing Structural Composites for U.S. Army Applications. *MRS Proc.* **2004**, *851*, NN4.6. Available online: <https://www.cambridge.org/core/journals/mrs-online-proceedings-library-archive/article/multifunctional-powergenerating-and-energystoring-structural-composites-for-us-army-applications/EE493315B815801CD4F5BB1BB97AB64A> (accessed on 11 October 2019). [CrossRef]
- Snyder, J.F.; Gienger, E.B.; Wetzel, E.D.; Xu, K.; Curtis, P.T. Multifunctional Structural Composite Batteries. In Proceedings of the Society for the Advancement of Materiel and Process Engineering (SAMPE) 2006 Fall Technical Conference, Dallas, TX, USA, 6–9 November 2010.
- Wong, E.L.; Baechle, D.M.; Xu, K.; Carter, R.H.; Snyder, J.F.; Wetzel, E.D. Design and Processing of Structural Composite Batteries. In Proceedings of the Society of Advancement of Material and Process Engineering, Baltimore, MD, USA, 3–7 June 2007.
- Kjell, M.H.; Jacques, E.; Zenkert, D.; Behm, M.; Lindbergh, G. PAN-Based Carbon Fiber Negative Electrodes for Structural Lithium-Ion Batteries. *J. Electrochem. Soc.* **2011**, *158*, A1455. [CrossRef]
- Arvidsson, R.; Janssen, M.; Nordelöf, A. Environmental Assessment of Emerging Technologies Recommendations for Prospective LCA. *J. Ind. Ecol.* **2017**, *22*, 1286–1294. [CrossRef]
- Nielsen, P.H.; Wenzel, H. Integration of environmental aspects in product development: A Stepwise Procedure Based on Quantitative Life Cycle Assessment. *J. Clean. Prod.* **2002**, *10*, 247–257. [CrossRef]
- Simon, M.; Poole, S.; Sweatman, A.; Evans, S.; Bhamra, T.; McAlone, T. Environmental Priorities in Strategic Product Development. *Bus Strateg. Environ.* **2000**, *9*, 367–377. [CrossRef]
- Zackrisson, M. *Product Orientation of Environmental Work: Barriers & Incentives*; Degree in Licentiate of Engineering, Department of Machine Design, Royal Institute of Technology; KTH: Stockholm, Sweden, 2009; Available online: <http://urn.kb.se/resolve?urn=urn:nbn:se:kth:diva-10585> (accessed on 11 October 2019).
- Johannisson, W.; Zenkert, D.; Lindbergh, G. Model of a structural battery and its potential for system level mass savings. *Multifunct. Mater.* **2019**, *2*, 035002. [CrossRef]
- Jacques, E.; Kjell, M.H.; Zenkert, D.; Lindbergh, G.; Behm, M.; Willgert, M. Impact of electrochemical cycling on the tensile properties of carbon fibres for structural lithium-ion composite batteries. *Compos. Sci. Technol.* **2012**, *72*, 792–798. [CrossRef]
- Jacques, E.H.; Kjell, M.; Zenkert, D.; Lindbergh, G. The effect of lithium-intercalation on the mechanical properties of carbon fibres. *Carbon N. Y.* **2014**, *68*, 725–733. [CrossRef]
- Hagberg, J.; Maples, H.A.; Alvim, K.S.P.; Xu, J.; Johannisson, W.; Bismarck, A.; Zenkert, D.; Lindbergh, G. Lithium iron phosphate coated carbon fiber electrodes for structural lithium ion batteries. *Compos. Sci. Technol.* **2018**, *162*, 235–243. [CrossRef]
- Zackrisson, M.; Fransson, K.; Hildenbrand, J.; Lampic, G.; O'Dwyer, C. Life cycle assessment of lithium-air battery cells. *J. Clean. Prod.* **2016**, *135*, 299–311. [CrossRef]
- European Commission. *Energy Roadmap 2050*; Publications Office of the European Union: Luxembourg, 2012.

18. Das, S. Life cycle assessment of carbon fiber-reinforced polymer composites. *Int. J. Life Cycle Assess.* **2011**, *16*, 268–282. [CrossRef]
19. Wernet, G.; Bauer, C.; Steubing, B.; Reinhard, J.; Moreno-Ruiz, E.; Weidema, B. The ecoinvent database version 3 (part I): overview and methodology. *Int. J. Life Cycle Assess.* **2016**, *21*, 1218–1230. [CrossRef]
20. Dunn, J.B.; Gaines, L.; Sullivan, J.; Wang, M.Q. Impact of recycling on cradle-to-gate energy consumption and greenhouse gas emissions of automotive lithium-ion batteries. *Environ. Sci. Technol.* **2012**, *46*, 12704–12710. [CrossRef]
21. Zackrisson, M.; Avellán, L.; Orlenius, J. Life cycle assessment of lithium-ion batteries for plug-in hybrid electric vehicles—Critical issues. *J. Clean. Prod.* **2010**, *18*, 1517–1527. [CrossRef]
22. Dunn, J.B.; Gaines, L.; Kelly, J.C.; James, C.; Gallagher, K.G. The significance of Li-ion batteries in electric vehicle life-cycle energy and emissions and recycling's role in its reduction. *Energy Environ. Sci.* **2014**, *8*, 158–168. [CrossRef]
23. Matheys, J.; Van Autenboer, W.; Van Mierlo, J. *Subat: Sustainable Batteries. Work Package 5: Overall Assessment; Final Public Report*; Vrije Universiteit Brussels-ETEC: Amsterdam, The Netherlands, 2005.
24. Forell, A.; Busa, A.; Wilbert, G. *Advanced High Volume Affordable Lightweighting for Future Electric Vehicles*; Thinkstep AG: Wolfsburg, Germany, 2016.
25. Cullbrand, F.K.; Fråne, A.; Jensen, C. *Utökad demontering av personbilar*; IVL Svenska Miljöinstitutet: Stockholm, Sweden, 2015.
26. Ec. Directive 2000/53/EC of the European Parliament and of the Council on end-of Life Vehicles. *Off. J. Eur. Communities* **2000**, 1–15. Available online: <https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX%3A32000L0053> (accessed on 11 October 2019).
27. Zackrisson, M.; Jönsson, C.; Olsson, E. Life Cycle Assessment and Life Cycle Cost of Waste Management—Plastic Cable Waste. *Adv. Chem. Eng. Sci.* **2014**, *4*, 221–232. [CrossRef]
28. Hagnell, M.K.; Åkermo, M. The economic and mechanical potential of closed loop material usage and recycling of fibre-reinforced composite materials. *J. Clean. Prod.* **2019**, *223*, 957–968. [CrossRef]
29. RECHARGE. *PEFCR—Product Environmental Footprint Category Rules for High Specific Energy Rechargeable Batteries for Mobile Applications*; The Advanced Rechargeable & Lithium Batteries Association: Brussels, Belgium, 2018.
30. Ellingsen, L.A.; Majeau-bettez, G.; Singh, B.; Srivastava, A.K.; Valøen, L.O.; Strømman, A.H. Life Cycle Assessment of a Lithium-Ion Battery Vehicle Pack. *J. Ind. Ecol.* **2013**, *18*, 113–124. [CrossRef]
31. Askham, C.; Gade, A.L.; Hanssen, O.J. Linking chemical risk information with life cycle assessment in product development. *J. Clean. Prod.* **2013**, *51*, 196–204. [CrossRef]
32. Barberio, G.; Scalbi, S.; Buttol, P.; Masoni, P.; Righi, S. Combining life cycle assessment and qualitative risk assessment: The case study of alumina nanofluid production. *Sci. Total Environ.* **2014**, *496*, 122–131. [CrossRef] [PubMed]
33. Harmon, J.P.; Otter, R. Green Chemistry and the Search for New Plasticizers. *ACS Sustain. Chem. Eng.* **2018**, *6*, 2078–2085. [CrossRef]
34. Jacobs, M.M.; Malloy, T.F.; Tickner, J.A.; Edwards, S. Alternatives assessment frameworks: Research needs for the informed substitution of hazardous chemicals. *Environ. Health Perspect.* **2016**, *124*, 265–280. [CrossRef]
35. European Commission. *Regulation (EC) No 1272/2008 of the European Parliament and of the Council of 16 December 2008 on Classification Labelling and Packaging of Substances and Mixtures, Amending and Repealing Directives 67/548/EEC and 1999/45/EC, and Amending Regulation (EC)*; Publications Office of the European Union: Luxembourg, 2008.
36. ECHA. European Chemicals Agency, Chemical Database. 2019. Available online: <https://echa.europa.eu/sv/home> (accessed on 27 May 2019).
37. European Commission. *Regulation (EC) No 1907/2006 of the European Parliament and of the Council of 18 December 2006 Concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH)*; Publications Office of the European Union: Luxembourg, 2006.
38. EU; European Commission. *Regulation (EC) No 850/2004 of the European Parliament and of the Council of 29 April 2004 on Persistent Organic Pollutants and Amending Directive 79/117/EEC*; Publications Office of the European Union: Luxembourg, 2004.
39. Bauer, C. *Ökobilanz Von Lithium-Ionen Batterien*; Paul Scherrer Institut: Villigen, Switzerland, 2010.

40. Peters, J.; Weil, M. A Critical Assessment of the Resource Depletion Potential of Current and Future Lithium-Ion Batteries. *Resources* **2016**, *5*, 46. [[CrossRef](#)]
41. Klinglmair, M.; Sala, S.; Brandão, M. Assessing resource depletion in LCA: A review of methods and methodological issues. *Int. J. Life Cycle Assess.* **2014**, *19*, 580–592. [[CrossRef](#)]



© 2019 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).

TOPICAL REVIEW

Structural battery composites: a review

To cite this article: Leif E Asp *et al* 2019 *Funct. Compos. Struct.* **1** 042001

View the [article online](#) for updates and enhancements.

Functional Composites and Structures



TOPICAL REVIEW

Structural battery composites: a review

RECEIVED
9 October 2019

REVISED
24 October 2019

ACCEPTED FOR PUBLICATION
5 November 2019

PUBLISHED
21 November 2019

Leif E Asp^{1,5}, Mats Johansson², Göran Lindbergh³, Johanna Xu¹ and Dan Zenkert⁴

¹ Department of Industrial and Materials Science, Chalmers University of Technology, SE-41296 Göteborg, Sweden

² Department of Fibre and Polymer Technology, KTH Royal Institute of Technology, SE-10044 Stockholm, Sweden

³ Department of Chemical Engineering, KTH Royal Institute of Technology, SE-10044 Stockholm, Sweden

⁴ Department of Aeronautical and Vehicle Engineering, KTH Royal Institute of Technology, SE-10044 Stockholm, Sweden

⁵ Author to whom any correspondence should be addressed.

E-mail: leif.asp@chalmers.se

Keywords: carbon fibre, lithium ion, mechanical properties, electrochemical performance

Abstract

This paper presents a comprehensive review of the state-of-the-art in structural battery composites research. Structural battery composites are a class of structural power composites aimed to provide mass-less energy storage for electrically powered structural systems. Structural battery composites are made from carbon fibres in a structural electrolyte matrix material. Neat carbon fibres are used as a structural negative electrode, exploiting their high mechanical properties, excellent lithium insertion capacity and high electrical conductivity. Lithium iron phosphate coated carbon fibres are used as the structural positive electrode. Here, the lithium iron phosphate is the electrochemically active substance and the fibres carry mechanical loads and conduct electrons. The surrounding structural electrolyte is lithium ion conductive and transfers mechanical loads between fibres. With these constituents, structural battery half-cells and full-cells are realised with a variety in device architecture. The paper also presents an overview of material modelling and characterisation performed to date. Particular reference is given to work performed in national and European research projects under the leadership of the authors, who are able to provide a unique insight into this emerging and exciting field of research.

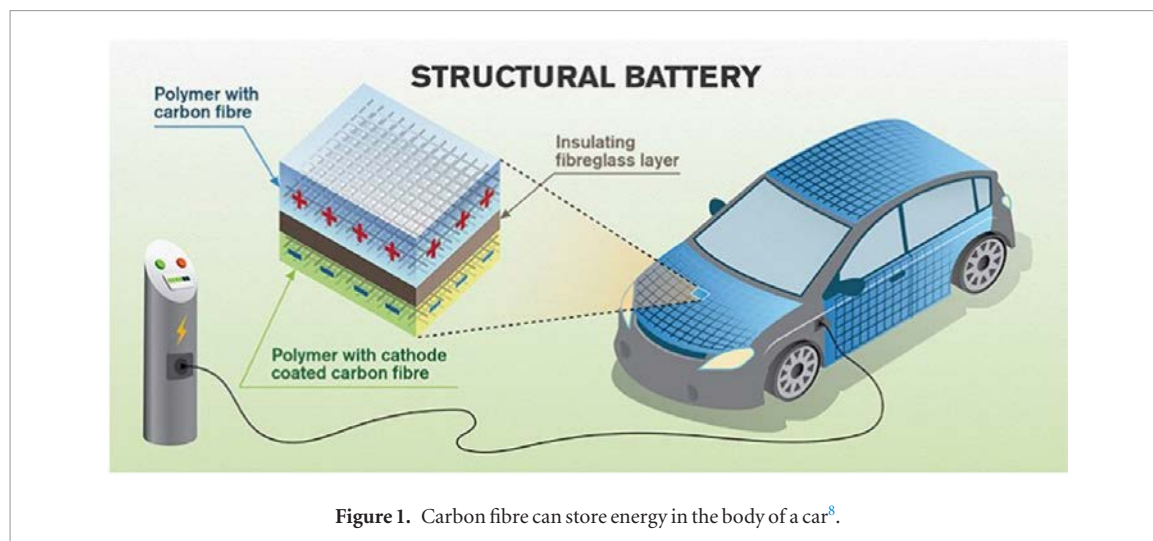
1. Introduction

This paper addresses a new type of multifunctional lightweight composite material desired for its potential to reduce vehicle weight and ease future electrification across transport modes. We refer to these materials as *structural battery composites*. The paper reviews the current status of structural battery composites. Focus is on the activities performed during the last decade by an interdisciplinary team of researchers in Sweden set to realise structural battery composites from carbon fibre reinforced polymers (CFRP).

The need to develop greener, safer and more competitive road and air transport has been recognised as of critical societal and commercial importance. In Europe, the ERTRAC and EPoSS strategy paper⁶ and Flight-path2050⁷ have been used by the European Commission to define the Green car initiative and Green vehicle as well as the Clean Sky Joint Undertaking in European Union FP7 and H2020 research funding frameworks. For road transport electrification of urban mobility and transport has been highlighted as a most urgent research area. In addition, the Green vehicle initiative identify the need for advanced lightweight materials to realise future lightweight electric vehicle solutions. To this, Airbus has expressed a vision for an all-electric regional aircraft for 100 passengers by year 2050! The research on structural battery composites is conducted in this setting with ambition to pave the road for ‘mass-less’ energy storage in future vehicle structures. This will be achieved by realisation of multifunctional lightweight composite materials that simultaneously can carry mechanical loads and store electrical energy. Such materials will allow radical weight savings for future electric and hybrid vehicles,

⁶ ERTRAC and EPoSS European Roadmap Electrification of Road Transport, Version 2.0/November 2010.

⁷ <http://ec.europa.eu/transport/air/doc/flightpath2050.pdf>



contributing to highly energy-efficient and emission-free vehicles ranging from bicycles, city-movers, cars and boats to aircraft, as illustrated in figure 1.

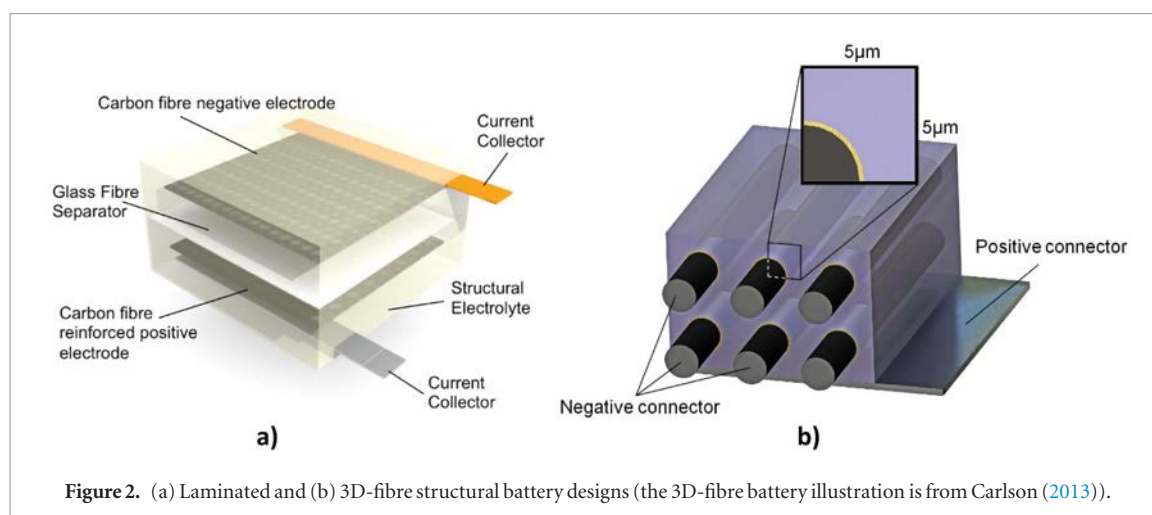
Benefits of multifunctional engineering materials are numerous and diverse. The use of structural battery composites, for instance, goes well-beyond transportation applications. We foresee that they will be used in transportable electronics as mobile phones and lap-tops. However, concerning emissions of greenhouse gases transport applications are most interesting. While electrification of the automotive sector is already underway electrification of aircraft is less developed. This is partly due to the relatively moderate energy densities of available battery technologies. For example, Airbus' vision to make all-electric regional aircraft by 2050 is very challenging. Consider a 1 h flight with a 100-passenger aircraft. If Airbus were to simply replace the approximately 30 kg of kerosene per passenger used for such a flight with batteries, they would need batteries at a weight of approximately 1000 kg/passenger. Consequently, means to make secondary structures or interior parts from structural battery composites are very appealing to aircraft manufacturers.

Structural battery composites belong to a new class of multifunctional composites called structural power composites (Asp and Greenhalgh 2014). These comprise of structural composites with an inherent ability to store electrical energy, such as structural capacitors (Carlson *et al* 2010, O'Brien *et al* 2011), supercapacitors (Shirshova *et al* 2013) and batteries. The current paper addresses only structural battery composites.

In the literature there are two different approaches to achieve combined mechanical and electrical performance in structures. One approach is to add functionalities in to a component. This is done by, for instance, embedding thin-film batteries within composite laminates. These are essentially sandwich structures (Thomas and Qidwai 2004, Thomas *et al* 2005, Ladpli *et al* 2019). Such devices do not rely on multifunctional material constituents but is rather an assembly of components (i.e. the composite face sheets, foam core and thin-film battery). We refer to these as multifunctional structures. The second approach is to make a multifunctional material in which every constituent performs multiple functions (Asp and Greenhalgh 2014, Lendlein and Trask 2018). In such structural battery composites carbon fibres function as reinforcement and electrode and the polymer acts as matrix and electrolyte. This paper focuses solely on multifunctional materials, i.e. the structural battery composite materials.

The first attempts to make a structural battery composite material from multifunctional constituents were made at the US Army Research Labs (ARL) (Wetzel 2004, Snyder *et al* 2007). Wetzel and his team at ARL did pioneering work utilising different reinforcing materials as structural electrodes and a glass weave separator in a common polymer electrolyte matrix as they built the first structural battery composite material (Wong *et al* 2007). The resulting structural battery material demonstrated promising mechanical performance but did not work electrically due to poor electrical insulation. Following the attempts at ARL, Liu *et al* (2009) designed a structural battery composite with short-fibre reinforced electrodes and a solid polymer electrolyte matrix material. However, they were not able to manufacture the composite electrodes and failed to identify a sufficiently ion-conductive polymer electrolyte. For these reasons they used a robust gel electrolyte as matrix. This resulted in a working battery with very low mechanical properties. Inspired by these works, Ekstedt *et al* (2010) made a functioning laminated structural battery employing a gel electrolyte reinforced with a carbon fibre weave negative electrode, a glass weave separator and a lithium iron phosphate (LiFePO_4)/aluminium fibre weave positive electrode. The structural battery, containing lithiated carbon and LiFePO_4 showed an Open Cell Potential of 3.3 V.

⁸ www.chalmers.se/en/departments/ims/news/Pages/carbon-fibre-can-store-energy.aspx



Early structural battery designs relied on a laminated structure where two electrode layers were separated by an electrically insulating (separator) layer. This design is the obvious choice as it is a common architectural feature for composite laminates and conventional batteries. However, the laminated design faces some substantial challenges that must be overcome in order to realise a working structural battery. As indicated above, one of these challenges is the ion-conductivity and mechanical properties of the combined electrolyte and matrix. Lack of highly ion-conductive and stiff polymer electrolyte systems will hamper realisation of structural battery composites. The second is the thickness of the separator layer. Thick separator layers will significantly reduce the power and energy density of the structural battery composite and internal resistances will cause high energy losses. Conventional batteries have a separator thickness of around 20–30 μm . This is much thinner than conventional composite plies, which typically are 100–200 μm in thickness. To overcome these challenges new structural battery electrolytes have been developed. This is reported in detail in chapter 3 of this paper. One approach for structural electrolyte development was first suggested by Snyder *et al* (2007) using block co-polymer electrolyte systems as composite matrix. These contain a cross-linking monomer as structural enhancer and an ethylene oxide (EO) rich monomer as diffusion enhancer of the polymer. An alternative approach used for structural supercapacitors is also considered for structural battery composites. Shirshova *et al* (2013) proposed a bi-continuous polymer/ionic liquid system. In such systems the hollow polymer structure transfers mechanical loads and the liquid diffuses ions in its hollow channels. With these approaches, structural electrolytes with stiffness of up to 1 GPa and ion-conductivity exceeding $10^{-4} \text{ S cm}^{-1}$ have been realised. Given the multifunctional properties of the available structural electrolytes two different structural battery designs have evolved: the laminated and the 3D fibre structural battery architectures. These are schematically illustrated in figure 2, and further discussed in chapter 5.

In this paper the state of the art of structural battery composites is presented. The paper addresses carbon fibre reinforced structural battery composites and discusses the multifunctional constituents, battery cell and half-cell designs and performance as well as their modelling and characterisation.

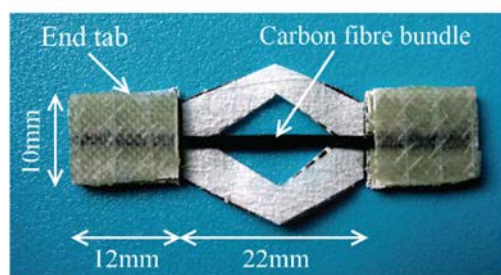
2. Carbon fibres as negative electrodes in structural battery composites

To realise structural battery composites, the carbon fibres must perform two functions simultaneously: carry mechanical loads and act as an active battery electrode. In the latter the carbon fibres must be able to store ions in the micro-structure of the fibre itself. This is when ions (in our case lithium ions) are inserted into the fibre during charge and removed on discharge, in our case also denoted lithiation and delithiation, respectively. In a full battery cell, lithium ions are inserted or lithiated into the negative carbon electrode during charge and removed or delithiated during discharge.

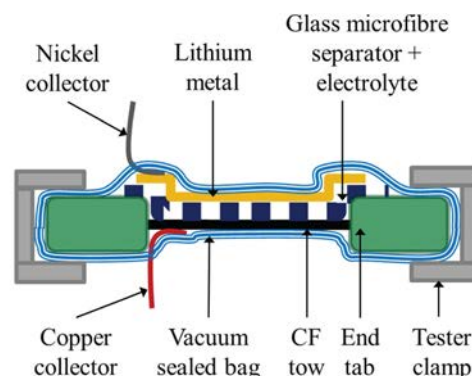
There are a few key issues to be studied in relation to the fibre itself. Can carbon fibre be lithiated and store lithium as a battery electrode? What type of fibres are most favourable for storing lithium? How large are the electrochemical losses during charge and discharge? Does mechanical load affect the process of lithiation and delithiation? What happens to the fibre as lithium occupies space in the fibre micro-structure and does that affect the mechanical properties of the fibre?

2.1. Mechanical properties of carbon fibres

Carbon fibres have perhaps the best specific mechanical properties of all commercially used materials in high performance structures. There are two main classes of carbon fibres stemming from the pre-cursor from which they are made: pitch-based and polyacrylonitrile (PAN)-based fibres. Pitch-based fibres usually exhibit very high



(a)



(b)

Figure 3. (a) Carbon fibre bundle with end-tabs and (b) schematic of electrochemical cell reprinted from (Jacques *et al* (2013b)), Copyright 2013, with permission from Elsevier.

stiffness (ranging up to around 800 GPa) but with moderate strength and with low failure strains in the order of less than 1%. They usually have a high graphitic content with large and oriented crystals. PAN-based fibres are the most commonly used fibres today and come in a wide range of qualities. By choice of precursor and process parameters, the microstructure can be varied considerably, especially with respect to crystallite size and orientation. Therefore, carbon fibres offer a wide range of mechanical and physical properties (Johnson 1987, Lavin 2001, Park 2015, Fredi *et al* 2018). Their modulus ranges from about 200–600 GPa and with strengths from around 3000–6000 MPa. The ones in the lower range of stiffness (and with high strength) are denoted HS (high strength) or HT (high tenacity) fibres. They have lower graphitic content and small and not very oriented crystals. The intermediate modulus (IM) fibres have a modulus of around 300–400 GPa, have both higher graphitic content and somewhat larger and more oriented crystals. There are also PAN-based ultra-high modulus fibres that are graphitised at very high temperatures, giving high graphitic content, high orientation and with a modulus over 500 GPa. Early work in Japan (Kanno *et al* 1989) and at ARL (Snyder *et al* 2009a) demonstrated PAN-fibres to be very good electrodes, whereas pitch-based carbon fibres were not. Extensive characterisation of contemporary carbon fibre performed by Kjell *et al* (2011, 2013) confirm high capacities of PAN-based carbon fibres, e.g. IMS65 and T800 fibres as discussed below.

2.2. Electrochemical properties of carbon fibres

A wide range of carbon fibres were tested electrochemically to study which types of fibres perform best as battery electrode (Kjell *et al* 2011, Fredi *et al* 2018). They ranged from Toray T300, which is a typical HT fibre, to Toho Tenax IMS65 and Toray M60J which are intermediate and high modulus fibres with moduli of 290 and 580 GPa, respectively. The carbon fibres were used either as received or with the sizing chemically removed before sample preparation.

In order to simplify the specimen preparation carbon fibre bundles were tabbed using two layers of standard glass fibre/epoxy pre-preg as seen in figure 3(a). The specimens were then placed in a cell with a microfibre separator and a lithium metal counter electrode. Current collectors were applied, liquid electrolyte was poured into the cell which was then vacuum sealed in a bag, see figure 3(b). This was all done inside a glovebox in an oxygen free and dry environment.

The cells were electrochemically cycled galvanostatically (using a constant current) between 0.002–1.5 V versus Li/Li⁺. Different current rates were used ranging from 1 C (a constant current that gives a charge and discharge time of 1 h) down to C/10 (1/10:th of the current at 1 C giving charge and discharge times of approximately 10 h).

All the tested carbon fibres exhibited some electrochemical capacity. However, the high modulus fibres had quite low capacity which was explained by staging as the prevailing lithiation mechanism. Lithiation in graphite occurs via staging. However, for the high modulus fibre staging was partially obstructed by the turbostratic graphitic structure of the carbon fibre (Fredi *et al* 2018). As consequence, its larger graphite crystal size and higher crystal orientation could not be efficiently exploited for lithium insertion. Hence, the studied high modulus fibres demonstrated low electrochemical capacity. In contrast, two IM fibres showed excellent electrochemical capacity: Toho Tenax IMS65 and Toray T800. They are very similar mechanically (modulus 290 GPa and strength around 5500 MPa). The capacities were 130 (T800) and 177 (IMS65) mAh g⁻¹ at 1 C, respectively (Kjell *et al* 2011). The intermediate modulus fibres were found to insert lithium with a mechanism like that found for disordered carbons. As consequence, the intermediate modulus fibres (IMS65 and T800) outperform high modulus fibres (M60J) as shown by Fredi *et al* (2018).

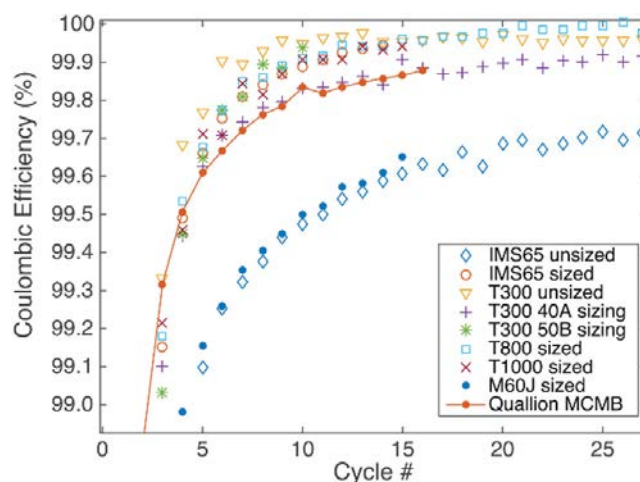


Figure 4. Coulombic efficiency as function of cycle number for various carbon fibre. Solid line is for a commercial MCMB (Quallion). Reproduced from (Hagberg *et al* (2016)). CC BY 4.0.

Some effect of the sizing was found but not for all fibre types. At low charge rates ($C/10$) the capacities were surprisingly high: 290 mAh g^{-1} for T800 and 357 mAh g^{-1} for IMS65, which is very close to the theoretical capacity of pure graphite, which is 372 mAh g^{-1} .

Kjell *et al* (2013) found that the high drop in capacity (about 50%) after the first charge cycle observed in the tests on fibre tows (capacity at first and tenth lithiation was 360 mAh g^{-1} and 177 mAh g^{-1} , respectively) was partly attributed to the bundle structure. In tests on single fibres the reversible capacity was reduced only by 25% compared to that at the first cycle. IMS65 single unsized fibres showed a reversible capacity of 250 mAh g^{-1} , whereas the capacity for the bundle was 177 mAh g^{-1} . Furthermore, a general lower influence of charge rate for single carbon fibres compared to that for carbon fibre tows was demonstrated. Consequently, Kjell *et al* (2013) found that a battery employing single fibre electrodes can be charged much faster than batteries made from carbon fibre tows. The tests on single fibres also showed that sized IMS65 fibres had the same electrochemical performance as unsized fibres.

In a later study by Hagberg *et al* (2016) the coulombic efficiency was measured using high precision coulometry. This relates to the electrochemical losses during charge and discharge cycles, which must be very low for a battery. This was done on several fibre types and compared with state-of-the-art graphitic battery electrodes from micro carbon meso beads (MCMB). The results are presented in figure 4.

As can be seen in figure 4 the coulombic efficiency is very high for some of the carbon fibres tested in this study, some even surpass that of state-of-the-art graphitic battery electrodes.

2.3. Effect of lithiation on mechanical properties

In a study by Jacques *et al* (2012) the effect on the mechanical properties of carbon fibres due to lithium insertion was studied. The same type of specimen as shown in figure 3 was used for tests on T800 and IMS65 fibre tows. They were cycled in a pouch cell (see figure 3(b)) at 1 C for up to 1000 cycles. The mechanical properties were measured after some intervals of cycling. Both the longitudinal stiffness and strength were measured. The result showed (in essence) that lithium insertion does not seem to affect the stiffness of the fibres, at least not during 1 C cycling up to 1000 cycles, as seen in figure 5(a). The tensile strength was reduced after lithiation (when the carbon fibre is charged) but some of it was regained as the fibres were delithiated (when the carbon fibre is discharged), see figure 5(b). This also indicates that some lithium is trapped inside the carbon fibres even after discharge.

In a later study (Jacques *et al* 2014) the same type of experiment was repeated but now the stiffness and strength was measured as function of capacity corresponding to the amount of lithium inserted into the fibre. It was found that the stiffness remained unchanged with capacity (lithium content). The strength decreased with capacity and with a drop of approximately 30% for the IMS65 fibre and approximately 20% for T800 at full capacity (above 300 mAh g^{-1}). At delithiated state the strength drop was approximately 15% for IMS65 and 5% for T800 at the slowest charge rate. Note that constant stiffness is not the same as constant modulus. In fact, as the fibre expands radially during lithium insertion the axial fibre modulus E_z is reduced (Jacques *et al* 2014). Work is currently in progress to determine the effect of lithiation on the radial and shear moduli of the fibres E_r and G_{zr} of IMS65, T800 and M60J carbon fibres (Duan *et al* 2019).

The opposite effect has also been investigated: the effect of mechanical loads on the electrochemical performance (Jacques *et al* 2011). In this case, no effect was found, and the carbon fibres had the same capacity whether there was a tensile strain applied to them or not during charge or discharge.

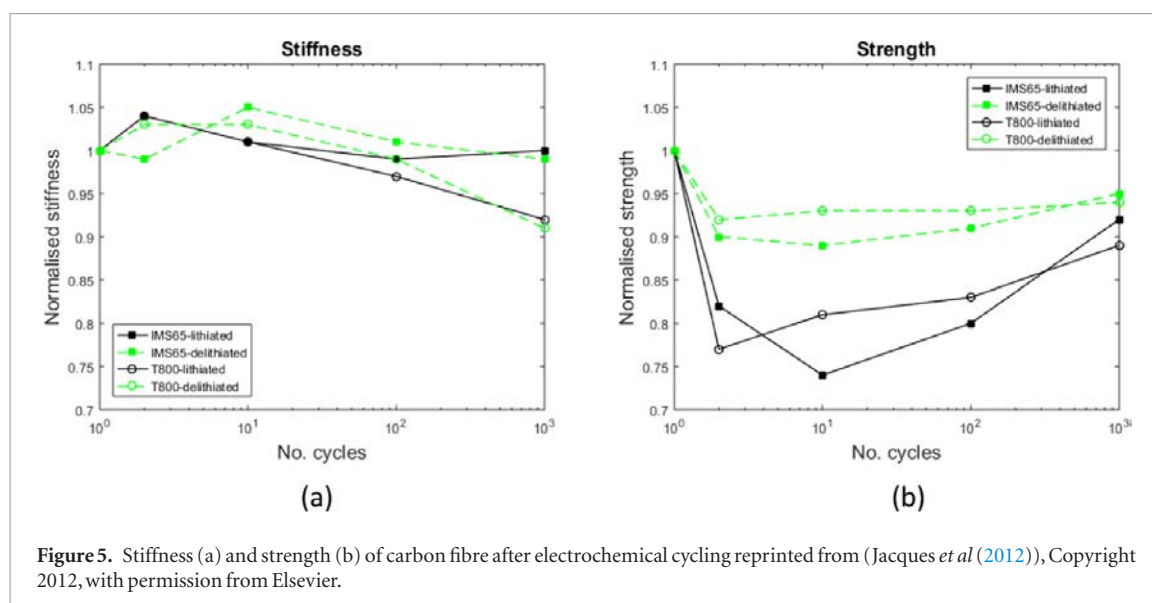


Figure 5. Stiffness (a) and strength (b) of carbon fibre after electrochemical cycling reprinted from (Jacques *et al* (2012)), Copyright 2012, with permission from Elsevier.

2.4. Fibre expansion during charge and discharge

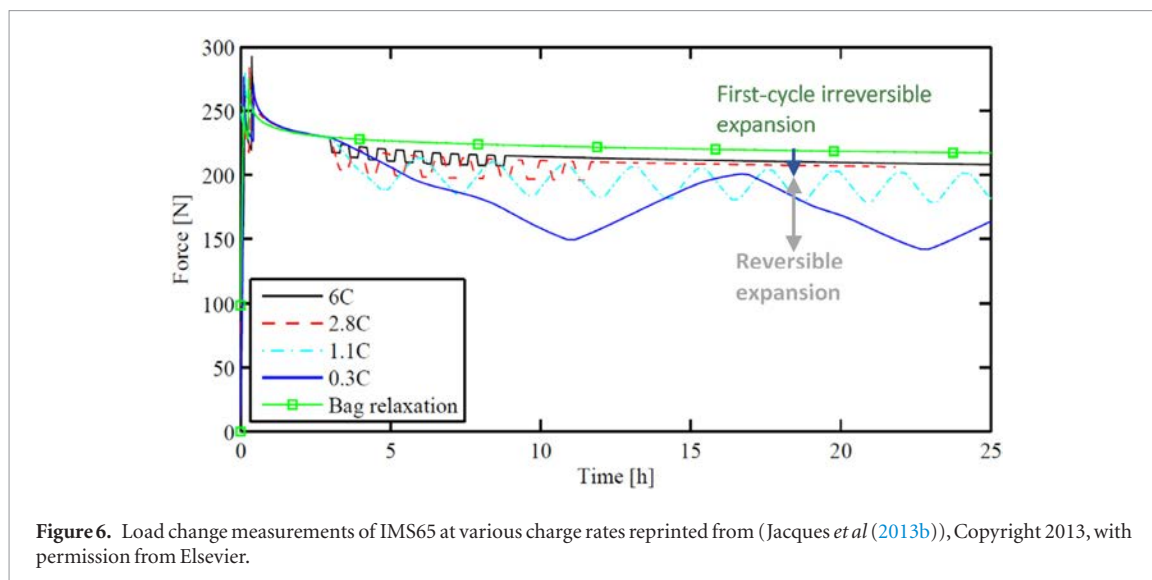
In the electrochemical cell, lithium ions move from one electrode to the other during charge, and the other way during discharge. These ions are moving in and out of the carbon fibres, which leads to volume changes. It is well known that graphitic electrodes change its volume during lithiation. A study was performed by Jacques *et al* (2013b) to measure the axial expansion of carbon fibres when used as battery electrodes. A cell as in figure 3 was placed in a tensile testing machine and a constant strain was applied. Since the carbon fibre bundle was in a pouch bag, the bag material was first allowed to relax. The carbon fibre was then lithiated at various galvanostatic currents (constant current charge/discharge), leading to different charge rates. Since the fibres expand when lithiated the load applied decreased (the strain was constant). In a second step the fibre bundle was delithiated and the applied load increased again corresponding to a contraction. Since the fibres have the same stiffness in lithiated and delithiated states the load decrease/increase can be directly related to the expansion and contraction of the fibre. As anticipated, the expansion depends on the charge rate, or rather the amount of lithium inserted. The force changes during these experiments are shown in figure 6. As seen, the axial expansions and contractions (changes in load) were large for low charge rates (see e.g. curve for 0.3 C in figure 6) and small for high charge rates (6 C). The axial expansion strains were unexpectedly large, reaching almost 1% in the axial direction at low charge rates. It was also found that some of the expansion was irreversible, i.e. the fibres did not contract back to their original length after discharge. This further supports that some lithium is trapped in the micro-structure after discharge. The axial expansion was not linear with capacity (lithium content) but still quite close to linear. No reliable method to measure radial expansion of carbon fibres from lithium insertion has yet been developed and validated. Preliminary measurements using scanning electron microscopy (SEM) suggests much higher radial expansions, up to 5% (Jacques *et al* 2013b).

2.5. Piezo-electrochemical effect

Carbon fibres are good electrical conductors but do not exhibit a piezo-electrical response. However, when lithium ions are inserted into their micro-structure, they do become piezo-electric, or as a more appropriate term this is named the piezo-electrochemical effect. The experiments used to measure this effect was in principal the same as described above (Jacques *et al* 2013a). A tabbed carbon fibre bundle in a pouch cell (see figure 3) was placed in a tensile tester. It was electrochemically cycled and at various states-of-charge the charging/discharging was interrupted leaving the cell in an open circuit potential (no currents running so the cell is at its resting potential). A load was applied and the potential between the carbon fibre electrode and the counter electrode (in this case a lithium metal foil) was measured. Interestingly, a change in the electrical potential was found, for both IMS65 and T800 fibres. The response was a few mV for a strain of approximately 0.3%. The response was not constant with capacity but seemed to have a maximum around 50% state-of-charge. The piezo-electrochemical response was about the same at full charge (high capacity) and at full discharge (Jacques *et al* 2015). Again, this support the fact that lithium is being trapped in the structure even when the fibre is fully discharged.

2.6. Resistivity of carbon fibres

To accurately model the electrical processes in the structural battery the resistivity of the constituents must be known. Schutzeichel *et al* (2019) measured the resistance of a polymer electrolyte coated carbon fibres (PeCCF) unidirectional composite. A temperature independent ohmic longitudinal resistance of the PeCCF, lying at the lower end of semi-conductors, was found. This is beneficial, since Joule heating and resulting temperature



predictions can be based on a temperature independent resistor. Temperature prediction is necessary to control/predict the mechanical behaviour of the compound. Furthermore, Schutzzeichel and co-workers presented a method to compute the number of fibres in the composite. Once the total averaged resistance and the measurement length are determined the number of fibres in the composite can be calculated using the measured specific resistance. The specific resistance of the IMS65 fibre was determined to $1.35 \cdot 10^{-3} \Omega \text{ cm}$.

3. Structural battery electrolytes

One of the main challenges for a structural battery electrolyte (SBE) is to make a composite matrix that simultaneously allow for lithium ion conduction and a mechanical load transfer between the carbon fibres. These two properties in many cases counteract each other, i.e. either a high ion conductivity and low mechanical performance or vice versa is achieved. A second challenge is that the SBE also needs to interact with the fibres via a suitable interface, i.e. the constituents must be possible to combine. These challenges have been addressed in different ways as described in the following sections.

3.1. Homogenous systems

The first SBE approach described by Snyder *et al* (2007) utilized the well-established fact that poly(ethylene glycol) (PEG) can dissolve lithium ions as already described in the 1970s (Fenton *et al* 1973, Wright 1975). Using acrylate functional PEGs this formed thermoset structures with a structural integrity as well as allowing for a lithium ion transport (Nest *et al* 1988, Snyder *et al* 2007, 2009b, Wysocki *et al* 2010, Willgert *et al* 2011, 2012, 2013). Parameters such as lithium ion content, crosslink density, and presence of plasticizers have been shown to improve the multifunctional performance to some extent, but these SBE's still suffer from the trade-off between mechanical properties and ion conductivity (Ihrner and Johansson 2017). One approach to increase the ion conductivity for solid polymer electrolytes is to make so-called gel polymer electrolytes (GPEs) that are obtained by swelling a sparsely crosslinked thermoset polymers with a liquid electrolyte. This concept has been applied to a wide range of different polymers to give ion conductivities up to $10^{-2} \text{ S cm}^{-1}$, see e.g. review paper by Stephan (2006). The relationship between the two counteracting properties however to a large extent remains why new approaches had to be taken.

3.2. In-homogenous systems

The first approach that was pursued in this context was to start with a GPE that was reinforced to form a composite polymer electrolyte (CPE). Numerous reinforcements ranging from inorganic particles (see e.g. Croce (1998)) to nano-cellulose and chitosan (see e.g. Willgert *et al* (2014)) have been tested and shown that significant multifunctional improvement can be obtained. For example, a modulus of 400 MPa and a conductivity of $5 \cdot 10^{-5} \text{ S cm}^{-1}$ have been reported by Willgert *et al* 2014. The main problem for these systems arose when the SBEs should be combined with carbon fibres as electrodes, i.e. there was no feasible route to assemble these to a half-cell. It should however be noted that this concept of CPE can be applied in other contexts e.g. a structural membrane.

Hence, new routes to resolve the problem of improved multifunctional performance and processability had to be developed. One route towards this goal is to start with a homogeneous liquid that upon polymerization/solidification transforms to a heterogeneous material with two percolating phases, where one phase determines

the ion transport and the other mechanical load transfer. The reason for the phase separation is that the solubility/miscibility of two components depend on the components' relative solubility parameters (Hansen 1967) and that the solubility parameters change when monomers transform to a polymer. By an appropriate choice of components with specific solubility parameters a system can be designed so that all components are totally miscible initially and totally immiscible after the monomers transformed to polymers. The initial liquid can then be infused into an electrode material and when polymerized form two intermingled continuous phases on a submicron scale. This technique is already well established and implemented into production in other areas where two counteracting properties are desired, e.g. in contact lenses (Seitz *et al* 2017). This concept has been demonstrated for several different systems (Shirshova *et al* 2013, 2014, Greenhalgh *et al* 2015, Yu *et al* 2016) to give a combination of relatively high modulus and conductivity. Ihrner *et al* (2017) utilized a combination very suitable for an SBE when combining a conventional liquid solvent/Li-salt electrolyte with a bis-phenol-A based methacrylate monomer that resembles a conventional vinyl ester resin often used for advanced composites. Fully phase separated SBE with two percolating intermingled phases was made utilizing photoinduced free radical polymerization of the monomer system. Using different monomer stiffness values in the range of 360–750 MPa were obtained while simultaneously having ion conductivities between $1\text{--}2 \cdot 10^{-4} \text{ S cm}^{-1}$. The presence of two percolating phases was verified since the SBEs showed structural integrity at the same time as the liquid electrolyte could be fully extracted from the SBE. The utilized photopolymerization is however limited to systems that are transparent in the UV-range why a thermally induced polymerization route more recently was developed (Schneider *et al* 2019). This thermally induced polymerization process makes conventional production processes used for composite manufacturing possible as later described in section 4. An optimized curing scheme was $80\text{--}90\text{ }^{\circ}\text{C}$ for 30 min which yielded a monomer conversion more than 90%. Schneider *et al* (2019) further demonstrated that the thermal curing could be performed in presence of carbon fibres without any impact on the curing rate.

Looking more in detail into the thermally cured systems it reveals SBEs with porous morphology as seen in the SEM pictures in figure 7. All liquid electrolyte was removed soaking the SBE in water demonstrating that there was no detectable amount of electrolyte trapped in closed voids. Approximately 39 wt% of electrolyte was used with a retained high structural integrity of the SBE.

All thermally cured SBEs exhibit a similar morphology with structural features in the submicron range, i.e. pore sizes in the range of 50–200 nm. Mechanical analysis using DMA (dynamic mechanical analysis) revealed a broad glass transition temperature and a modulus at ambient temperature around 500 MPa. The ionic conductivities were for all samples around $2 \cdot 10^{-4} \text{ S cm}^{-1}$.

Recently He *et al* (2019) proposed an alternative structural battery electrolyte. They proposed a particle reinforced poly(ethylene oxide) (PEO) solid-state electrolyte. The composite polymer electrolyte was realised reinforcing PEO with $\text{Li}_{6.4}\text{La}_3\text{Zr}_{1.4}\text{Nb}_{0.6}\text{O}_{12}$ (LLZNO) fillers. He and co-workers found that the incorporation of LLZNO fillers significantly improved the ionic conductivity of the composite electrolytes. The improvement was explained to be a combined result of increased amorphous region of PEO and pathways of ion transport. A wide electrochemical window of 5.2 V was demonstrated. The assembled solid $\text{LiFePO}_4/\text{PEO-0.5LLZNO}/\text{Li}$ batteries were shown to possess a discharge capacity of 153 mAh g^{-1} at the rate of 0.5 C and $60\text{ }^{\circ}\text{C}$.

4. Structural battery half-cells

In this section we describe some paths on the integration of carbon fibres and SBE to make structural battery half-cells, both negative and positive.

4.1. Laminated negative half-cells

In order make laminated carbon fibre structural negative half-cells, one needs to combine carbon fibres and the SBE described in section 3.2 into a load carrying composite lamina. This was recently done by Johannisson *et al* (2018) by using a standard vacuum infusion technique of a dry spread fibre bundle. The infusion was done on a glass plate with vacuum bag so the lamina could be cured through the glass plate after infusion using UV-light, see figure 8.

After curing the lamina was tested both electrochemically and mechanically, the latter both before and after electrochemical cycling. The results are very promising. The electrochemical capacity was around 230 mAh g^{-1} of carbon fibre after 10 galvanostatic charge/discharge cycles at C/10. Manufacturing of a single layer, and a very thin lamina, resulted in low fibre volume fraction, around 20% only. Still, the measured mechanical properties were quite good and are summarised in table 1.

As seen in table 1, the modulus in the fibre direction is moderate due to the low volume fraction. This value will increase with a higher fibre volume fraction. The transverse modulus and the estimated shear modulus on the other hand are not that much lower than for structural carbon composite laminas showing that the SBE has quite good mechanical properties. The strength values are preliminary but still quite promising. There was a

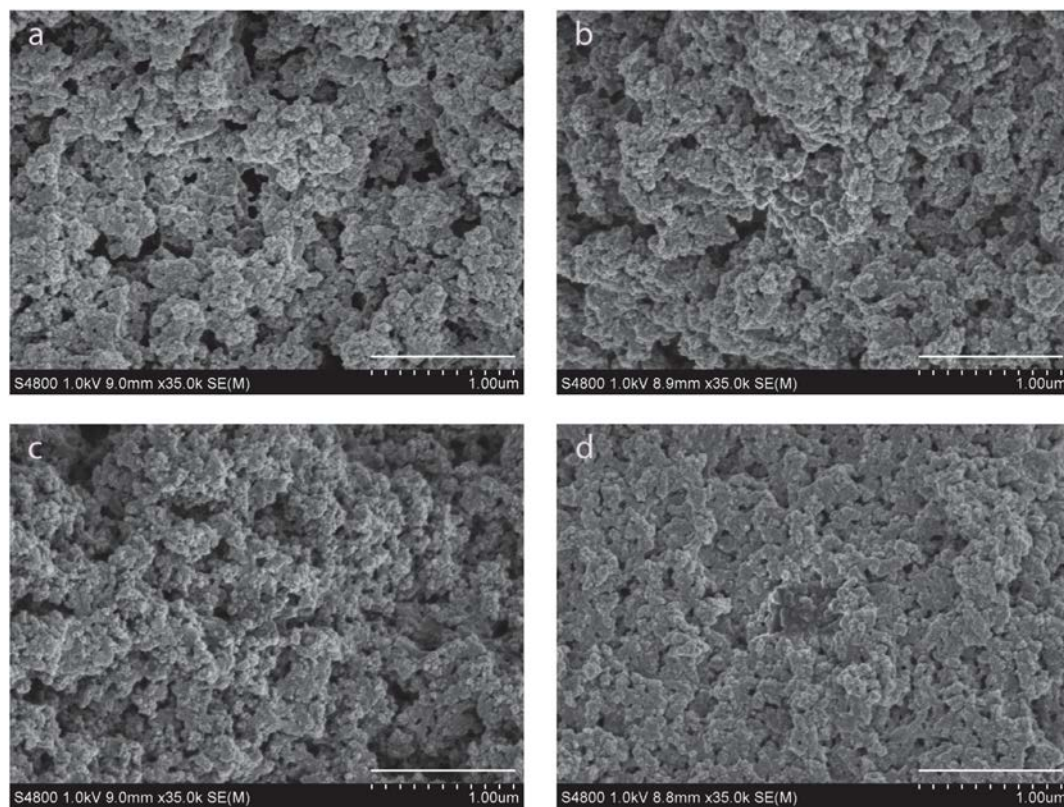


Figure 7. SEM images of SBEs cured at 70, 80, 90 °C ((a)–(c), respectively) in comparison to the corresponding system cured photoinduced polymerization (d) reprinted with permission from (Schneider *et al* (2019)). Copyright 2019 American Chemical Society.

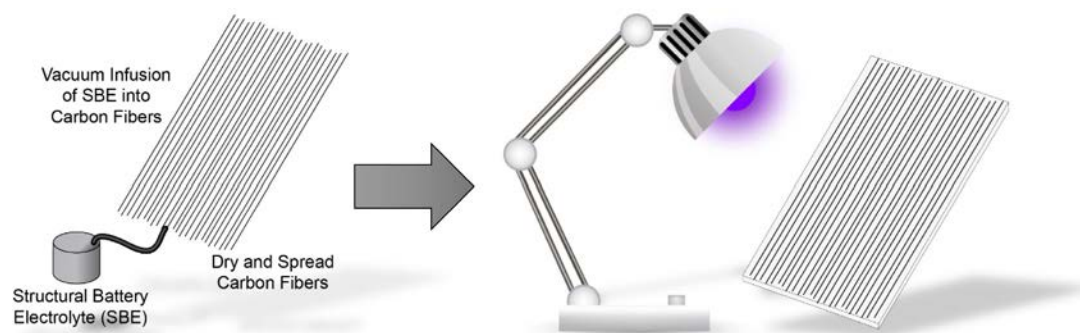


Figure 8. Schematic of infusion of a structural carbon fibre/SBE half-cell lamina.

Table 1. Mechanical properties of carbon fibre lamina half-cell reprinted from (from Johansson *et al* (2018)), Copyright 2018, with permission from Elsevier.

Modulus and strength	Before cycling	After cycling
E_L (GPa)	52	52
E_T (GPa)	1.7	1.9
G_{LT} (GPa)	1.5	1.6
σ_L^t (MPa)	980	960
σ_T^t (MPa)	12	15
σ_L^c (MPa)	980	850
σ_T^c (MPa)	12	12
τ_{LT} (MPa)	13	14

worry that the volume changes in the fibres during charge and discharge (described in section 2.4) would potentially decrease the fibre to SBE adhesion. However, this does not seem to be the case as both the transverse and shear strengths remain unchanged, at least after 10 cycles. This was further supported by SEM imaging, which

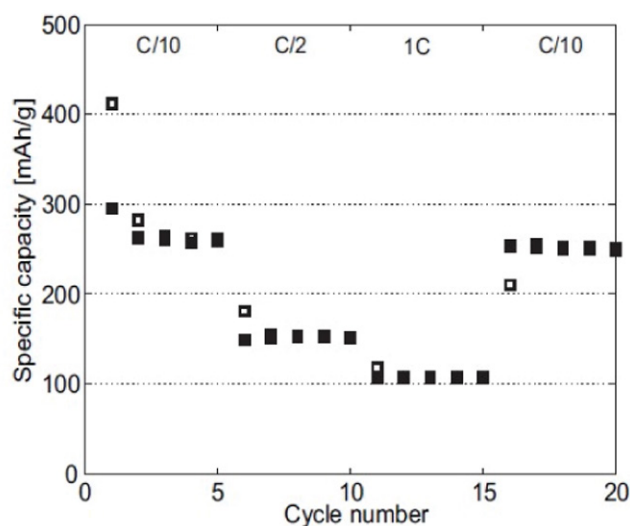


Figure 9. Lithiation (unfilled squares) and delithiation (filled squares) of electrocoated, reprinted from (Leijonmarck *et al* (2013)), Copyright 2013, with permission from Elsevier.

confirmed two things: the SBE phase separation was the same at the fibre/SBE interface as in bulk SBE, confirming ion transport through the interface, and fracture surfaces from before and after cycling looked essentially the same, both leaving SBE residue on the fibres indicating good adhesion.

Yu *et al* (2017) made laminated structural battery half-cells from thicker (0.21 mm) carbon fibre electrodes with T700 fibres employing an epoxy/ionic liquid structural electrolyte. The battery half-cells were made into coin cells and electrochemically cycled versus Li metal. A reversible capacity of approximately 15 mAh g^{-1} at best was reported by Yu *et al* (2017). Tensile stiffness data presented for the structural battery half-cells was for the fibre direction and hence dominated by the carbon fibres.

4.2. Micro-battery negative half-cells

Laminated structural battery composites, where the electrode layers are separated by an insulating material of a significant thickness, rely on highly ion conductive structural battery electrolytes. Current homogenous electrolytes (see section 3.1) require very small separator thickness (Asp and Greenhalgh 2014). For this reason, Asp and co-workers (Leijonmarck *et al* 2013, Carlson 2013) developed negative half-cells and battery full cells (alias the 3D-fibre battery) from individual polymer electrolyte coated carbon fibres, as illustrated in figure 2(b).

Leijonmarck *et al* (2013) developed a method to coat individual carbon fibres in a yarn with a homogeneous thin solid polymer electrolyte (SPE), see section 3.1. Approximately 500 nm thick methyl methacrylate coatings were applied onto the carbon fibres via an electro-polymerisation process in solution with a Li-triflate salt as supporting electrolyte. The Li-ion content in the solid polymer coating was enough to allow for the battery function. Under these conditions, being electrically insulating the SPE coating works as separator between fibres as well as between the fibres and any surrounding positive electrode material in a battery application. The electrochemical performance of a negative electrode from coated IMS65 fibres in a half-cell using lithium metal as counter electrode is depicted in figure 9. The coating does not deteriorate the cycling characteristics of the carbon fibre type used. At low currents (C/10) a specific capacity $250\text{--}260 \text{ mAh g}^{-1}$ was measured and after the first two cycles and at high currents (1 C) up to 107 mAh g^{-1} was recorded. These results are in line with studies on unsized IMS65 carbon fibres used as negative electrodes by Kjell *et al* (2011).

4.3. Positive half-cells

To date only a limited number of studies on the design, manufacture and characterisation of the positive electrode have been published. Hagberg *et al* (2018) described a path to manufacture structural positive electrodes via electrophoretic deposition (EPD) of LiFePO_4 (LFP), carbon black and polyvinylidene fluoride (PVDF) onto carbon fibres, see figure 10. The carbon fibres simultaneously act as reinforcement and current collectors. Electrochemical characterisation demonstrated a specific capacity of up to 110 mAh g^{-1} with good rate performance and high coulombic efficiency. Furthermore, the cell was stable during cycling, with a capacity retention of approximately 50% after 1000 cycles. Mechanical tests on coated and uncoated carbon fibres demonstrated good adhesion between the coating and the fibre.

In a recent study, Bouton *et al* (2019) present an alternative method to coat the carbon fibres with LFP particles. The method is a repeated dip coating process to generate a layer-by-layer (LbL) assembly of LFP particles has been chosen. The process results in a few hundred nanometre thick coating layers. The dipped carbon fibres are

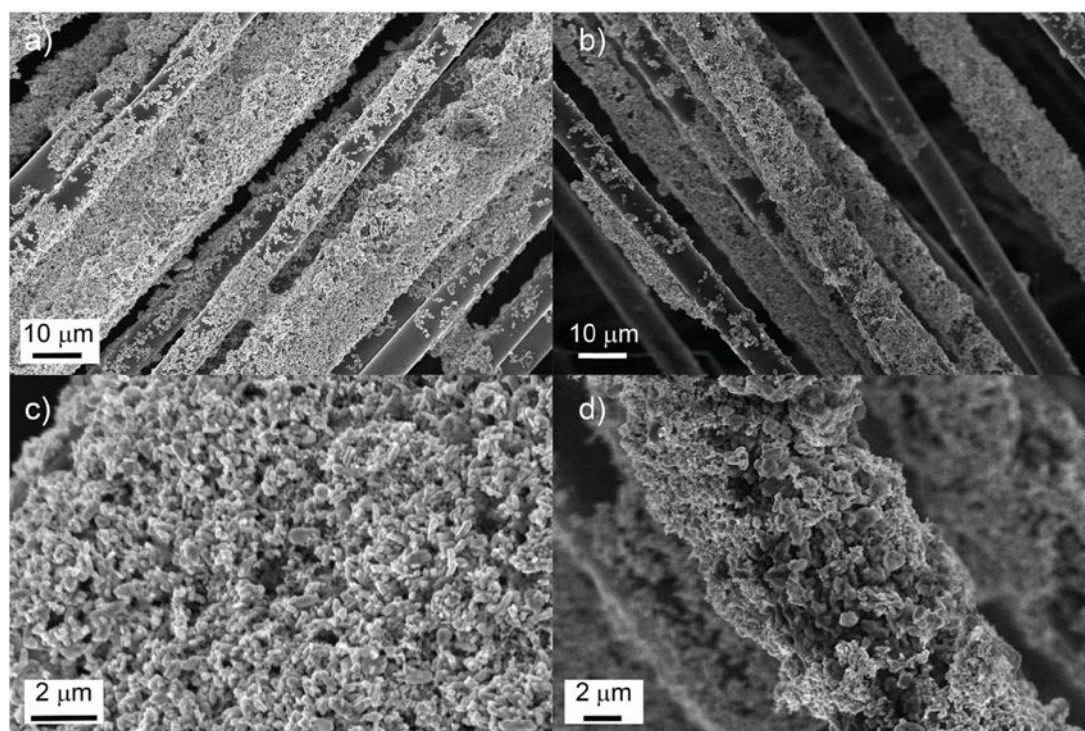


Figure 10. SEM images of LFP coated carbon fibres using electrophoretic deposition. (a) and (c) before cycling, (b) and (d) after cycling. Magnifications (a) 1000x, (b) 1000x, (c) 7000x, (d) 4000x. The active electrode material (LFP particles), conductive additive (carbon black) and binder (PVDF) were found to be well dispersed on the surface of the fibres (reprinted from (Hagberg *et al* (2018)), Copyright 2018, with permission from Elsevier).

heated up to 450 °C to carbonise the organic binders used in the solution. The LbL-electrodes showed a specific capacity close to 100 mAh g⁻¹. This is close to the capacity of LFP-coated aluminium foils, commonly used as commercial positive electrodes in conventional battery cells.

5. Architectures

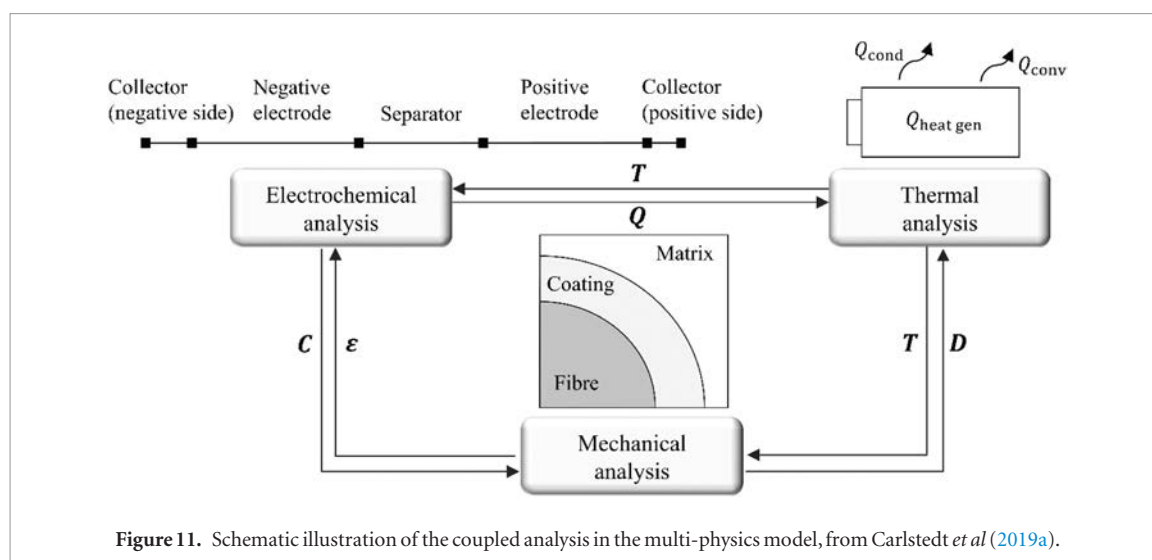
The need for high energy and power density has immediate implication on the architectural designs of structural battery composites. In this section two material architectures for structural battery composites are presented: the laminated and the 3D-fibre battery designs schematically illustrated in figure 2. We start and describe the obvious laminate lay-out, separating the positive and negative electrodes with an electrically insulating, lithium ion conductive, separator layer (i.e. the traditional battery and composite laminate design). Following this, an approach making each carbon fibre into a negative electrode in a 3D-fibre battery design by coating carbon fibres with an approximately 500 nm thick SPE sheath is presented.

5.1. Laminated structural battery

As mentioned above the laminated structural battery is what first comes to mind to make a structural battery composite. Both conventional batteries and composites are laminated structures. However, there is an inherent problem to make laminated structural battery composites: the use of a solid polymer electrolyte/matrix material.

Wetzel (2004) and his team at ARL developed the first laminated structural battery composite material. ARL built a device using a metal mesh coated with a positive electrode material, a carbon fibre fabric acting as a negative electrode, a fibre glass separator layer, and a structural solid block co-polymer electrolyte matrix (Wong *et al* 2007). However, the composite did not work as a battery due to poor electrical insulation. Later, Ekstedt *et al* (2010) and Carlson (2013) were able to build working laminated structural battery composites. Carlson (2013) used an IMS65 carbon fibre woven fabric as the negative electrode, a bi-continuous multifunctional polymer electrolyte system with an ionic liquid, developed for structural supercapacitors by Imperial College London, on a LiFePO₄ coated metal foil positive electrode. The negative and positive electrode had copper and aluminium connectors, respectively.

A schematic illustration of a state-of-the-art laminated structural battery composite is presented in figure 2(a). The device consists of two electrodes. The negative electrode is made from carbon fibres. The positive electrode is made from carbon fibres coated with e.g. a lithium metal oxide or phosphate, such as LiFePO₄. The two electrodes are separated by an electrically insulating thin film, typically a polymer. The separator needs to be thin to reduce losses from ion currents in the battery. The three plies, i.e. the electrodes and the separator



are infused by a structural battery electrolyte, as those discussed in section 3. Bi-continuous structural battery electrolytes (Ihrner *et al* 2017, Schneider *et al* 2019) are preferred due their higher multifunctional performance compared to homogenous block co-polymer electrolytes. Finally, current collectors are introduced for electron currents. To date, no data are available for the laminated structural battery device.

5.2. 3D-fibre structural battery

Asp and co-workers (Carlson 2013, Asp *et al* 2016) prepared a semi-structural 3D carbon fibre battery cell, as schematically illustrated in figure 2(b). The battery was made from a tow of approximately one thousand IMS65 carbon fibres. The tow had been coated and dried according to the procedure described by Leijonmarck *et al* (2013). The coating was polymerised in a polytetrafluoroethylene (PTFE) rig from a solution containing monofunctional SR550 monomer from Sartomer, DMF and Li-triflate, leaving grafted polymer chains on the fibres. The battery was built under argon atmosphere where coated fibres made up a structure containing electrode material, current collector and a thin separator. The rig, containing the coated CFs, was attached to an aluminium sheet (current collector), in such a way that the coated CFs were in contact with the metal. A slurry consisting of LiFePO_4 :Super-P carbon:PVDF 54:34:12 by weight in DMF was applied onto the CFs, where after the DMF was evaporated leaving a positive electrode introduced in contact with both the coated CFs and the aluminium current collector. The 3D-battery was electrochemically cycled at $C/5$. The capacity of this battery was at best 60% of the used LiFePO_4 (102 mAh g^{-1} compared to theoretically 170 mAh g^{-1}). Nevertheless, the result is promising for the concept of carbon fibre batteries. However, extensive work remains to up-scale the manufacturing process of this material. Currently, only stamp-sized 3D-batteries, from a few thousand carbon fibres can be made.

6. Modelling

To model the coupled mechanical, thermal and electrochemical processes that occur in a structural battery multi-physics models must be developed. Recently, Carlstedt *et al* (2019a) presented a coupled analysis for structural battery composites, see figure 11. The essential couplings between the physical domains are illustrated as arrows between boxes where T is the temperature field, C is the lithium concentration in the active electrode materials, ϵ are the mechanical strains, Q is the generated heat due electrochemical cycling and D is the energy dissipation.

To estimate the electrical performance, related to the battery functionality of this material, electrochemical analysis needs to be performed. This analysis allows estimation of the electrical performance of the material related to electrical power, current, etc. During electrochemical cycling heat is generated or absorbed (Q) and the lithium concentration in the active electrode materials (C) is altered. It has been shown that the volume and elastic properties of electrode materials such as carbon fibres and positive electrode particles are affected by lithium-ion concentration (Qi *et al* 2010, Jacques *et al* 2013b). This means that the battery functionality is coupled with the thermal and mechanical analysis. Moreover, mechanical strains (ϵ) will affect the electrochemical process, e.g. mechanical fracture of constituents, etc and energy dissipation (D) will generate heat. Finally, the heat distribution inside the material and exchange with the surroundings (T) will affect both the mechanical and electrical properties of the material. Hence, to estimate the complete performance of the material with respect to the different physical phenomena refined modelling techniques that allow for two-way data exchange between the different physical models are required.

6.1. Constituent-level analysis

6.1.1. Effect of galvanostatic cycling on 3D-fibre battery constitutive properties.

Given that the electrode materials undergo significant volume change during electrochemical cycling the elastic properties of the composite may be affected by the state of charge (SOC). Substantial volume change will effectively result in a variation of fibre volume fraction in the composite for different SOC. In addition, the constituents may undergo change in their elastic properties. In fact, since the carbon fibre tow stiffness is constant for different levels of lithiation the fibres longitudinal modulus must be reduced. Jacques *et al* (2013b) indicated that the diameter increases approximately five percent as it becomes fully lithiated. A change in fibre moduli (i.e. E_z , E_r and G_{zr}) may significantly change the composite's mechanical properties. Carlstedt *et al* (2019b) developed an analytical model to investigate how the elastic properties of the 3D-fibre structural battery composite are affected by changes in volume and stiffness of the constituents associated with a change in SOC. Carlstedt *et al* (2019b) present results from a parametric study performed to analyse how different design parameters such as volume fraction of active materials, stiffness of constituents, type of positive electrode material, etc affect the moduli of the structural battery composite for extremes in SOC. Indeed, the composite's transverse elastic properties E_T and G_{TT} and the in-plane shear modulus G_{LT} were found to be highly affected by the SOC for critical configurations, while the longitudinal stiffness E_L was not. Fibre volume fraction and properties of the coating (stiffness and Poisson's ratio) were identified as critical design parameters. For configurations with a high fibre volume fraction ($V_f \geq 0.6$) and Young's modulus of the solid polymer electrolyte coating of 1 GPa or higher a change in transverse stiffness E_T up to 30% from electrochemical cycling was predicted. This shows that the effects of SOC on the elastic properties may be crucial to consider when designing a 3D structural battery.

In addition to the volume changes heat will be generated during electrochemical cycling. Potentially, the generated heat will additionally affect the elastic properties of the structural battery composite as well as alter the internal stress state. To date, only one study has been reported which considers diffusion induced stresses in combination with heat generation from ion and electron currents in a structural battery (Carlstedt and Asp 2019). Note that heat generated in a structural battery is generally higher than in conventional batteries due to the lower ion and electron conductivities in the SBE and carbon fibre than in their liquid electrolyte and copper connector counterparts.

Carlstedt and Asp (2019) present predictions of the internal stress state in a 3D-fibre structural battery composite due to a combination of heat generation and volume change of electrode materials occurring during electrochemical cycling. The results show that heat generation during electrochemical cycling must be accounted for when evaluating the internal stress state. For a C-rate of 1 and large lamina dimensions a temperature increase of approximately 35 °C is predicted at full charge. Such temperature increase will significantly affect the internal stress state and change the elastic properties of the structural battery composite.

6.1.2. Damage analysis

A multi-scale physics based electrochemical model to describe the 3D-fibre battery containing a coupled system of nonlinear partial differential equations (PDE) was proposed by Xu *et al* (2018a, 2018b). The PDEs describe the spatial and time-dependent variation in Li concentration in the constituents. At the beginning of charging, all available Li is stored in the active material of the matrix. As the charging progresses via electrochemical reactions, lithium ions are transported to the fibre, starting at the coating/matrix interface, see figure 2(b). The difference in Li concentration at the centre of the fibre and the fibre surface is negligible. However, due to low ionic conductivity in the matrix, there is a Li concentration gradient arising in the matrix during charging. This concentration gradient is equalized closer to full charge. At full charge, the Li distribution in both fibre and matrix is uniform.

The insertion expansion-induced stresses in the transversely isotropic carbon fibres are calculated through a thermo-mechanical analogy (Xu *et al* 2018a, 2018b, Xu and Varna 2019, Carlstedt and Asp 2019). Figure 12 shows the stress distributions in the fibre (F), coating (C) and matrix (M) at four instants in time at 1 C-charging in absence of mechanical loads. The initial state, corresponding to completely delithiated fibre and fully lithiated matrix, is assumed stress free.

As shown in figure 12, all stresses are highest at full charge. Consequently, damage is most likely to form at full charge. The high tensile hoop stress, σ_θ , built up during charging indicates that radial cracks may form at the coating/matrix interface. Radial cracks are important as they may contribute to debonding, and even failure, under mechanical in-service loading. Furthermore, such debonding is likely to impair electrochemical performance since Li-ion transport is hindered.

Xu and Varna (2019) used linear elastic fracture mechanics to study propagation of radial matrix cracks and subsequent debond at the coating/matrix interface in a 3D-fibre structural battery composite (figure 13). The load case considered was pure electrochemical loading (1 C charging), i.e. only battery operation with no mechanical load. Crack propagation was studied by calculating energy release rate (ERR) in 2D FEM models assuming square packing of fibres with a radial crack introduced at the SBE/matrix interface.

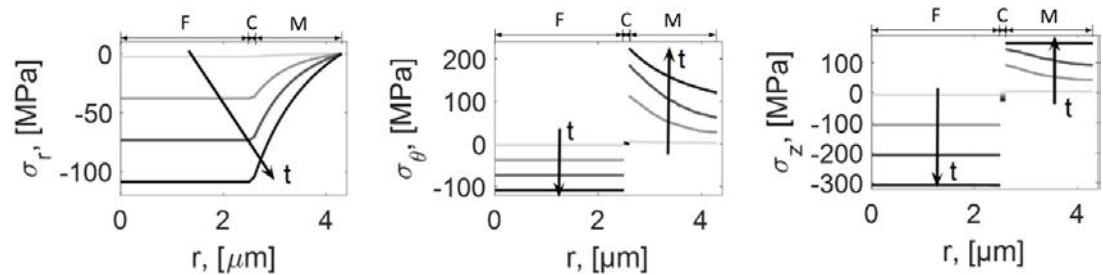


Figure 12. Stress distribution in the constituents during charging. (a) Radial stress. (b) Hoop stress. (c) Axial stress. Radial position, r , is zero at the fibre centre Reproduced with permission from (Xu and Varna (2019)).

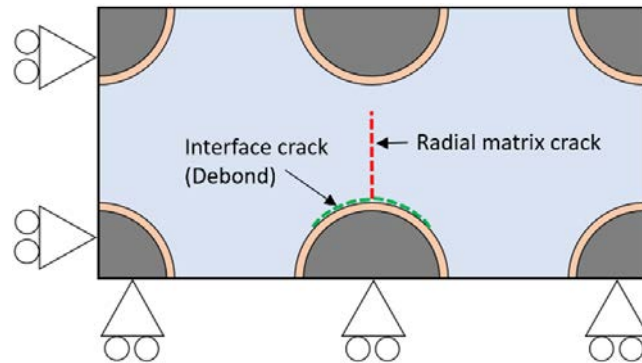


Figure 13. Model geometry and boundary conditions for crack analysis in a 3D-fibre structural battery composite material.

For an electrochemically balanced 3D-fibre structural battery ($V_f = 0.34$), results show that crack growth is unstable. The crack is found to grow towards its closest neighbour. For an undamaged composite, there is no risk for debonding to occur. However, in the presence of a radial crack, large tensile radial and shear stresses at the coating/matrix interface may cause debonding. Results for ERR show that debond crack growth occurs in Mode II. Consequently, the formed interface crack is expected to remain closed, with the constituents remaining in contact through sliding. This may be beneficial for the electrochemical performance of the structural battery.

6.1.3. Effect of mechanical stress state on ion conductivity of structural polymer electrolytes

In a very recent study Grazioli *et al* (2019) proposed a coupled electrochemical-mechanical model for analysis of solid polymer electrolytes. They studied the effect of an applied mechanical load on the performance of the solid polymer electrolyte. They found the predicted conductivity of the solid polymer electrolyte to change considerably when a mechanical contribution was included in the analysis. Thus, stresses and deformations need to be accounted for in the design of structural batteries as they are expected to experience high mechanical stresses from in-service loads.

6.2. Laminate level analysis

As discussed above, the carbon fibres in the negative electrode expand and contract during charge and discharge. In a laminated battery there are also positive electrodes, for example carbon fibres coated with an active material (e.g. LiFePO_4 particles). These particles will also expand and contract during charge and discharge. Thus, both the negative and positive electrodes will expand and contract, however, not the same amount and not the same in the fibre direction as in the transverse direction.

An analytical model was developed for the prediction of the shape change of an arbitrary laminated structural battery laminate by Dionisi *et al* (2017). The aim of this model was to be able to make lay-ups that would minimise overall deformations of the battery laminate by alternating the stacking sequence, and possibly also by finding elaborate schemes for charging and discharging the cells individually. The aim was also to predict the free edge stresses which could potentially lead to delaminations in the laminate. The model was based on an extension of classical lamination theory and leads to closed form solutions of deformation, strains and stresses, although the stress solution eventually must be solved numerically.

In terms of overall deformation of the laminated structural battery composites one must of course rely on symmetric stacking sequences in order to avoid bending (ensuring a zero B -matrix). Still, it is not possible to avoid any in-plane deformation although they can be smaller or larger depending on the stacking. Regarding

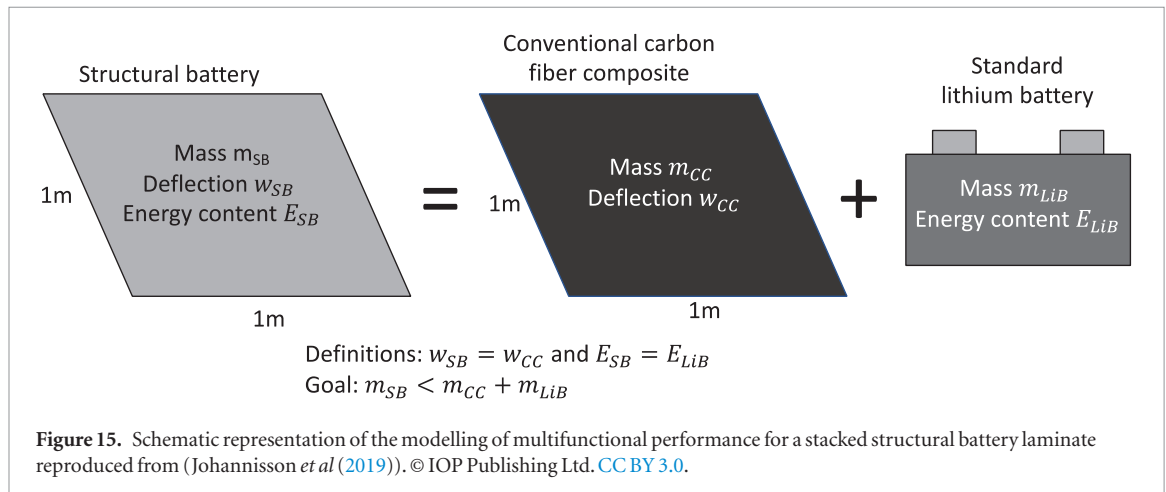
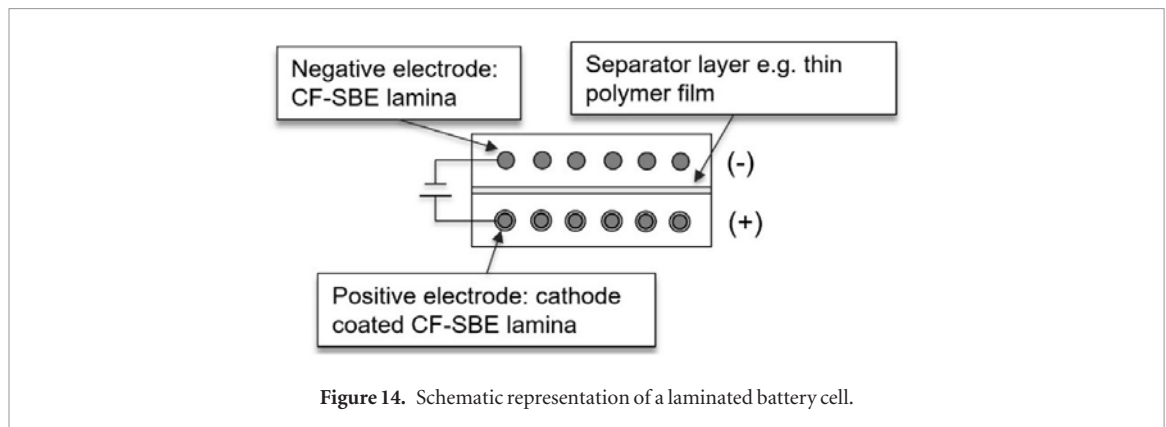


Table 2. Mass saving potential for structural battery composites (data from Johannisson *et al* (2019)).

Application	Today's design	Weight saving potential 'target' (in %)
Aircraft interior panel	Glass fibre composite sandwich structure	67
Car roof in steel	Steel 0.8 mm	62
Hull of electric ferry	Carbon fibre composite sandwich structure	11
Lap-top casing	Aluminium	38

interlaminar stresses it was seen that it is beneficial to place the negative electrodes on the outside of the laminate and keeping the positive electrodes closer to the middle surface, at least for simple cross-ply laminates.

6.3. Conceptual battery design and multifunctional performance

The laminated battery cell is a material that can potentially save significant weight on a systems level compared to separate components for structural and battery functions. As schematic representation of a laminated battery cell is illustrated in figure 14.

In this set-up the negative electrode lamina consists of structural battery electrolyte (SBE) developed by Ihrner *et al* (2017) reinforced with carbon fibres. The positive electrode lamina also consists of SBE but is instead reinforced with lithium-based electrode material (e.g. LiFePO_4) coated carbon fibres. A separator layer is also needed between the two laminae to avoid short-circuit. The mechanical and electrical performance of the laminated structural battery composites can be assessed by estimating the in-plane elastic properties of the laminate using Classical Laminate Theory and the specific capacity and energy density of the complete component.

Based on these performance metrics it is possible to estimate the overall multifunctional performance of the laminated battery cell and to compare the performance with that of monofunctional based systems. To identify the key parameters to improve multifunctionality and their impact on the performance, the framework has been extended by refining the modelling of the mechanical and electrical performance and defining parametric variables for the design parameters of the battery cell. To identify possible weight reductions the performance of the structural battery is compared with the performance of the separate structural and battery components.

Here, a structural battery is modelled with the dimensions $1\text{ m} \times 1\text{ m}$, built up by stacked positive and negative electrodes with SBE. The structural battery has a known mass m_{SB} and energy storage E_{SB} , see figure 15. This

structural battery is then loaded with a distributed pressure and simply supported boundary conditions which results in a deflection at its midpoint (w_{SB}) to find a single stiffness metric for the laminate. For comparison a state-of-the-art carbon fibre and epoxy composite plate is modelled to have the same deflection due to the same load (same global stiffness), as well as a standard lithium ion battery with the same energy content as the structural battery. Then one can find the mass of the two monofunctional systems m_{CC} and m_{LiB} that performs like the multifunctional structural battery. The goal of the modelling is to find parameters which maximize the mass saving potential of the structural battery with respect to the separate structure and battery.

Potential mass saving offered by replacing conventional carbon fibre composite and standard lithium ion battery with a structural battery can be estimated for any application. In a recent study Johannisson *et al* (2019) employed this model and compared weight savings for several scenarios. The benchmark model uses targeted performance metrics (conductivity, thicknesses, rate dependence, capacities, etc) for the structural battery. Mass saving estimates were presented for several applications; a composite aircraft interior panel, a car roof made from steel, a carbon fibre composite boat hull and an aluminium lap-top casing. The mass saving by using a multifunctional structural battery, compared to a monofunctional structural material and a separate lithium ion battery is given by the mass saving in percent by:

$$MS\% = \frac{m_{CC} + m_{LiB} - m_{SB}}{m_{CC} + m_{LiB}} \cdot 100.$$

The results are very promising leading the mass saving potential estimates given in table 2.

7. Concluding remarks

The structural battery composite is a novel lightweight material. Not only is the density of the composite material constituents low, these constituents also demonstrate exceptional ability to perform two vital functions for lightweighting. Firstly, carbon fibres are stiff and strong, with unprecedented specific mechanical properties. Carbon fibres also have exceptional electrochemical characteristics, with very high specific capacity and coulombic efficiency. Secondly, structural battery electrolytes are now available that can efficiently transfer mechanical loads and transport Li-ions. As consequence, numerous structural battery composite architectures can now be realised. Having said that, there is still little research performed on how to design and manufacture positive structural electrodes. Similarly, only a few attempts to make structural battery full cells have been reported to date. This is partly due to the lack of structural positive electrodes. Finally, new modelling approaches, considering the coupled thermomechanical-electrochemical problem are being developed. Multifunctional performance analyses with such tools rely on an extensive data base, which is currently lacking.

In this paper we provide an overview of research performed on structural battery composites to date. Substantial work has been performed. However, significant work on the structural battery full cell and its manufacture and validation remains before structural battery composites offer a solution for mass-less energy storage in future electric road, air and sea transport applications. To date, no show-stoppers for the realisation of structural battery composites have been identified. Nevertheless, issues related to up-scaling of the manufacture process, power management and connectivity as well as recycling are still to be addressed (Asp and Greenhalgh 2015).

Acknowledgments

The authors would like to thank the following sources for funding this research: Swedish Energy Agency grant #37712-1, the Swedish Research Council, projects 2017-03898 and 621-2014-4577, the strategic innovation program LIGHTer (funding provided by Vinnova, the Swedish Energy Agency and Formas), H2020 Clean Sky II project SORCERER no. 738085 and work supported by the Air Force Office of Scientific Research under award number FA9550-17-1-0244. The entire research group within the program is acknowledged for valuable discussion and input on this work.

ORCID iDs

Leif E Asp  <https://orcid.org/0000-0003-0630-2037>

References

- Asp L E and Greenhalgh E S 2014 Structural power composites *Compos. Sci. Technol.* **101** 41–61
- Asp L E and Greenhalgh E S 2015 Multi-functional composites for load bearing and electrical power storage *Multi-Functionality of Polymer Composites* ed K Friedrich and U Breuer (Amsterdam: Elsevier)
- Asp L E, Bismarck A, Carlson T, Lindbergh G, Leijonmarck S and Kjell M 2016 A structural battery half-cell, a structural battery and their manufacture, PCT Patent No. EP 2 893 582 B1 (*International Application* No. WO 2014/033276)

- Bouton K, Chen B, Zenkert M and Lindbergh G 2019 Structural positive electrodes for multifunctional composite materials *Proc. 22nd Int. Conf. on Composite Materials (ICCM22) (Melbourne, Australia)*
- Carlson T 2013 Multifunctional composite materials—design, manufacture and experimental characterisation *Doctoral Thesis* Luleå University of Technology, Sweden
- Carlson T, Ordéus D, Wysocki M and Asp L E 2010 Structural capacitor materials made from carbon fibre epoxy composites *Compos. Sci. Technol.* **70** 1135–40
- Carlstedt D and Asp L E 2019 Thermal and diffusion induced stresses in a structural battery under galvanostatic cycling *Compos. Sci. Technol.* **179** 69–78
- Carlstedt D, Marklund E and Asp L E 2019b Effects of state of charge on elastic properties of 3D structural battery composites *Compos. Sci. Technol.* **169** 26–33
- Carlstedt D, Xu J, Runesson K, Larsson F and Asp L E 2019a Unit cells for multiphysics modelling of structural battery composites *Proc. 22nd Int. Conf. on Composite Materials (ICCM22) (Melbourne, Australia)*
- Croce F, Appetecchi G B, Persi L and Scrosati B 1998 Nanocomposite polymer electrolytes for lithium batteries *Nature* **394** 456–8
- Dionisi F, Harnden R and Zenkert D 2017 A model to analyse deformations and stresses in structural batteries due to electrode expansions *Compos. Struct.* **179** 580–9
- Duan S, Liu F, Pettersson T, Creighton C and Asp L E 2019 Transverse modulus measurement of carbon fibre by atomic force microscope and nanoindentation *Proc. 22nd Int. Conf. on Composite Materials (ICCM22) (Melbourne, Australia)*
- Ekstedt S, Wysocki M and Asp L E 2010 Structural batteries made from fibre reinforced composites *Plast. Rubber Compos.* **39** 148–50
- Fenton D E, Parker J M and Wright P V 1973 Complexes of alkali metal ions with poly(ethylene oxide) *Polymer* **14** 589
- Fredi G et al 2018 Graphitic microstructure and performance of carbon fibre Li-ion battery electrodes *Multifunct. Mater.* **1** 015003
- Grazioli D, Verners O, Zadin V, Brandell D and Simone A 2019 Electrochemical-mechanical modeling of solid polymer electrolytes: impact of mechanical stresses on Li-ion battery performance *Electrochim. Acta* **296** 1122–41
- Greenhalgh E S et al 2015 Mechanical, electrical and microstructural characterisation of multifunctional structural power composites *J. Compos. Mater.* **49** 1823–34
- Hagberg J, Leijonmarck S and Lindbergh G 2016 High precision coulometry of commercial PAN-based carbon fibres as electrodes in structural batteries *J. Electrochem. Soc.* **163** A1790–7
- Hagberg J, Maples H A, Alvim K S P, Xu J, Johannisson W, Bismarck A, Zenkert D and Lindbergh G 2018 Lithium iron phosphate coated carbon fibre electrodes for structural lithium ion batteries *Compos. Sci. Technol.* **162** 235–43
- Hansen C M 1967 *The Three Dimensional Solubility Parameter and Solvent Diffusion Coefficient, Their Importance in Surface Coating Formulation* (Copenhagen: Technical University of Denmark, Danish Technical Press)
- He K, Chen C, Fan R, Liu C, Liao C, Xu Y, Tang J and Li R K Y 2019 Polyethylene oxide/garnet-type $\text{Li}_{6.4}\text{La}_3\text{Zr}_{1.4}\text{Nb}_{0.6}\text{O}_{12}$ composite electrolytes with improved electrochemical performance for solid state lithium rechargeable batteries *Compos. Sci. Technol.* **175** 28–34
- Ihrner N and Johansson M 2017 Improved performance of solid polymer electrolytes for structural batteries utilizing plasticizing co-solvents *J. Appl. Polym. Sci.* **134** 44917
- Ihrner N, Johannisson W, Sieland F, Zenkert D and Johansson M 2017 Structural lithium ion battery electrolytes via reaction induced phase-separation *J. Mater. Chem. A* **5** 25652–9
- Jacques E, Kjell M H, Zenkert D and Lindbergh G 2013a Piezo-electrochemical effect in lithium-intercalated carbon fibres *Electrochem. Commun.* **35** 65–7
- Jacques E, Kjell M H, Zenkert D and Lindbergh G 2014 The effect of lithium-intercalation on the mechanical properties of carbon fibres *Carbon* **68** 725–33
- Jacques E, Kjell M H, Zenkert D, Lindbergh G and Behm M 2011 Impact of the mechanical loading on the electrochemical capacity of carbon fibres for use in energy storage composite materials *ICCM-18 (Korea, August 2011)*
- Jacques E, Kjell M H, Zenkert D, Lindbergh G and Behm M 2013b Expansion of carbon fibres induced by lithium intercalation for structural electrode applications *Carbon* **59** 246–54
- Jacques E, Kjell M H, Zenkert D, Lindbergh G, Behm M and Willgert M 2012 Impact of electrochemical cycling on the tensile properties of carbon fibres for structural lithium-ion composite batteries *Compos. Sci. Technol.* **72** 792–8
- Jacques E, Lindbergh G, Zenkert D, Leijonmarck S and Hellqvist Kjell M 2015 Piezo-electrochemical energy harvesting with lithium-intercalating carbon fibres *ACS Appl. Mater. Interfaces* **7** 13898–904
- Johannisson W, Ihrner N, Zenkert D, Johansson M, Carlstedt D, Asp L E and Sieland F 2018 Multifunctional performance of a carbon fibre UD lamina electrode for structural batteries *Compos. Sci. Technol.* **168** 81–7
- Johannisson W, Zenkert D and Lindbergh G 2019 Modelling of multifunctional performance of a carbon fibre structural battery *Multifunct. Mater.* **2** 035002
- Johnson D J 1987 Structure-property relationships in carbon fibres *J. Phys. D: Appl. Phys.* **20** 286–91
- Kanno R, Takeda Y, Ichikawa T, Nakanishi K and Yamamoto O 1989 Carbon as negative electrodes in lithium secondary cells *J. Power Sources* **26** 535–43
- Kjell M H, Jacques E, Zenkert D, Behm M and Lindbergh G 2011 PAN-based carbon fibre electrodes for structural lithium-ion batteries *J. Electrochem. Soc.* **158** A1455–60
- Kjell M H, Zavalis T G, Behm M and Lindbergh G 2013 Electrochemical characterization of lithium intercalation processes of PAN-based carbon fibres in a microelectrode system *J. Electrochem. Soc.* **160** A1473–81
- Ladpli P, Nardari R, Kopsaftopoulos F and Chang F K 2019 Multifunctional energy storage composite structures with embedded lithium-ion batteries *J. Power Sources* **414** 517–29
- Lavin G J 2001 Carbon fibres *High-Performance Fibres* J W S Hearle (Cambridge, MA: Woodhead Publishing) ch 5, pp 156–90
- Leijonmarck S, Carlson T, Lindbergh G, Asp L E, Maples H and Bismarck A 2013 Solid polymer electrolyte coated carbon fibres for structural and novel micro batteries *Compos. Sci. Technol.* **89** 149–57
- Lendlein A and Trask R S 2018 Multifunctional materials: concepts, function-structure relationships, knowledge-based design, translational materials research (editorial) *Multifunct. Mater.* **1** 010201
- Liu P, Sherman E and Jacobsen A 2009 Design and fabrication of multifunctional structural batteries *J. Power Sources* **189** 646–50
- Nest J-F L, Gandini A and Cheradame H 1988 Crosslinked polyethers as media for ionic conduction *Br. Polym. J.* **20** 253–68
- O'Brien D J, Baechle D M and Wetzel E D 2011 Design and performance of multifunctional structural composite capacitors *J. Compos. Mater.* **45** 2797–809
- Park S-J 2015 *Carbon Fibres (Springer Series in Materials Science vol 210)* (Dordrecht: Springer)
- Qi Y, Guo H, Hector L G and Timmons A 2010 Threefold increase in the Young's modulus of graphite negative electrode during lithium intercalation *J. Electrochem. Soc.* **157** A558–66

- Schneider L, Ihrner N, Zenkert D and Johansson M 2019 Bicontinuous electrolytes via thermally initiated polymerization for structural lithium ion batteries *ACS Appl. Energy Mater.* **2** 4362–9
- Schutzzeichel M O H, Kletschkowski T, Linde P and Asp L E 2019 Experimental characterization of multifunctional polymer electrolyte coated carbon fibres *Funct. Compos. Struct.* **1** 025001
- Seitz M E *et al* 2017 Influence of silicone distribution and mobility on the oxygen permeability of model silicone hydrogels *Polymer* **118** 150–62
- Shirshova N, Bismarck A, Greenhalgh E S, Johansson P, Kalinka G, Marczewski M, Shaffer M S P and Wienrich M 2014 Composition as a means to control morphology and properties of epoxy based dual-phase structural electrolytes *J. Phys. Chem. C* **118** 28377–87
- Shirshova N, Qian H, Shaffer M S P, Greenhalgh E S, Curtis P T, Kucernak A and Bismarck A 2013 Structural composite supercapacitors *Composites A* **46** 96–107
- Snyder J F, Carter R H and Wetzel E D 2007 Electrochemical and mechanical behavior in mechanically robust solid polymer electrolytes for use in multifunctional structural batteries *Chem. Mater.* **19** 3793–801
- Snyder J F, Wetzel E D and Watson C M 2009b Improving multifunctional behaviour in structural electrolytes through copolymerisation of structure- and conductivity-promoting monomers *Polymer* **50** 4906–16
- Snyder J F, Wong E L and Hubbard C W 2009a Evaluation of commercially available carbon fibres, fabrics and papers for potential use in multifunctional energy storage applications *J. Electrochem. Soc.* **56** A215
- Stephan M A 2006 Review on gel polymer electrolytes for lithium batteries *Eur. Polym. J.* **42** 21–42
- Thomas J and Qidwai S 2004 Mechanical design and performance of composite multifunctional materials *Acta Mater.* **52** 2155–64
- Thomas J, Qidwai S, Pouge W III and Pham G 2005 The design and application of multifunctional structure-battery materials systems *JOM* **57** 18–24
- Wetzel E D 2004 Reducing weight: multifunctional composites integrate power, communications and structures *AMPTIAC Q.* **8** 91–5
- Willgert M, Kjell M H and Johansson M 2012 Effect of lithium salt content on the performance of thermoset lithium battery electrolytes *Polymers for Energy Storage and Delivery: Polyelectrolytes for Batteries and Fuel Cells* ACS Symposium series K Page *et al* (Washington, DC: American Chemical Society) pp 55–65
- Willgert M, Kjell M H, Jacques E, Behm M, Lindbergh G and Johansson M 2011 Photoinduced free radical polymerization of thermoset lithium battery electrolytes *Eur. Polym. J.* **47** 2372–8
- Willgert M, Kjell M H, Lindbergh G and Johansson M 2013 New structural lithium battery electrolytes using thiolene chemistry *Solid State Ion.* **236** 22–9
- Willgert M, Leijonmarck S, Lindbergh G, Malmström E and Johansson M 2014 Cellulose nanofibril reinforced composite electrolytes for lithium ion battery applications *J. Mater. Chem. A* **2** 13556–64
- Wong E L, Baechele D M, Xu K, Carter R H, Snyder J F and Wetzel E D 2007 Design and processing of structural composite batteries *Proc. SAMPE 2007 (Baltimore, MD, USA, June 2007)* (SAMPE)
- Wright P V 1975 Electrical conductivity in ionic complexes of poly(ethylene oxide) *Br. Polym. J.* **7** 319–27
- Wysocki M, Asp L E and Ekstedt S 2010 Structural polymer electrolyte for use in multifunctional energy storage devices *ECCM 14 (Budapest, Hungary)*
- Xu J and Varna J 2019 Matrix and interface microcracking in carbon fiber/polymer structural micro-battery *J. Compos. Mater.* **53** 3615–28
- Xu J, Lindbergh G and Varna J 2018a Carbon fiber composites with battery function: stresses and dimensional changes due to Li-ion diffusion *J. Compos. Mater.* **52** 2729–42
- Xu J, Lindbergh G and Varna J 2018b Multiphysics modeling of mechanical and electrochemical phenomena in structural composites for energy storage: Single carbon fiber micro-battery *J. Reinf. Plast. Compos.* **37** 701–15
- Yu Y, Zhang B, Feng M, Qi G, Tian F, Feng Q, Yang J and Wang S 2017 Multifunctional structural lithium ion batteries based on carbon fiber reinforced plastic composites *Compos. Sci. Technol.* **147** 62–70
- Yu Y, Zhang B, Wang Y, Qi G, Tian F, Yang J and Wang S 2016 Co-continuous structural electrolytes based on ionic liquid, epoxy resin and organoclay: effects of organoclay content *Mater. Des.* **104** 126–33

PAPER • OPEN ACCESS

A residual performance methodology to evaluate multifunctional systems

To cite this article: Wilhelm Johannisson *et al* 2020 *Multifunct. Mater.* **3** 025002

View the [article online](#) for updates and enhancements.

Multifunctional Materials



PAPER

OPEN ACCESS

RECEIVED

28 March 2020

ACCEPTED FOR PUBLICATION

29 April 2020

PUBLISHED

28 May 2020

Original content from this work may be used under the terms of the [Creative Commons Attribution 4.0 licence](#).

Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI.



A residual performance methodology to evaluate multifunctional systems

Wilhelm Johannisson¹ , Sang Nguyen², Göran Lindbergh³, Dan Zenkert¹ , Emile S Greenhalgh², Milo S P Shaffer⁴ and Anthony R J Kucernak⁴

¹ Department of Aeronautical and Vehicle Engineering, KTH Royal Institute of Technology, SE-100 44, Stockholm, Sweden

² Aeronautics Department, Imperial College London, South Kensington, London SW7 2AZ, United Kingdom

³ Department of Chemical Engineering, KTH Royal Institute of Technology, SE-100 44, Stockholm, Sweden

⁴ Department of Chemistry, Imperial College London, South Kensington, London SW7 2AZ, United Kingdom

E-mail: wjoh@kth.se

Keywords: multifunctional, residual, performance, metric

Abstract

The development of multifunctional materials and structures is receiving increasing interest for many applications and industries; it is a promising way to increase system-wide efficiency and improve the ability to meet environmental targets. However, quantifying the advantages of a multifunctional solution over monofunctional systems can be challenging. One approach is to calculate a reduction in mass, volume or other penalty function. Another approach is to use a multifunctional efficiency metric. However, either approach can lead to results that are unfamiliar or difficult to interpret and implement for an audience without a multifunctional materials or structures background.

Instead, we introduce a comparative metric for multifunctional materials that correlates with familiar design parameters for monofunctional materials. This metric allows the potential benefits of the multifunctional system to be understood easily without needing a holistic viewpoint. The analysis is applied to two different examples of multifunctional systems; a structural battery and a structural supercapacitor, demonstrating the methodology and its potential for state-of-the-art structural power materials to offer a weight saving over conventional systems. This metric offers a new way to communicate research on structural power which could help identify and prioritise future research.

1. Introduction

There is a growing interest in adopting multifunctionality to produce more efficient and environmentally-friendly materials and structures to address the challenges of lightweighting and energy storage [1]. For instance, NASA regards multifunctionality as a critical attribute for future deep space missions [2]. Multifunctionality is achieved by combining one or more, conventionally disparate, functions into a single material or structure [3], which can include load carrying, structural health monitoring, morphing, self-healing, energy storage, etc [4, 5]. Fibre composite materials are a particularly attractive platform for developing multifunctional systems, as they already deliver excellent mechanical performance whilst offering considerable versatility in composition and microstructure. Furthermore, the relatively benign fabrication conditions for carbon fibre reinforced polymer (CFRP) composites (moderate temperatures and pressures) permits the incorporation of processing-sensitive functions. Introducing functions beyond structural load bearing can be achieved with or without modifying the constituents of the composite material [6], however, this typically results in some compromise in the structural performance. In *multifunctional materials* [7], the constituents (e.g. fibres, matrices, etc) undertake more than one function throughout the whole material, whilst in *multifunctional structures*, the multiple functions are provided by distinct monofunctional materials which have been assembled together. Carbon fibre reinforced polymer composites are particularly appropriate choices for multifunctional applications [8], because the carbon

fibres offer both attractive mechanical and electrical properties [9]. One class of multifunctional material which is currently receiving considerable attention is structural power composites [10], which store electrochemical energy within the composite component: various devices have been fabricated, including structural batteries [11], structural capacitors [12], structural supercapacitors [13] and structural fuel cells [14]. Structural power composites typically contain a structural electrolyte which needs to satisfy two contrasting requirements: high ionic conductivity for good electrochemical performance and high elastic modulus for good mechanical performance.

1.1. Structural batteries

Structural batteries use the same lithium-ion battery technology as their conventional monofunctional counterparts: two electrodes, the cathode (positive electrode) and the anode (negative electrode), and a separator layer placed in an ion-conducting electrolyte. When current is applied and the battery charges, lithium ions shuttle from the cathode to the anode, creating an electrical potential difference between the electrodes. The opposite reactions enable the battery to deliver electrical power. First developed in a structural form by the US Army Research Laboratory [15], researchers have taken different approaches to exploit this technology. The first, laminated structural batteries (LSB), are effectively fibre-matrix laminates, in which each layer is designed for both electrochemical and mechanical properties [16]. Carbon fibres are used as electrodes for their excellent load carrying capability and good lithium ion intercalation properties, which is essential for efficient battery design [17]. While in conventional batteries a liquid electrolyte is used, LSBs require a solid electrolyte to maintain rigidity and load-carrying capability. A structural battery electrolyte (SBE) [18] based on a two-phase percolating network has been developed, which allows ionic redox reactions to take place while ensuring structural rigidity. Research has also been targeted towards improving the performance of the anode, with silicon-coated carbon nanotubes presenting a 2.5 times higher specific capacity than previous anodes [19].

In parallel, a different approach to making structural batteries has also been developed [20]: instead of using laminates of carbon fibres as electrodes, they use individual fibres. By depositing the cathode and electrolyte onto the carbon fibre and encapsulating the coated fibres in a multifunctional matrix, a 3D structural battery was created.

1.2. Structural supercapacitors

Supercapacitors are appropriate electrochemical energy storage devices when high power and high cyclability are required. Unlike batteries, supercapacitors harness electrical energy from electrostatics. Two high surface area electrodes are separated by an ionically-conducting but electrically-insulating separator all soaked in an electrolyte. The accumulated charge at the interface between each electrode and the electrolyte stores the electrical energy. Structural supercapacitors operate in the same manner whilst also providing mechanical load carrying capabilities. A structural supercapacitor has been developed using two woven carbon fibre electrodes in a multifunctional matrix, separated by a woven glass fibre separator [21]. Increasing the surface area of the electrodes results in a higher capacitance [22]. Carbon aerogel modified electrodes have been used to greatly increase the surface area of the electrodes and yield specific power values up to 1.2 kW kg^{-1} [23]. However, their specific energy, around 1 Wh kg^{-1} , remains lower than that of conventional supercapacitors and the cell working voltage is limited by the electrolyte breakdown voltage, which is typically around 2.7 V [24].

1.3. Multifunctional efficiency and performance metrics

For multifunctional materials or structures to be advantageous compared to conventional, compartmentalised, monofunctional constituents, they need to demonstrate an improvement in, for instance, overall system mass, volume or cost. A common metric to rank the performance of multifunctional systems in comparison to monofunctional systems is through a single metric called the multifunctional efficiency index: $\eta_{mf} = \eta_s + \eta_d$, where η_s and η_d are the structural and device efficiencies (i.e. multifunctional performance divided by monofunctional performance [25–27]). If η_{mf} exceeds unity, the multifunctional material offers a mass or volume saving over the conventional monofunctional system. A more complex analysis methodology for multifunctional composites is a material-architecture index [28], which has been applied to structural battery laminate designs. This method involves eight steps similar to those used for typical design optimisation problems to derive the indices for stiffness and strength-limited designs at minimum weight. This methodology is limited to symmetric composite beams with uniform cross-sections and materials. However, one difficulty with applying such metrics is that few publications provide enough data to fully compare multifunctional with monofunctional system properties.

To enable engineers to decide how well a multifunctional material can perform for a given application, there is a need for a more robust comparative methodology. One major challenge for a multifunctional

material is that a single separate function alone will never outperform a corresponding state-of-the-art monofunctional material or device. Hence, if only considering a single function (such as bending deflection) of a multifunctional system, the gain of the multifunctional system can easily be overlooked. To address this challenge, we present a new metric to permit a holistic comparison of the properties in multifunctional systems against the equivalent monofunctional reference properties. The approach is to project the properties from the multifunctional design space to the monofunctional parameter space by normalizing by the additional material requirement, rather than the total quantity of material. The resulting residual specific properties for the multifunctional material can be compared to specific properties of the monofunctional systems.

The residual specific properties are demonstrated using two application examples; a structural battery and a structural supercapacitor using current state-of-the-art performance data for commercial devices and projected performance data for the multifunctional systems. These examples show how the methodology can be implemented, and the resulting residual specific properties indicate how structural power composites can potentially outperform equivalent monofunctional systems.

2. Methodology

The methodology herein is described for a system which has some defined requirements for electrical properties and mechanical properties. The best monofunctional solution, which can satisfy these requirements and minimize a penalty-parameter that depends on the desired outcome of the design process is considered known. Traditionally, mass is used for transport applications, whereas volume may be more important for consumer electronics. Herein, we will for simplicity consider mass saving, though the methodology is the same for any penalty-parameter. Traditionally, system mass savings are made by decreasing the mass of the sub-systems independently, e.g. the mass of a battery pack and the mass of the load-carrying structure. Alternatively, a multifunctional design can be considered which also satisfies the same system requirements. The multifunctional design combines the electrical and mechanical properties into the same material or structure as shown in figure 1.

For the monofunctional electrical sub-system, it has given electrical requirements of energy w and power p . To decrease the mass, a screening is made of different solutions and an optimal selection with the highest specific properties $\bar{w}$ and $\bar{p}$ is chosen, since it reaches the lowest electrical sub-system mass m_1 given by:

$$m_1 = \max \left(\frac{w}{\bar{w}}, \frac{p}{\bar{p}} \right). \quad (1)$$

Similarly, the monofunctional structural sub-system can have many different requirements, including stiffnesses and strengths. These could include limitations on bending deflection z , in-plane stiffness A_x , shear strength τ_{xy} , etc. The optimal solution for maximizing the mass saving then has the best corresponding specific properties $\bar{z}$, $\bar{A}_x$, $\bar{\tau}_{xy}$, providing a structural sub-system mass m_2 as:

$$m_2 = \max \left(\frac{z}{\bar{z}}, \frac{A_x}{\bar{A}_x}, \frac{\tau_{xy}}{\bar{\tau}_{xy}} \right). \quad (2)$$

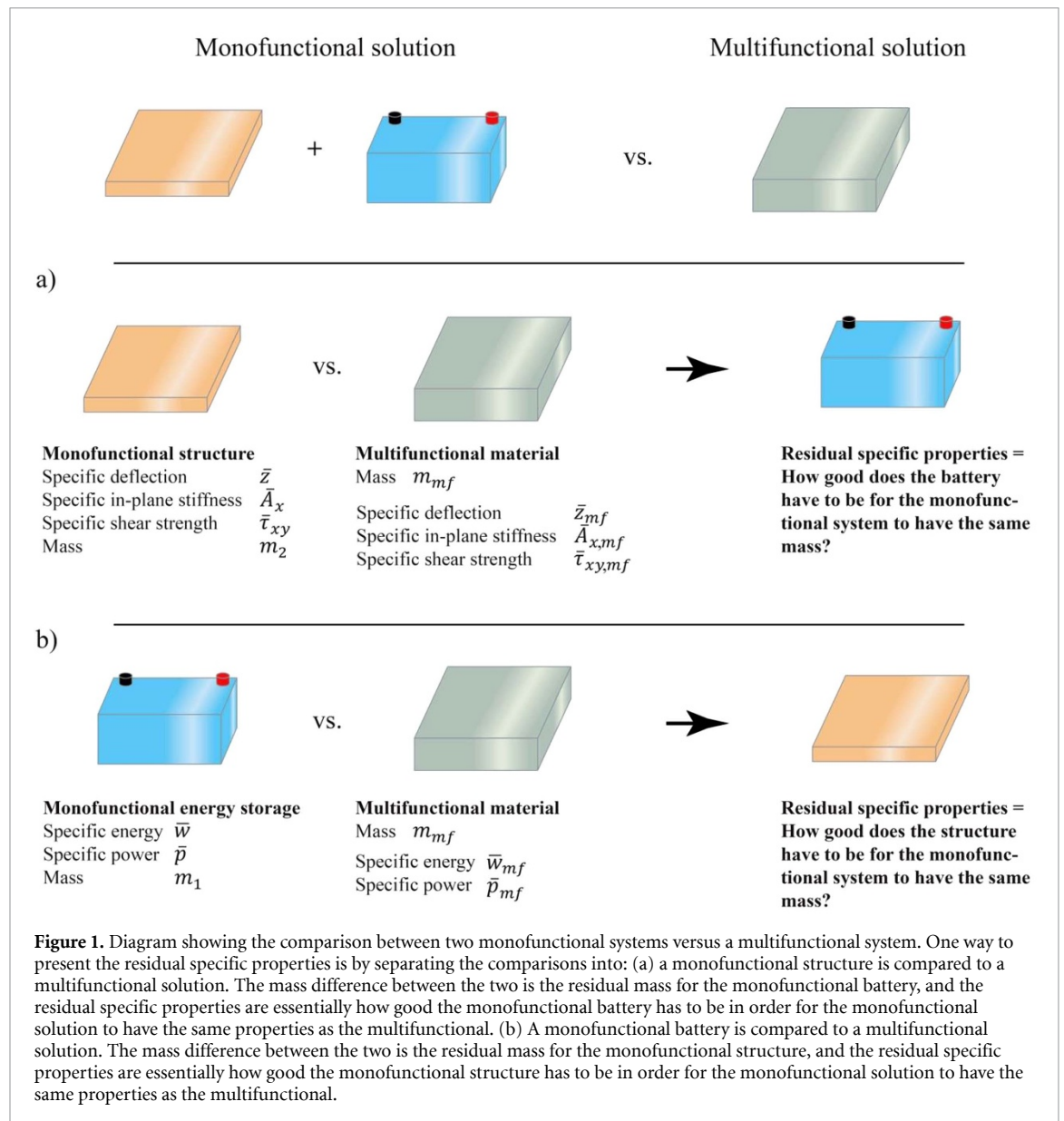
Often, the design of a system stops here, since a lowest possible system mass ($m_1 + m_2$) has been reached. Any further design considerations would follow the same procedure, possibly finding a solution with better specific properties which incrementally reduces the mass of that sub-system.

Alternatively, a multifunctional material can be used to fulfil all the requirements w , p , z etc. Traditionally, if such a multifunctional material is included in the design choices above, its specific properties are calculated by $\bar{w}_{mf} = \frac{w}{m_{mf}}$, $\bar{p}_{mf} = \frac{p}{m_{mf}}$, $\bar{z}_{mf} = \frac{z}{m_{mf}}$ and so on, where m_{mf} is the total mass of the multifunctional material. The challenge with multifunctionality in this case is that any multifunctional material can never have a larger $\bar{w}_{mf}$ than $\bar{w}$ or $\bar{p}_{mf}$ than $\bar{p}$, etc. and thus will always be considered inferior to monofunctional solutions and rejected. This is because the addition of a new function will invariably add some mass to the multifunctional system, and so there are lower bounds on the multifunctional system mass as given in equation (3).

$$m_{mf} > m_2 \text{ and } m_{mf} > m_1. \quad (3)$$

These lower limits are directly linked to the quality and performance of the systems that are being compared: i.e. it is not possible to compare a high-performance multifunctional system with low performance monofunctional systems.

We now present two relative masses to be considered when comparing a multifunctional system with two monofunctional sub-systems. These *residual masses* are the differences in mass between the multifunctional



system and the corresponding monofunctional sub-systems providing equal functional performance and are given as:

$$m_{res,1} = m_{mf} - m_2 \quad (4)$$

$$m_{res,2} = m_{mf} - m_1. \quad (5)$$

Essentially, $m_{res,2}$ is the surplus mass for the monofunctional energy-storing system, such that the monofunctional sub-systems have the same total mass as the multifunctional system (figure 1(a)), and similarly $m_{res,1}$ is the surplus mass for the monofunctional structural system, such that the monofunctional sub-systems have the same total mass as the multifunctional system (figure 1(b)). The multifunctional residual specific properties are then calculated as:

$$\bar{w}_{res} = \frac{w}{m_{res,i}}, \bar{p}_{res} = \frac{p}{m_{res,i}}, \bar{z}_{res} = \frac{z}{m_{res,i}}, \text{ etc} \quad (6)$$

where $m_{res,i}$ (i = parameter 1, parameter 2) is defined as the residual mass of function i in the multifunctional system and the parameter number specifies the multifunctional aspect begin considered.

Utilizing these residual specific properties in the design choices for the systems above could highlight the benefits from incorporating a multifunctional material and allow direct comparisons to be made with the traditional monofunctional design parameters for monofunctional sub-systems. Essentially, this

Table 1. Data for a structural battery, a CFRP panel and a lithium ion battery given from [29].

System demands	Monofunctional data		Multifunctional data	
Midpoint deflection limit z	Total mass m	3.54 kg	Structural battery mass	2.64 kg
0.65 mm	Structure mass m_2	1.87 kg	Residual structure mass $m_{res,2}$	0.97 kg
Total energy w	Battery mass m_1	1.67 kg	Residual battery mass $m_{res,1}$	0.77 kg
286 Wh	Battery specific energy $\bar{w}$	171 Wh kg ⁻¹	Residual specific energy $\bar{w}_{res}$	371 Wh kg ⁻¹
			Multifunctional efficiency index η_{mf}	1.26

methodology identifies what specific performance level the monofunctional components would need to achieve to match the weight saving of a multifunctional system. If the monofunctional component performance levels are below the residual specific values identified, the multifunctional system represents a preferable holistic design solution.

3. Examples

As a demonstration, the methodology presented in Section 2 it has been applied to two structural energy storage materials: a structural battery and a structural supercapacitor. The results from these examples are also evaluated using the multifunctional efficiency index approach as presented by Snyder *et al* [25].

3.1. Structural battery

Consider an example system that requires an energy w of 286 Wh and can simultaneously support a uniformly distributed pressure of 1 N m⁻² (as presented in [29]) with minimal deflection for a given system mass. In this example, other requirements such as power or strength are not considered because structural battery data for these properties have not yet been determined.

An optimised *monofunctional* system could contain an electrical sub-system (mass $m_1 \approx 1.67$ kg) made from standard Li-ion batteries with a specific energy $\bar{w}$ of 171 Wh kg⁻¹ [29]. The structural sub-system could be a 1 m × 1 m × 1 mm simply-supported CFRP panel [29]. This panel is made from unidirectional epoxy prepreg with a quasi-isotropic (QI) lay-up ([0, 90, -45, 45]_s) and $m_2 \approx 1.87$ kg [29]. Excluding the panel's self-weight, the midpoint bending deflection z under this pressure loading would be 0.65 mm.

Now consider an optimised *multifunctional* structural battery composite panel with the same area and QI lay-up capable of storing the same required energy (286 Wh) [29]. For this structural battery panel to not exceed the midpoint deflection limit reached by the CFRP panel under the same 1 N m⁻² load case, the thickness of the structural battery panel needs to be 1.4 mm [29]. This structural battery that can match the monofunctional energy requirement and deflection limit (w and z) has a total mass of about 2.64 kg. Thus, the residual analysis for this structural battery yields a residual specific energy $\bar{w}_{res}$ of 371 Wh kg⁻¹ (table 1), and a multifunctional efficiency index [25] of 1.26.

An insight into interpreting the values in table 1 is the following: by utilizing a 2.64 kg structural battery, and comparing this to a 1.87 kg monofunctional structure, the 0.77 kg residual mass (according to equation (4)) of the structural battery is the equivalent 'energy storing' constituent of the whole system. Thus, a monofunctional battery containing the same amount of energy would need a specific energy of 286 Wh/0.77 kg = 371 Wh kg⁻¹ (equation (6)).

3.2. Structural supercapacitor

For the purpose of demonstrating the applicability of the residual analysis method, here we consider a slightly different design scenario and assume that equation (1) leads to two functions being the limiting properties: electrochemical power and midpoint bending deflection. This example system needs a power p of 2.80 kW and must also support a uniformly distributed pressure of 1 N m⁻² with minimal deflection.

An optimised *monofunctional* system could contain an electrical sub-system (mass $m_1 = 0.68$ kg) made from state-of-the-art commercial supercapacitors with a specific power $\bar{p}$ of 4.10 kW kg⁻¹ [30]. The structural sub-system is the same 1 m × 1 m × 1 mm simply-supported CFRP panel described in the structural battery example ($m_2 = 1.90$ kg) [29].

Now consider an optimised *multifunctional* structural supercapacitor [31] panel with the same area and capable of delivering the same required power (2.80 kW). For this structural supercapacitor panel to not exceed the midpoint deflection limit reached by the CFRP panel under the same 1 N m⁻² load case, the mass of the structural supercapacitor panel needs to be 2.55 kg. Thus, the residual analysis for this structural supercapacitor yields a residual specific power $\bar{p}_{res} = 4.33$ kW kg⁻¹ (table 2) whilst the multifunctional efficiency index [25] is 1.01.

Table 2. Structural supercapacitor [31], CFRP panel and Maxwell 150 F supercapacitors [30] data.

System demands	Monofunctional data		Multifunctional data	
Midpoint deflection limit z	Total mass m	2.58 kg	Structural supercapacitor mass	2.55 kg
0.65 mm	Structure mass m_2	1.90 kg	Residual structure mass $m_{res,2}$	1.87 kg
Total power p	Supercapacitor mass m_1	0.68 kg	Residual supercapacitor mass $m_{res,1}$	0.65 kg
2.80 kW	Supercapacitor specific power $\bar{p}$	4.10 kW kg ⁻¹	Residual specific power $\bar{p}_{res}$	4.33 kW kg ⁻¹
			Multifunctional efficiency index η_{mf}	1.01

The data in table 2 can be interpreted as using a 2.55 kg structural supercapacitor compared to a 1.90 kg monofunctional structure yields a residual mass of 0.65 kg according to equation (4). Thus, a monofunctional supercapacitor must have a specific power (equation (6)) of 2.80 kW/0.65 kg = 4.33 kW kg⁻¹ for the combined monofunctional components to have equal mass to the structural supercapacitor. Conversely, a structural supercapacitor of 2.55 kg compared to 0.68 kg of monofunctional supercapacitors leaves 1.87 kg residual mass (equation (5)). The residual specific power slightly exceeds the monofunctional specific power. This comparison indicated that the state-of-the-art structural supercapacitor merits consideration as a potential solution. Further analysis may be performed to investigate other benefits achievable from using the multifunctional system, such as potential safety improvements from having a distributed rather than concentrated energy source.

4. Discussion and conclusion

This paper introduces a new methodology to compare residual specific properties of a multifunctional system to well-known conventional specific properties of monofunctional sub-systems. The residual specific properties are based on a residual mass, which is the difference in mass between the multifunctional system and the corresponding monofunctional component mass. The methodology computes the required performance of selected monofunctional components so that the combined mass of the monofunctional components is the same as that of the multifunctional material system.

This approach has an advantage over other multifunctional efficiency metrics [25–27] in that it provides values that are already familiar to engineers or scientists working in the respective fields. Besides, this residual metric can be directly compared in a screening of different material or energy/power storage options and does not require a holistic system viewpoint to be understood. This metric could also be expanded to evaluate potential volume or cost savings instead of mass, or one can incorporate other properties for comparing with monofunctional materials, structures or systems.

The residual specific properties presented in this paper has an inherent limitation, it cannot compare the systems if the mass of the multifunctional system is smaller than any of the monofunctional systems. This constraint is inherently fulfilled, since a material will almost certainly gain mass with added functions. But it imposes a restraint on the comparative monofunctional systems; they need to be of similar performance.

To gain a complete understanding of the performance enhancements provided by a multifunctional system, it is essential to have baseline monofunctional performance data with which to compare against. However, publications in this field presenting new multifunctional systems often lack this corresponding benchmark monofunctional data. Therefore, we recommend that future studies on new multifunctional systems (both multifunctional materials and multifunctional structures) would benefit from being accompanied by equivalent monofunctional performance results and the key limiting material properties for a given component/application corresponding to both functions. This complete data set would enable researchers in the field to accurately quantify and evaluate the relative improvements offered by the multifunctional system, facilitate progress in this field and potentially promote adoption of the new multifunctional system.

The residual specific metric presented here offers a new perspective on multifunctionality; it relates multifunctional performance parameters to common monofunctional performance parameters. This residual perspective can help to disseminate and emphasize the considerable potential of multifunctional materials, which could help identify needs for future research in the field.

Acknowledgments

This work has been carried out by combined efforts from KTH Royal Institute of Technology (departments of Aeronautical and Vehicle Engineering and Chemical Engineering) and Imperial College London

(departments of Aeronautics and Chemistry) through the joint research program EU Clean Sky 2 (SORCERER Project number 738085). The Swedish research group Kombatt is acknowledged for its synergism throughout this work.

The work was financed by the Swedish Research Council, projects 2017-03898 and 621-2014-4577, the strategic innovation program LIGHTer (funding provided by Vinnova, the Swedish Energy Agency and Formas), the Air Force Office of Scientific Research under award number FA9550-17-1-0244, the EPSRC Beyond Structural project (EP/P007465/1), the European Office of Aerospace Research and Development (IOE Grant FA9550-17-1-0251). Additionally, this work was supported by the Engineering and Physical Sciences Research Council [Grant Numbers EP/P006701/1], as part of the EPSRC Future Composites Manufacturing Research Hub.

ORCID iDs

Wilhelm Johannisson  <https://orcid.org/0000-0002-1194-9479>

Dan Zenkert  <https://orcid.org/0000-0002-9744-4550>

Anthony R J Kucernak  <https://orcid.org/0000-0002-5790-9683>

References

- [1] Narayana K J and Burela R G 2018 A review of recent research on multifunctional composite materials and structures with their applications *Mater. Today Proc.* **5** 5580–90
- [2] NASA 2015 SBIR 2015 Phase I Solicitation
- [3] González C, Vilatela J J, Molina-Aldareguía J M, Lopes C S and LLorca J 2017 Structural composites for multifunctional applications: current challenges and future trends *Prog. Mater. Sci.* **89** 194–251
- [4] Gibson R F 2010 A review of recent research on mechanics of multifunctional composite materials and structures *Compos. Struct.* **92** 2793–810
- [5] Bennett B 2010 Future multifunctional structures: composites needed *Composites World, High-Performance Composites*
- [6] Chung D D L 2019 A review of multifunctional polymer-matrix structural composites *Compos. Part B: Eng.* **160** 644–60
- [7] Saloni K, Pandremenos J, Paralikas J and Chrysosouris G 2009 Multifunctional Materials Used In Automotive Industry: A Critical Review *Engineering Against Fracture* ed S G Pantelakis and C A Rodopoulos (<https://www.springer.com/gp/book/9781402094019#aboutBook>) (Dordrecht: Springer Netherlands) pp 59–70
- [8] Friedrich K 2015 Chapter 1—routes for achieving multifunctionality in reinforced polymers and composite structures *Multifunctionality of Polymer Composites* ed K Friedrich and U Breuer (Oxford: William Andrew) pp 3–41
- [9] Forintos N and Czigany T 2019 Multifunctional application of carbon fiber reinforced polymer composites: electrical properties of the reinforcing carbon fibers—a short review *Compos. Part B: Eng.* **162** 331–43
- [10] Asp L E and Greenhalgh E S 2014 Structural power composites *Compos. Sci. Technol.* **101** 41–61
- [11] Zhang Y, Ma J, Singh A K, Cao L, Seo J, Rahn C D, Bakis C E and Hickner M A 2017 Multifunctional structural lithium-ion battery for electric vehicles *J. Intell. Mater. Syst. Struct.* **28** 1603–13
- [12] Chan K-Y, Jia B, Lin H, Hameed N, Lee J-H and Lau K-T 2018 A critical review on multifunctional composites as structural capacitors for energy storage *Compos. Struct.* **188** 126–42
- [13] Deka B K, Hazarika A, Kim J, Park Y-B and Park H W 2017 Recent development and challenges of multifunctional structural supercapacitors for automotive industries *Int. J. Energy Res.* **41** 1397–411
- [14] Hilton C D, Peairs D M, Lesko J J and Case S W 2011 A metric for characterization of multifunctional fuel cell designs *J. Fuel Cell Sci. Technol.* **8** 051008
- [15] Snyder J F, Carter R H and Wetzel E D 2007 Multifunctional structural composite batteries *Chem. Mater.* **19** 3793–801
- [16] Wong E L, Baechle D M, Xu K, Carter R H, Snyder J F and Wetzel E D 2007 Design and processing of structural composite batteries *Proc. of Society for the Advancement of Material and Process Engineering (SAMPE) Symp. and Exhibition* pp 1–15
- [17] Fredi G et al 2018 Graphitic microstructure and performance of carbon fibre Li-ion structural battery electrodes *Multifunct. Mater.* **1** 015003
- [18] Johannisson W, Ihrner N, Zenkert D, Johansson M, Carlstedt D, Asp L E and Sieland F 2018 Multifunctional performance of a carbon fiber UD lamina electrode for structural batteries *Compos. Sci. Technol.* **168** 81–87
- [19] Evanoff K, Benson J, Schauer M, Kovalenko I, Lashmore D, Ready W J and Yushin G 2012 Ultra strong silicon-coated carbon nanotube nonwoven fabric as a multifunctional lithium-ion battery anode *ACS Nano* **6** 9837–45
- [20] Asp L E, Carlson T, Leijonmarck S and Lindbergh G 2015 Realisation of structural battery composite materials *20th Int. Conf. on Composite Materials*
- [21] Greenhalgh E S et al 2015 Mechanical, electrical and microstructural characterisation of multifunctional structural power composites *J. Compos. Mater.* **49**
- [22] Zhang L et al 2013 Controlling the effective surface area and pore size distribution of sp² carbon materials and their impact on the capacitance performance of these materials *J. Am. Chem. Soc.* **135** 5921–9
- [23] Qian H, Kucernak A R, Greenhalgh E S, Bismarck A and Shaffer M S P 2013 Multifunctional structural supercapacitor composites based on carbon aerogel modified high performance carbon fiber fabric *ACS Appl. Mater. Interfaces* **5** 6113–22
- [24] Zang X, Shen C, Sanghadasa M and Lin L 2019 High-voltage supercapacitors based on aqueous electrolytes *ChemElectroChem* **6** 976–88
- [25] Snyder J F, Gienger E and Wetzel E D 2015 Performance metrics for structural composites with electrochemical multifunctionality *J. Compos. Mater.* **49**
- [26] O'Brien D J, Baechle D M and Wetzel E D 2011 Design and performance of multifunctional structural composite capacitors *J. Compos. Mater.* **45** 2797–809
- [27] Freund R, Lächelt U, Gruber T, Rühle B and Wuttke S 2018 Multifunctional efficiency: extending the concept of atom economy to functional nanomaterials *ACS Nano* **12** 2094–105

- [28] Thomas J P and Qidwai M A 2004 Mechanical design and performance of composite multifunctional materials *Acta Mater.* **52** 2155–64
- [29] Johansson W, Zerkert D and Lindbergh G 2019 Model of a structural battery and its potential for system level mass savings *Multifunct. Mater.* **2** 035002
- [30] Maxwell HC series ultracapacitors datasheet (available at: https://www.maxwell.com/images/documents/2_7_1_100_100_150F_ds_3001957_datasheet.pdf)
- [31] Greenhalgh E S *et al* Future challenges and industrial adoption strategies for structural supercapacitors *ICCM22 (Melbourne, Australia, 11-16 August)* pp 1–23

Shape-morphing carbon fiber composite using electrochemical actuation

Wilhelm Johannisson^a, Ross Harnden^a, Dan Zenkert^{a,1}, and Göran Lindbergh^b

^aDepartment of Aeronautical and Vehicle Engineering, KTH Royal Institute of Technology, SE-100 44 Stockholm, Sweden; and ^bDepartment of Chemical Engineering, KTH Royal Institute of Technology, SE-100 44 Stockholm, Sweden

Edited by David A. Weitz, Harvard University, Cambridge, MA, and approved February 28, 2020 (received for review December 5, 2019)

Structures that are capable of changing shape can increase efficiency in many applications, but are often heavy and maintenance intensive. To reduce the mass and mechanical complexity solid-state morphing materials are desirable but are typically nonstructural and problematic to control. Here we present an electrically controlled solid-state morphing composite material that is lightweight and has a stiffness higher than aluminum. It is capable of producing large deformations and holding them with no additional power, albeit at low rates. The material is manufactured from commercial carbon fibers and a structural battery electrolyte, and uses lithium-ion insertion to produce shape changes at low voltages. A proof-of-concept material in a cantilever setup is used to show morphing, and analytical modeling shows good correlation with experimental observations. The concept presented shows considerable promise and paves the way for stiff, solid-state morphing materials.

solid state | zero-power hold | structural composites | high stiffness | electrically controlled

Structures that can change their shape by morphing between two or more stable geometries are advantageous in a wide variety of applications such as aerospace, renewables, and robotics: for example, trimming of aerodynamic surfaces for steady-state conditions in aircraft and wind turbines, and deployment of satellite booms. The problem with current state-of-the-art morphing technologies is that they use systems of heavy mechanical motors, hydraulic/pneumatic pumps, or solenoids to create shape changes. These systems add parasitic weight, and are mechanically complex, adding to maintenance costs. One way to reduce the mechanical complexity is to use solid-state morphing materials.

A wide range of materials have been shown to exhibit controllable solid-state shape-changing capabilities. Typically, actuation devices can be characterized in terms of actuation force, strain, stiffness, operating frequency, and efficiency, among other parameters (1). Piezoelectric materials have proven to offer high operating frequencies and reliability; however, they are most often nonstructural, and rely on high operating voltages in order to deliver high actuation forces (2–4). Pseudocapacitive actuation materials are capable of delivering high actuation frequencies and high actuation strains at low operating voltages (5–12); however, they are most often reliant on liquid electrolytes for operation, which discounts their use as structural components. Shape-memory alloys are good actuation materials, and have been demonstrated in many applications in aerospace (13). Their use is however limited to applications where shape changes can be triggered by changes in temperature or pressure. All of the above also rely on a constant supply of power in order to maintain deformations, which limits their use in energy-sensitive applications. Intercalation-based actuation can offer high actuation forces at low voltages, as well as inherently having the ability to maintain deformations without a constant supply of power, known as a zero-power hold. However, intercalation actuation devices are limited by low operating frequency and have relied on liquid electrolytes to allow ion transport between

electrodes which has prevented any practical use in structural components (14–17).

In order for morphing structures to become more widely used—and hence enable more efficient design—there is a need for a morphable solid-state material that is lightweight and stiff, exhibits a zero-power hold, and is easy to control and integrate into existing structures. A material that can fulfill these needs is still to be conceived.

This article demonstrates a proof-of-concept for a stiff, morphable solid-state composite material. It is made from commercial carbon fibers and a structural battery electrolyte (SBE). By combining these elements we show that it is possible to form a low-density material with a stiffness higher than that of aluminum, that is morphable at voltages up to 1.5 V, exhibits an inherent zero-power hold, and can produce large deformations and high gravimetric actuation energies. The morphing material is characterized mechanically, and its behavior agrees well with modeling predictions.

Carbon fibers are a good candidate for creating multifunctional materials, having some of the best strength and stiffness to weight ratios of any commercially available material, and being electrically conductive. The microstructure of polyacrylonitrile-based carbon fibers is turbostratic and consists of graphitic and amorphous carbon (18). This structure is amenable to lithium (Li) storage, allowing carbon fibers to be used as negative electrodes in Li-ion batteries, with good electrochemical efficiency (19, 20). Graphite expands linearly by as much as 4.2% when Li is inserted into its microstructure through a well-known process known as intercalation (16). There is, however, no consensus on

Significance

Structures that can change their shape are advantageous in a wide variety of applications such as aerospace, renewables, and robotics. The problem with current shape-changing technologies is that they are either heavy, lack mechanical stiffness, or are hard to control. This paper demonstrates a shape-changing carbon fiber composite material, which is lightweight, has a stiffness higher than aluminum, and is electrically controlled. Future applications for this material could include trimming of aerodynamic surfaces for steady-state conditions in aircraft and wind turbines, and deployment of satellite booms.

Author contributions: W.J., R.H., D.Z., and G.L. designed research; W.J., R.H., and D.Z. performed research; W.J., R.H., and D.Z. contributed new reagents/analytic tools; W.J., R.H., D.Z., and G.L. analyzed data; and W.J., R.H., D.Z., and G.L. wrote the paper.

The authors declare no competing interest.

This article is a PNAS Direct Submission.

This open access article is distributed under [Creative Commons Attribution-NonCommercial-NoDerivatives License 4.0 \(CC BY-NC-ND\)](https://creativecommons.org/licenses/by-nc-nd/4.0/).

Data deposition: The raw data for Figs. 3 and 4 and *SI Appendix, Figs. S1 and S2 and Tables S1 and S2* are available in Mendeley Data (<https://doi.org/10.17632/4zky6h8w3v.1>).

¹To whom correspondence may be addressed. Email: danz@kth.se.

This article contains supporting information online at <https://www.pnas.org/lookup/suppl/doi:10.1073/pnas.1921132117/-DCSupplemental>.

First published March 25, 2020.

how Li inserts into amorphous carbon (21). Measurements on carbon fibers have shown that they expand along their fiber direction by up to 1% when inserted with Li (22). This expansion is reversible and approximately linear with the state of charge, which corresponds to the amount of inserted Li in the carbon fibers. The electrochemical insertion reaction requires low electrical potentials. The fibers will remain expanded when no current is running, thus exhibiting a zero-power hold. Such expansions have been proposed as a possible way to create linear actuation using liquid electrolytes (22). Additionally, it has been shown that even after 1,000 repeated Li insertion cycles the mechanical properties of carbon fibers remain largely unaffected (23). However, to realize a solid-state morphing material, a matrix is required that can both transfer mechanical load between fibers and conduct ions which enables the electrochemical functionality of the carbon fibers.

Solid electrolytes are being developed in order to improve conductivity, safety, and stability of Li batteries (24). However, these are structurally low performing and cannot be used to transfer mechanical load. An SBE has been developed recently for structural battery applications that adheres to carbon fibers, transfers mechanical load, conducts Li ions, and allows Li insertion into carbon fibers (25–27). The SBE consists of two

phases: a structural polymer backbone for mechanical load transfer and a liquid for ion conductivity, forming an interpenetrating and percolating network on a nanoscale (Fig. 1A). The properties can be tailored by choice of SBE constituents and curing process. The SBE therefore fulfills the necessary multifunctional matrix requirements for realizing a solid-state morphing material.

The morphing material presented here is formed from two Li-activated carbon fiber layers, electrically insulated from one another by a commercial ceramic separator layer and embedded in the SBE to form a structural composite laminate (Fig. 1B). By applying an electrical current Li ions are transferred through the SBE from one carbon fiber layer to the other, causing the discharging layer to contract, while the charging layer expands, morphing the entire laminate in a bending motion (Fig. 1C). The morphing mechanism is thus provided by the load-carrying material itself, forming a truly multifunctional material that adds little to no parasitic mass to a structure and is electrically controlled.

Results

Preparation and Characterization. The composite material is fabricated using two layers of spread unidirectional carbon fibers separated by a layer of ceramic Li-ion battery separator material

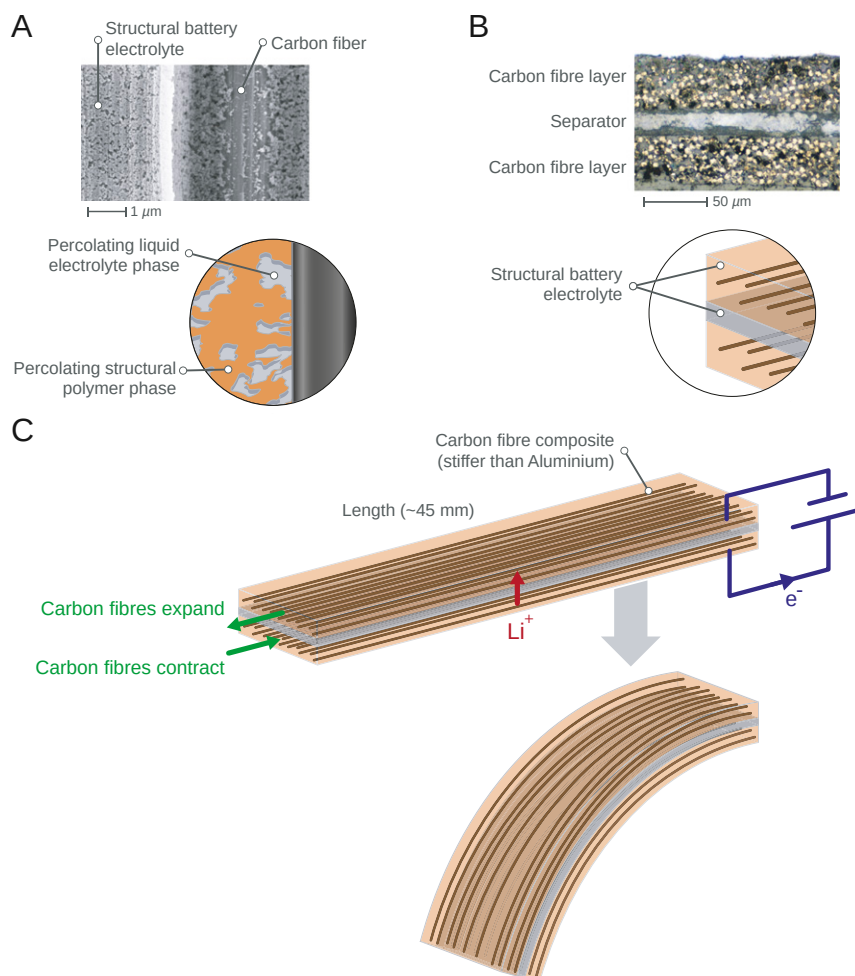


Fig. 1. Solid-state carbon fiber composite morphing material in a cantilever setup. (A) SEM image and schematic of carbon fiber and SBE. (B) The composite material consists of two unidirectional Li-activated carbon fiber layers, and one ceramic-based Li-ion battery separator layer. All three layers are embedded in an SBE. A representative cross-section of the material captured using a light microscope is also shown. (C) Li ions are discharged from one carbon fiber layer to the other by application of a current, causing the discharging layer to contract in the fiber direction, and the charging layer to expand. This creates an overall bending deformation.

(Fig. 2A). Current collectors are attached to the two carbon fiber layers for electrical connection. The three layers are assembled on a flat mold and vacuum infused with SBE and subsequently heat cured (Fig. 2B). The resulting composite material (Fig. 2C) has an approximate density of $1,600 \text{ kg m}^{-3}$. The carbon fiber layers are activated as follows: the cured composite material is placed into a pouch cell bag with a layer of Li metal foil on either side, separated from the carbon fiber layers by a glass fiber paper, soaked in liquid electrolyte, and vacuum sealed in the pouch cell (Fig. 2D). The two carbon fiber layers are then fully charged/discharged at a low constant current density for several cycles before being left at 50% state of charge (see *SI Appendix, Fig. S1* for charge/discharge profiles). This activation partially expands the carbon fiber layers by an equal amount. The cell was then disassembled, the laminate taken out and sealed with a thin, low-density polyethylene film to prevent solvent evaporation. The laminate was then placed in a custom-made bending rig forming a cantilever, with morphing controlled by a potentiostat as a current source (Fig. 2E). All morphing experiments were carried out in a dry argon atmosphere.

Layer thicknesses were obtained by measuring cross-sections using a light microscope, giving carbon fiber layer thicknesses of $\sim 50 \text{ }\mu\text{m}$, and a separator layer thickness of $\sim 20 \text{ }\mu\text{m}$ (*SI Appendix, Table S1*). An example cross-section is shown in Fig. 1B. Theoretical predictions and material testing results in a homogenized longitudinal in-plane modulus of the laminate, including the separator layer, of over 100 GPa, higher than the 69 GPa of aluminum (*SI Appendix, Table S2*). This is three orders of magnitude higher than the stiffness reported for similar morphing materials elsewhere in the literature (15, 16, 28).

Morphing Performance. The morphing experiments were carried out by applying a constant current between the two carbon fiber layers using voltage cutoff limits of -1.5 and 1.5 V . This creates a

bending deformation in the composite material due to the transfer of Li, as one carbon fiber layer charges and expands, while the other discharges and contracts. The morphing was captured using a video camera, and the resulting films were processed using image tracking and digital image correlation to calculate the displacements. Fig. 3 shows one full upward and downward stroke at a current density of 14.5 mA g^{-1} , with regard to the mass of one of the carbon fiber layers. For a cantilever length of 48 mm this resulted in a maximum tip displacement of $\sim 35 \text{ mm}$, with one full stroke to either the upward or downward positions taking just over 5 h .

Movie S1 shows a time-lapse film of the morphing of a cantilever at two different current densities. The time lapse is recorded such that 1 s of video corresponds to 15 min in real time. Firstly, a downward stroke is shown followed by a return stroke to the neutral position. A similar movement is then shown beginning with an upward stroke. These are carried out at a current density of 44.2 mA g^{-1} and take $\sim 20 \text{ min}$ per stroke. Secondly, a new stroke is performed using a lower current density (14.5 mA g^{-1}) which produces larger displacements due to a higher charge transfer, albeit with a time per stroke of just over 5 h , snapshots of which are shown in Fig. 3. A 1-h period of no current is applied between each stroke to allow any Li concentration gradients to relax and additionally shows that the morphing composite material exhibits a zero-power hold. With an open circuit no currents are running and the potential difference between the carbon fiber layers is maintained, producing the zero-power hold.

Morphing Predictions. The morphing deformation is created by one carbon fiber layer expanding while the other contracts, corresponding to strains ϵ^+/ϵ^- , respectively. These strains, together with layer thicknesses and elastic moduli, are used as inputs to an analytical model based on beam theory, which is analogous to the analysis of a bimetal thermostat (29).

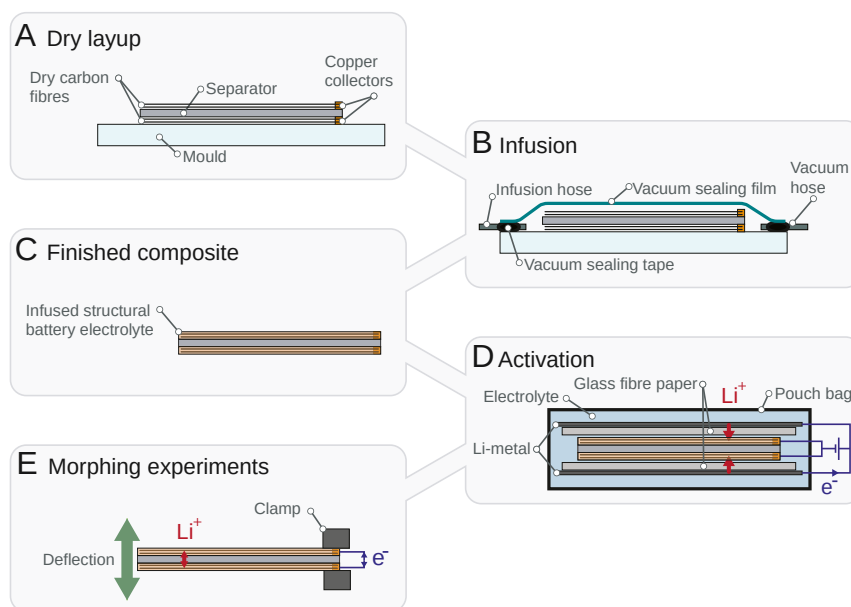


Fig. 2. Fabrication process for the carbon fiber composite morphing material. (A) Two unidirectional carbon fiber layers and one ceramic separator layer are laid up on a mold. Copper current collectors are attached to the carbon fiber layers. (B) The layup is sealed with a vacuum-sealing film and tape, and the SBE is infused into the three layers under vacuum, before being heat cured for 45 min at $90 \text{ }^{\circ}\text{C}$. (C) The cured three-layer composite material, with a density of $\sim 1,600 \text{ kg m}^{-3}$, is ready for the activation process. (D) Two layers of Li metal foil are used as a source of Li ions and are placed on either side of the composite material, separated from the carbon fiber layers by layers of glass fiber paper soaked with liquid electrolyte. This is then sealed under vacuum inside a pouch bag. A current is applied (18.6 mA g^{-1}) between the Li foil and the carbon fibers and the carbon fiber layers are charged/discharged several times before being left charged at 50% state of charge. (E) The composite material is removed from the pouch bag and clamped to form a cantilever. A current is applied between the two carbon fiber layers, charging/discharging the layers between -1.5 and 1.5 V causing the cantilever to bend.

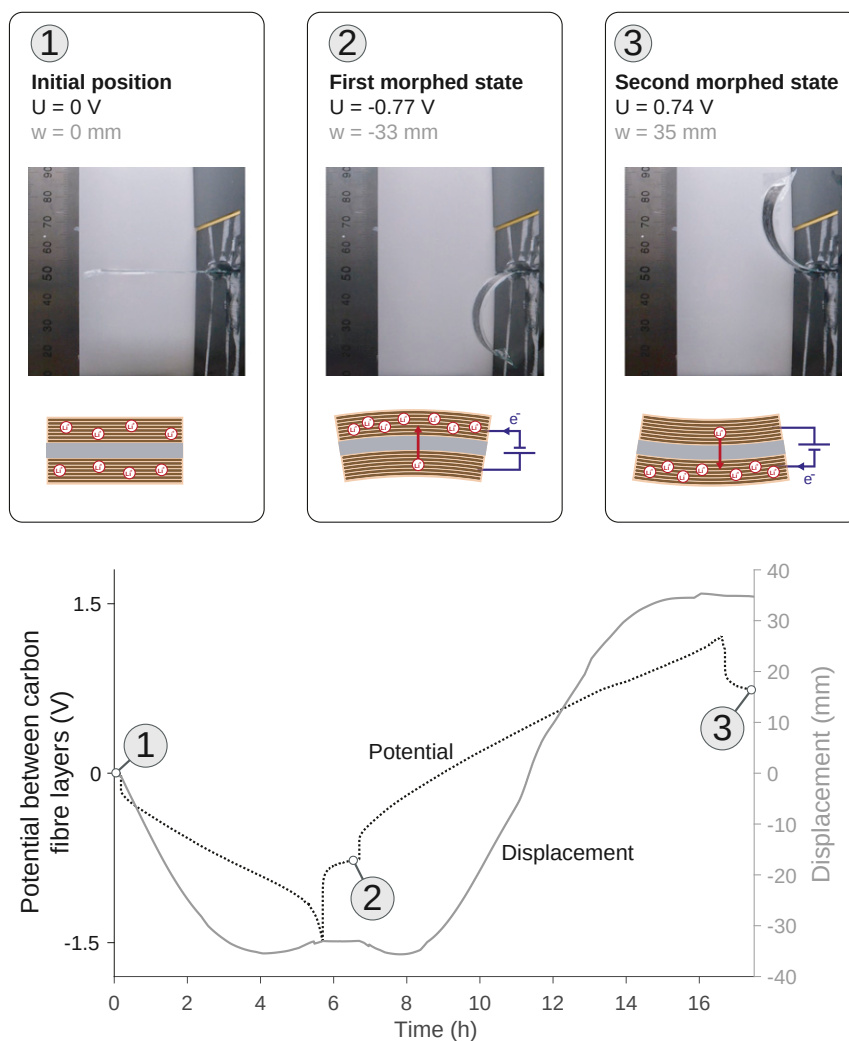


Fig. 3. Experiment showing the morphing carbon fiber composite material in a cantilever setup. A current is applied between the carbon fiber layers with cutoff voltages of -1.5 and 1.5 V. This causes Li to transfer from one carbon fiber layer to the other. The charging carbon fiber expands in the fiber direction as it reaches a higher state of charge, while the carbon fiber layer that is discharging contracts, creating a bending deformation. Potential difference between the carbon fiber layers and cantilever tip displacement are shown as functions of time. Images showing displacements of the morphing material are also shown. For a cantilever length of 48 mm a maximum tip displacement of 35 mm is reached for a charge transfer of 79.6 mAhg^{-1} . The specimen here has average layer thicknesses: carbon fiber $53.4 \text{ }\mu\text{m}$ and separator $21.0 \text{ }\mu\text{m}$.

The expansion/contraction strains are proportional to the change in charge (ΔQ) in each of the carbon fiber layers through

$$\varepsilon^+ = \beta \cdot \Delta Q \text{ and } \varepsilon^- = -\beta \cdot \Delta Q, \quad [1]$$

where β is an expansion coefficient. This was calculated as being $\beta = 2.6 \times 10^{-5} \text{ g(mAh)}^{-1}$ (*SI Appendix, Fig. S2*) measured using a previously described methodology (22). Thus, for a ΔQ of 100 mAhg^{-1} the strain in one layer is 0.26% and in the other -0.26% . The separator does not expand or contract during charge and discharge. The expansion strains create a lengthwise constant curvature of the cantilever, which is related geometrically to the cantilever tip displacement. To validate the analytical model the experiments were also analyzed the finite-element method (FEM) assuming linear elastic materials and large displacements (geometrically nonlinear). The expansion coefficient β was implemented as a thermal expansion. These predicted results are compared to an experimentally measured tip displacement and curvature in Fig. 4, where deviations at large charge difference ΔQ are due to the tip touching the vertical wall in the experiment.

The energy consumed in driving the morphing process is an important parameter to consider. Here, the energy consumed is not just the energy input to the system, as the majority of the energy is stored electrochemically and is recovered by running currents in the opposite direction. Only a small amount of the electrical energy put into the system is converted to elastic strain energy with a conversion around 0.05% . The only real losses are those coming from electrochemical losses similar to those in a conventional Li-ion battery. The gravimetric mechanical strain energies are 22 and 27 Jkg^{-1} for the experiments shown in Figs. 3 and 4, respectively. In bending, strains are varying through the thickness of the material, meaning mechanical strain energy from the tension/compression of the carbon fibers is not fully exploited, resulting in seemingly low actuation energies. Linear actuation could be exploited albeit without creating any bending motion. Both carbon fiber layers would be expanded (or contracted) simultaneously using an external lithium source, similar to the activation step. The linear gravimetric mechanical strain energy would then be around 500 Jkg^{-1} similar to previously reported data (16).

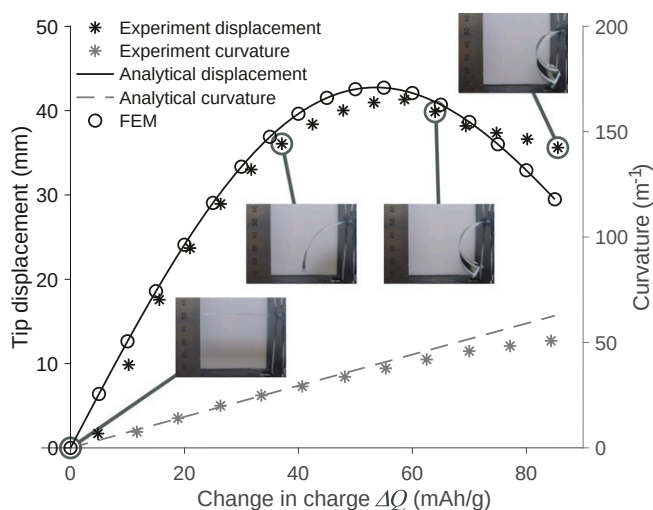


Fig. 4. Comparison between experiment, analytical prediction, and FE model prediction of tip displacement and curvature vs. change in charge for the carbon fiber composite morphing material in a cantilever setup. The specimen here has average layer thicknesses: carbon fiber 40.4 μm and separator 21.3 μm , and a cantilever length of 59 mm.

Discussion

In this paper we have shown it is possible to create a lightweight and stiff material, which is solid-state, morphable with large deformations, exhibits a zero-power hold, and is easy to control at low currents and voltages. It is made from commercial carbon fibers and an SBE using standard manufacturing techniques used in the composite industry, meaning it can be integrated into existing composite structures. Electrochemical actuation means no moving parts are required, enables electrical control at low voltages, and an inherent zero-power hold.

A limitation is that the actuation rate is low, as with any other actuation that exploits ion insertion, since diffusion in solids is generally a slow process. Rate can be improved by increasing the ionic conductivity of the SBE, however it is limited by the ionic conductivities of state-of-the-art Li-ion battery electrolytes. Decreasing layer thicknesses and carbon fiber diameter would also increase morphing rate, as the rate of ion transfer is inversely proportional to the layer thicknesses and inversely proportional to the square of the carbon fiber diameter (30). However, such geometry improvements are limited by the ionic conductivity of the SBE. With these system improvements it is realistic to consider a rate increase of around 10 times. Although this would still constitute comparably slow morphing, there are applications where this is required and even advantageous, such as the trimming of aerodynamic surfaces for steady-state conditions in aircraft and wind turbines, and the deployment of satellite booms in space.

Another limitation is that this morphing composite material is not yet operable in an ambient environment due to the inserted Li and presence of solvents, but this can be remedied by a suitable outer barrier such as layers of ultrathin glass (31).

The concept has potential for future development by tailoring for different applications. For example, the scale of the material could be adjusted, with the lower limit being the size of two single carbon fibers, which could be on the nanoscale. Larger structures could be conceived by adding more and thicker layers of carbon fiber, albeit at the expense of morphing rate. Different modes of morphing such as twisting and rolling deformations could be envisaged by altering the carbon fiber layer orientations. Differing layups would result in trade-offs between material stiffness, magnitude of deformation, mode of deformation, and actuation frequency. This technology could also be combined with

a positive electrode layer which would allow the material to inherently store the electrochemical energy required for morphing.

Conclusions

In summary, an electrically controlled solid-state morphing composite material has been manufactured and tested. It is capable of producing large deformations and holding them with no additional power, albeit at low rates. The material is lightweight and has a stiffness higher than aluminum. It consists of two layers of commercial carbon fiber and a separator layer embedded in a structural battery electrolyte. The carbon fibers expand and contract using lithium-ion insertion/extraction at low voltages leading to an overall bending motion. A proof-of-concept morphing material has been presented in a cantilever setup. Analytical modeling shows good correlation with experiments. In conclusion, the composite material presented here shows considerable promise to become a viable alternative for creating stiff solid-state morphing materials.

Experimental

Materials Used. Carbon fibers of the type T800SC-12K-50C manufactured by Toray Composite Materials America, Inc. were used (density 1,800 kgm^{-3}) (32). The carbon fiber tow was spread by Oxeon AB to an approximate width of 10 mm in order to make thin layers. The SBE consists of Bisphenol A ethoxylate dimethacrylate (BAED), $M = 364.43 \text{ g mol}^{-1}$, propylene carbonate (99% anhydrous) (PC), ethylene carbonate (99% anhydrous) (EC), lithium trifluoromethanesulfonate (LiTFS) (96%), and 2,2'-Azobis(2-methylpropionitrile) (AIBN), all were supplied by Sigma-Aldrich. The resulting cured SBE has a measured density of 1,100 kgm^{-3} . The separator is a layer of Freudenberg FS 3011-23 (areal weight 0.033 kgm^{-2}) (33). Current collectors were made from copper (17 μm , 99.95% purity) and nickel foil (15 μm , 99.95% purity). Lithium metal foil (0.38 mm, 99.9% purity, Sigma-Aldrich), Whatman GF/A (260- μm) glass fiber paper, and pouch cell bags (PET/Al/PE from Skultuna Flexible) were used during the activation process. DeltaPreg AX003 epoxy adhesive was used to attach the tabs during expansion measurements. All materials were used as received.

Manufacturing. The manufacturing of the composite material was made by stacking of dry layers. First a layer of carbon fiber was laid onto a glass plate mold. A ceramic separator (Freudenberg FS 3011-23) was used as the separator layer, followed by the second layer of carbon fiber. Current collectors on the carbon fiber layers were made from copper foil, and were adhered with Electrolube silver conductive paint. The stack was sealed with vacuum sealing film and dried for 12 h in vacuum at 60 °C before being inserted into dry argon atmosphere (<2 ppm H_2O , <2 ppm O_2). The SBE was prepared in the same argon atmosphere with 60.2 wt % BAED, 0.6 wt % AIBN, and 39.2 wt % liquid electrolyte, which is made from 1.0 M LiTFS in EC:PC 1:1 wt/wt. Vacuum-assisted infusion was used in order to impregnate the SBE into the layup which was then cured at 90 °C for 45 min. The resulting material density of 1,600 kgm^{-3} is based on the constituent densities and their volume fractions.

Activation Process. The activation was done by electrochemically charging and discharging of the carbon layers against Li metal. Nickel current collectors were used to contact the Li metal foils. Electrical insulation between the carbon fiber layers and the Li metal foils was ensured by layers of Whatman GF/A (260- μm) glass fiber paper (Fig. 2D). The glass fiber papers were saturated with the liquid electrolyte part of the SBE (1.0 M LiTFS in EC:PC 1:1 wt/wt) for ion conduction. The carbon fibers were electrochemically charged and discharged between 0.002 and 1.5 V vs. Li/Li^+ for about 10 cycles, with a constant current of 18.6 mA per gram of carbon fibers followed by a short potentiostatic step, using a Biologic VSP potentiostat. The current corresponds to a charging time of ~9.5 h and all cycling was carried out at a temperature of 25 ± 1 °C. The cycling was stopped at ~50% of the last full cycle charge (SI Appendix, Fig. S1), corresponding to 0.85 V vs. Li/Li^+ .

Expansion Measurements. The expansion coefficient β for the same carbon fiber and electrolyte as used in the morphing experiments was obtained using the following experimental setup. Glass fiber tabs were attached to single carbon fiber tows using DeltaPreg AX003 epoxy adhesive to provide a means of gripping the fibers in a tensile tester. First, tabbed carbon fiber specimens were tested in tension to obtain the axial stiffness of the tow, giving a value of 1,025 Nmm^{-1} . Next, tabbed carbon fiber specimens were placed in a half-cell setup in a pouch bag with Li metal as the common counter and reference electrode, and a glass fiber paper soaked with electrolyte as a separator. The pouch-cell specimen was mounted in a Shimadzu AGS-X 5kN tensile tester and a

constant strain was applied. The pouch-cell specimen was allowed to relax for 3 h, in order to minimize the load contribution of the viscoelastic pouch bag material. A constant current was applied between the carbon fibers and the Li metal using a Biologic VSP potentiostat in order to charge and discharge the carbon fibers. During the carbon fibers expand, resulting in a load drop, and the opposite occurs during discharge. These are correlated to axial expansions/contractions of the carbon fibers through the measured axial stiffness of the tow, since the carbon fiber stiffness remains constant with charge (22). A typical strain per unit charge ratio of $\beta = 2.6 \times 10^{-5} \text{ g(mAh)}^{-1}$ was measured (SI Appendix, Fig. S2).

Actuation Experiment Details. After activation, the pouch was opened in a dry argon atmosphere, with a temperature around 25 °C. The composite material was removed and encapsulated in a low-density polyethylene film with thickness 15 μm . This was clamped in a rig forming a cantilever structure and the copper collectors connected to a Biologic SP-50 potentiostat as a current source. Depending on desired morphing rate, constant currents ranging from 14 to 45 mA h g^{-1} were applied, charging one carbon fiber layer while discharging the other until the potential between the carbon fiber layers reached 1.5 V. The system was then relaxed with a zero-current hold for 60 min. Next, the current was reversed until reaching -1.5 V , followed by 60-min relax time and so on. Deflections were measured at the tip of the cantilever from the time-lapse video obtained using a GoPro Hero4 Session camera. Displacements were acquired using image tracking provided by MATLAB's Image Processing Toolbox. Curvatures were measured from video snapshots using MATLAB image processing and least-square fit of circles to image data points. An example of an actuation experiment video is shown in Movie S1.

Mechanical Characterization. Scanning electron microscope (SEM) imaging was conducted using a Zeiss Leo Ultra 55 field-emission gun SEM at 5-kV acceleration voltage. Prior to imaging all samples were soaked in water for one full day to remove the liquid component of the SBE, dried overnight at 60 °C, and sputter coated with Pt/Pd using an Emitech K500X sputter coater. Cut surfaces were obtained using a scalpel. An example image is shown in Fig. 1A. Layer thicknesses of the composite material were measured using an Olympus BX53M light microscope with Olympus Stream Basic (v2.3.3) software, from cut and potted samples, polished to obtain a smooth surface. An example image is shown in Fig. 1B. These layer thicknesses were used to calculate the fiber volume fraction of the carbon fiber layers V_f , knowing the tow count [12,000 fibrils (32)] and the carbon fiber diameter (5 μm) (32). The longitudinal elastic modulus E_{cf} of the carbon fiber layers was calculated using the rule of mixtures (34)

$$E_{cf} = E_f V_f + E_m (1 - V_f), \quad [2]$$

where E_f is the elastic modulus of the fibers (294 GPa) (32) and E_m is the elastic modulus of the SBE [0.4 GPa (25)]. The layer thicknesses of the carbon fiber t_{cf} and separator t_s , as well as the longitudinal elastic moduli of the carbon fiber layers are given in SI Appendix, Table S1.

Tension tests were performed on the composite material including the two carbon fiber layers and the separator. The size of the specimen was 10 mm wide and 15 mm long. These were performed in an Instron 5567 tensile tester with a 500-N load cell, under a fixed displacement rate of 0.1 mm min^{-1} . The strain was measured using an optical strain mapping system, GOM Aramis. The experimental longitudinal stiffness of the composite material A is calculated as the linear slope of the load-strain curve by

$$A = P/\varepsilon, \quad [3]$$

where P is the load per unit width and ε the measured strain. This is compared to the theoretically predicted longitudinal stiffness defined by

$$A = 2t_{cf}E_{cf} + t_sE_s, \quad [4]$$

assuming an elastic modulus of the separator layer ($E_s = 1 \text{ GPa}$). The homogenized longitudinal in-plane elastic modulus of the composite material (E_{mat}) is given by

$$E_{mat} = \frac{A}{2t_{cf} + t_s}. \quad [5]$$

Both the experimental and the theoretically predicted stiffnesses are given in SI Appendix, Table S2.

Bending tests were performed in the fiber direction using an Instron 5567 testing machine in a three-point bending setup using specimen width of 10 mm and supported length L of 12 mm and a fixed displacement rate of

1 mm min^{-1} . The experimentally measured bending stiffness D is given by the load-displacement relationship as

$$D = \frac{PL^3}{48\delta} \quad [6]$$

where δ is the midpoint displacement and P the load per unit width. This is compared to the theoretically predicted bending stiffness given by

$$D = \frac{2}{3}E_{cf} \left(\left(t_{cf} + \frac{t_s}{2} \right)^3 - \left(\frac{t_s}{2} \right)^3 \right) + \frac{E_s t_s^3}{12}. \quad [7]$$

The theoretical and experimentally measured stiffness values are given in SI Appendix, Table S2.

Modeling of Morphing Behavior. The deflection of the cantilever was analytically predicted using the expansion strains of the two carbon fiber electrode layers. A schematic representation of the composite material and its internal expansion strains is shown in SI Appendix, Fig. S3. Herein we use that the expansion strain $\varepsilon^+ = -\varepsilon^-$ and that the strain is proportional to the change in charge, ΔQ in the carbon fibers through Eq. 1. These expansion strains correspond to a constant bending moment M per unit width calculated using classical lamination theory (34):

$$M = \frac{E_{cf}}{2} \left[\left(t_{cf} + \frac{t_s}{2} \right)^2 - \left(\frac{t_s}{2} \right)^2 \right] (\varepsilon^+ - \varepsilon^-). \quad [8]$$

The lengthwise constant curvature is given by

$$\kappa = \frac{M}{D}. \quad [9]$$

Since the displacements are large, the cantilever tip displacement cannot be calculated from linear beam theory. The expansion strains cause the cantilever to bend with lengthwise constant curvature, forming a circle segment with an arc length equal to the cantilever length L and curvature κ . With a radius of curvature $R = 1/\kappa$ the circle segment angle is $\theta = \kappa L$. Geometry gives that $\cos\theta = (R-w)/R$ and thus the cantilever tip displacement w is

$$w = \frac{1}{\kappa} (1 - \cos \kappa L). \quad [10]$$

The total strains at the top and bottom of each carbon fiber layer are calculated as

$$\varepsilon_{top}^{tot} = \kappa \left(t_{cf} + \frac{t_s}{2} \right), \quad \varepsilon_{bottom}^{tot} = \kappa \frac{t_s}{2}, \quad [11]$$

and vary linearly within the layer. The mechanical strain is the total strain minus the expansion strain ($\varepsilon^{mech} = \varepsilon^{tot} - \varepsilon^{expansion}$) and the stress in the carbon fiber layers is then $\sigma_{cf} = E_{cf} \varepsilon^{mech}$. The strain energy due to bending is calculated as

$$U_{se} = \frac{1}{2} \int \sigma \varepsilon dV = \int_0^{t_s} \frac{\sigma_{cf}^2}{E_{cf}} dz \cdot L \cdot W = \frac{1}{E_{cf}} \left[\sigma_{cf,top}^2 t_c + \sigma_{cf,top} \kappa t_c^2 + \kappa^2 \frac{t_c^3}{3} \right] \cdot L \cdot W, \quad [12]$$

where $k = (\sigma_{cf, bottom} - \sigma_{cf, top})/2$, L is the beam length, and W is the beam width. The contribution from the separator is neglected, having low elastic modulus and subjected to low mechanical strains.

To validate the analytical model the cantilever was also modeled in the FE code ABAQUS (35) using four-noded shell elements of the type S4R consisting of three orthotropic layers corresponding to the two carbon fiber layers and the separator. The materials were linear elastic but the analysis accounted for large displacements (geometrically nonlinear) and applying a temperature change to the two carbon fiber layers. The temperature was correlated to ΔQ of the carbon fiber layers such that 0 °C corresponded to the initial condition (both carbon fiber layers have the same state of charge) and 100 °C to the maximum change in charge (positive in one layer and negative in the other).

The total electrical energy U_{elec} in one cycle going from zero displacement to maximum displacement in the experiments was calculated from (e.g., the potential curve in Fig. 3)

$$U_{elec} = I \int_0^T V dt, \quad [14]$$

where I is the applied constant current, V the electrical potential between the carbon fiber layers as function of time, and T the time at maximum displacement.

The conversion from electrical to mechanical energy in the cantilever is

$$\text{conversion} = \frac{U_{se}}{U_{elec}} \quad [15]$$

Data Availability. The raw data for Figs. 3 and 4 and *SI Appendix, Figs. S1 and S2 and Tables S1 and S2* are available at <https://doi.org/10.17632/4zky6h8w3v.1>.

1. J. E. Huber, N. A. Fleck, M. F. Ashby, The selection of mechanical actuators based on performance indices. *Proc. R. Soc. London, Ser. A* **453**, 2185–2205 (1997).
2. P. Portela, P. Camanho, P. Weaver, I. Bond, Analysis of morphing, multi stable structures actuated by piezoelectric patches. *Comput. Struct.* **86**, 347–356 (2008).
3. J. N. Reddy, On laminated composite plates with integrated sensors and actuators. *Eng. Struct.* **21**, 568–593 (1999).
4. M. Sunar, S. S. Rao, Recent advances in sensing and control of flexible structures via piezoelectric materials technology. *Appl. Mech. Rev.* **52**, 1–16 (1999).
5. L. Kong, W. Chen, Carbon nanotube and graphene-based bioinspired electrochemical actuators. *Adv. Mater.* **26**, 1025–1043 (2014).
6. S. Mehraeen, S. A. Gürsel, M. Papila, F. Ç. Cebeci, Investigation of electrochemical actuation by polyaniline nanofibers. *Smart Mater. Struct.* **26**, 095021 (2017).
7. S. Liu et al., High electromechanical response of ionic polymer actuators with controlled-morphology aligned carbon nanotube/naion nanocomposite electrodes. *Adv. Funct. Mater.* **20**, 3266–3271 (2010).
8. O. Kim, T. J. Shin, M. J. Park, Fast low-voltage electroactive actuators using nanostructured polymer electrolytes. *Nat. Commun.* **4**, 2208 (2013).
9. J. Liang et al., Electromechanical actuators based on Graphene and Graphene/Fe₃O₄ hybrid paper. *Adv. Funct. Mater.* **21**, 3778–3784 (2011).
10. R. H. Baughman et al., Carbon nanotube actuators. *Science* **284**, 1340–1344 (1999).
11. G. Gu et al., V₂O₅ nanofibre sheet actuators. *Nat. Mater.* **2**, 316–319 (2003).
12. G. Wu et al., Graphitic carbon nitride nanosheet electrode-based high-performance ionic actuator. *Nat. Commun.* **6**, 7258 (2015).
13. S. Barbarino, E. I. Saavedra Flores, R. M. Ajaj, I. Dayyani, M. I. Friswell, A review on shape memory alloys with applications to morphing aircraft. *Smart Mater. Struct.* **23**, 063001 (2014).
14. C. Massey, G. McKnight, W. Barvosa-Carter, P. Liu, “Reversible work by electrochemical intercalation of graphitic materials” in *Proceedings of SPIE Smart Structures and Materials 2005: Electroactive Polymer Actuators and Devices (EAPAD)* (International Society for Optics and Photonics, Bellingham, WA, 2005), vol. 5759.
15. T. E. Chin, U. Rhyner, Y. Koyama, S. R. Hall, Y.-M. Chiang, Lithium rechargeable batteries as electromechanical actuators. *Electrochem. Solid-State Lett.* **9**, A134–A138 (2006).
16. Y. Koyama et al., Harnessing the actuation potential of solid-state intercalation compounds. *Adv. Funct. Mater.* **16**, 492–498 (2006).
17. H. Zhang, P. S. Grant, An electrochemical microactuator based on highly textured LiCoO₂. *Sens. Actuators B Chem.* **176**, 52–57 (2013).
18. D. J. Johnson, Structural-property relationships in carbon fibres. *J. Phys. D Appl. Phys.* **20**, 286–291 (1987).
19. R. Kanno, Y. Takeda, T. Ichikawa, K. Nakanishi, O. Yamamoto, Carbon as negative electrodes in lithium secondary cells. *J. Power Sources* **26**, 535–543 (1989).
20. J. Hagberg, S. Leijonmarck, G. Lindbergh, High precision coulometry of commercial PAN-based carbon fibers as electrodes in structural batteries. *J. Electrochem. Soc.* **163**, A1790–A1797 (2016).
21. H. Kawaura et al., Operando measurement of solid electrolyte interphase formation at working electrode of Li-ion battery by time-slicing neutron reflectometry. *ACS Appl. Mater. Interfaces* **8**, 9540–9544 (2016).
22. E. Jacques, M. Hellqvist Kjell, D. Zenkert, G. Lindbergh, M. Behm, Expansion of carbon fibres induced by lithium intercalation for structural electrode applications. *Carbon* **59**, 246–254 (2013).
23. E. Jacques et al., Impact of electrochemical cycling on the tensile properties of carbon fibres for structural lithium-ion composite batteries. *Compos. Sci. Technol.* **72**, 792–798 (2012).
24. Z. Wu et al., Utmost limits of various solid electrolyte in all-solid state lithium batteries: A critical review. *Renew. Sustain. Energy Rev.* **109**, 367–385 (2019).
25. N. Ihrner, W. Johansson, F. Sieland, D. Zenkert, M. Johansson, Structural lithium ion battery electrolytes via reaction induced phase-separation. *J. Mater. Chem. A* **5**, 25652–25659 (2017).
26. W. Johansson et al., Multifunctional performance of a carbon fiber UD lamina electrode for structural batteries. *Compos. Sci. Technol.* **168**, 81–87 (2018).
27. L. M. Schneider, N. Ihrner, D. Zenkert, M. Johansson, Bicontinuous electrolytes via thermally initiated polymerization for structural lithium ion batteries. *ACS Appl. Energy Mater.* **2**, 4362–4369 (2019).
28. G. Alici, N. N. Huynh, Predicting force output of trilayer polymer actuators. *Sens. Actuators A Phys.* **132**, 616–625 (2006).
29. S. Timoshenko, Analysis of bi-metal thermostats. *J. Opt. Soc. Am.* **11**, 233–255 (1925).
30. J. Newman, K. E. Thomas-Alyea, *Electrochemical Systems* (Wiley, ed. 3, 2012).
31. A. Sepúlveda, J. Speulmanns, P. M. Vereecken, Bending impact on the performance of a flexible Li₄Ti₅O₁₂-based all-solid-state thin-film battery. *Sci. Technol. Adv. Mater.* **19**, 454–464 (2018).
32. Toray Composite Materials America Inc., T800S intermediate modulus carbon fiber. https://www.toraycma.com/file_viewer.php?id=5126. Accessed 2 September 2019.
33. Freudenberg Performance Materials, Lithium-ion battery separator. https://www.freudenberg-pm.com/-/media/Files/separators,-d-,freudenbergpm,-d-,com/LI_Ion%20Overview%20April%202018%20PRELIMINARY.PDF. Accessed 2 September 2019.
34. I. M. Daniel, O. Ishai, *Engineering Mechanics of Composites* (Oxford University Press, New York, 1994).
35. M. Smith, ABAQUS/Standard User's Manual (Version 6.9, Simulia, Providence, RI, 2009).

ACKNOWLEDGMENTS. The authors would like to acknowledge Anton Shipsha for help in building the FE model, Kevin Geiger for assistance with the initial experiments, and Oxeon AB for supplying spread tow carbon fibers. The Swedish research group Kombatt is acknowledged for its synergism throughout this work. This work was supported by the Swedish Research Council, Projects 2017-03898 and 621-2014-4577, the strategic innovation program LIGHTer (funding provided by Vinnova, the Swedish Energy Agency and Formas), H2020 Clean Sky II Project 738085, and by the Air Force Office of Scientific Research under Award FA9550-17-1-0244.



Research Article

Potassium-insertion in polyacrylonitrile-based carbon fibres for multifunctional energy storage, morphing, and strain-sensing

Ross Harnden^{a,*}, Dan Zenkert^a, Göran Lindbergh^b^a Lightweight Structures, Department of Engineering Mechanics, KTH Royal Institute of Technology, SE-100 44, Stockholm, Sweden^b Applied Electrochemistry, Department of Chemical Engineering, KTH Royal Institute of Technology, SE-100 44, Stockholm, Sweden

ARTICLE INFO

Article history:

Received 28 May 2020

Received in revised form

4 September 2020

Accepted 12 September 2020

Available online 18 September 2020

Keywords:

Composites

Intercalation

Ion-insertion

Lightweight

Structural

ABSTRACT

By increasing the number of functions a structure performs it is possible to save weight and volume on a systems level. Ion-insertion in carbon fibres (CFs) is a way to create multifunctional structures for energy storage, morphing, and strain-sensing. Previous studies have focussed on lithium- and sodium-insertion to create multifunctionality. However, with a larger ionic radius and a chemistry more amenable to insertion in polyacrylonitrile (PAN)-based CFs, potassium-insertion is a promising way forward. Here, a study is conducted to examine potassium-insertion in intermediate modulus PAN-based CFs for multifunctionality. Electrochemical cycling shows a maximum reversible capacity of 170 mAh/g, with ex-situ mechanical testing showing a small impact on the CFs' mechanical properties post-cycling. Operando measurements show a maximum reversible CF expansion during potassium-insertion of 0.24%, and analytical modelling illustrates that such strains can generate significant deformations in a morphing structure. A voltage-strain coupling of 0.26 V/unit strain is also found. Results are compared with previous work on lithium- and sodium-insertion, with the conclusion that potassium-insertion is more promising than sodium-insertion, but less so than lithium-insertion for multifunctional structures.

© 2020 The Author(s). Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

1. Introduction

By combining two or more functionalities into the same structure it is possible to save weight and volume on a systems level [1]. In vehicle structures, these savings result in lower fuel consumption and hence lowered CO₂ emissions. As carbon fibre (CF) composites are already used in many weight-sensitive applications in the transport industry, they are good candidates to augment with further functionality.

It is possible to exploit the favourable structural properties of polyacrylonitrile (PAN)-based CFs, as well as their ability to store lithium (Li) and sodium (Na) [2], to create different types of ion-functionalised multifunctional materials. In this study the ion-functionalisation of CFs with potassium (K) is investigated.

By combining CFs with an electrochemically-active matrix system [3,4], as well as a coated positive electrode [5,6], it is possible to form a structural composite battery [7]. Such structural batteries have shown the potential to reduce mass in various applications [8]. A recent review on the development of structural batteries can be

found in Asp et al. [9].

Using the same electrochemical properties it is possible to use ion-insertion strains in PAN-based CFs to create morphing materials. This concept was demonstrated by Johannisson et al. [10] where reversible expansions of CFs created by lithium-insertion were exploited to create a morphing cantilever. Similar reversible expansions of PAN-based CFs have also been demonstrated for sodium-insertion [11].

Lithiated and sodiated PAN-based CFs have also been shown to exhibit a voltage-strain coupling through the piezo-electrochemical effect [11,12]. This has paved the way for a new class of strain-sensing composite materials, similar to piezo-electric and light-diffraction methods proposed elsewhere [13–15]. The voltage-strain coupling also enables energy to be harvested from mechanical strains during lithiation/delithiation cycles [16].

Recently, concerns about lithium resource shortages, and sodium's inability to intercalate in graphite (Table 1), have led to a resurgence in interest for potassium-ion chemistries in the battery community [17–19]. Potassium, like sodium, is a significantly more abundant element than lithium, making it cheap to extract (Table 1), and more environmentally sustainable than lithium [20].

Sodium-insertion in PAN-based CFs for multifunctional

* Corresponding author.

E-mail address: harnden@kth.se (R. Harnden).

Table 1

Summary of economic and electrochemical characteristics of potassium, lithium, and sodium. Data taken from Pramudita et al. [23].

	K	Li	Na
Atomic Radius (pm)	220	145	180
Voltage vs. Standard Hydrogen Electrode (V)	−2.93	−3.04	−2.71
Cost of industrial grade metal (USD/ton)	13,000	100,000	3000
Reversible Capacity in Graphite (mAh/g)	≈200	≈370	≈5
Reversible Capacity in Hard Carbon (mAh/g)	≈200	≈500	≈300

materials was investigated previously, finding that insertion-expansions and the magnitude of the voltage-strain coupling were considerably lower than for lithium-insertion [11]. However, there have been no studies to-date focussing on the use of potassium-based CFs for multifunctional structures.

Potassium has a larger atomic radius than sodium (Table 1), but inserts with significant capacity in both graphite and hard carbon – making potassium-insertion in PAN-based CFs an interesting way forward for creating multifunctional structures.

The PAN-based CF used in this study is intermediate modulus Toray T800HB. Its microstructure has previously been characterised by Fredi et al. [21] and Hagberg et al. [22]. High Resolution Transmission Electron Microscopy shows that the microstructure is highly disordered with substantial variability in the orientation of the graphene layers [21]. Broad Raman spectroscopy peaks indicate a high degree of amorphous carbon, with a d_{002} spacing of 3.7 Å [22]. The density of the CFs is 1.81 g/cm³, making them denser than the majority of hard carbons, while the Brunauer-Emmett-Teller surface area is comparatively low at 0.52 m²/g [22].

In this study we present the electrochemical functionalisation of PAN-based CFs with potassium for application in structural energy storage, morphing, and strain-sensing. A comparison is given between potassium-functionalisation and previous studies carried out using lithium and sodium.

2. Experimental

The experimental setups for the potassium measurements is largely the same as for the lithium and sodium measurements reported previously [11,12,16,24], with small differences in specimen preparation including: CF fibre count, current collectors, electrolyte, and type of metal foil; while the main difference in electrochemical cycling was the voltage cut-off limits used. Importantly the same kind of CF was used for all ion-insertion experiments. A summary of the key differences between the three sets of testing is given in Table 2.

2.1. CF specimen preparation

The CF specimens manufactured for potassium cycling consisted of a tow of CF adhered between glass fibre tabs (DeltaPreg W105P/DT806W) using DeltaPreg AX003 epoxy adhesive (Fig. 1). The tabs

allowed the specimens to be gripped in a tensile tester for mechanical testing. A section of 260 µm thick glass microfibre filter paper (Whatman GF/A) was adhered between the two tabs to act as a separator layer, and the resulting specimens were heat-cured under vacuum at 120 °C for 1 h. A schematic of the specimens used is shown in Fig. 1. The CF sizing — a thin coating applied to the CFs during manufacture to aid handling — was partially removed by immersing the specimens in an acetone bath overnight. This was done to ensure a fair comparison with the sodiated CFs, for which this process resulted in more stable cycling [11]. The resulting specimens were dried overnight in a vacuum oven at 70 °C, before being placed in an argon-filled glovebox ready for cell manufacture. A number of the specimens were subjected to destructive tensile testing in order to establish the specimen axial stiffnesses and strengths.

2.2. Electrochemical cells

Half-cells in pouch cell format were used for all cycling. In this setup the CFs act as the working electrode, the potassium metal foil (manufactured from Sigma-Aldrich 99.5% purity cubes) act as the counter-electrode, and the glass microfibre filter paper act as a separator. The pouch cell bags were laminated constructions of PET/Al/PE from Skultuna Flexible with layer thicknesses of 12 µm/9 µm/75 µm respectively. Aluminium current collectors were attached to both the potassium foil and CFs. Prior to sealing the pouches, the separator was impregnated with 200 µL of electrolyte made up with 0.5 M KPF₆ (Sigma Aldrich, 99% purity) in propylene carbonate (PC, Sigma Aldrich, 99.7% purity, anhydrous). A number of cells were tested using 0.8 M KPF₆ in ethylene carbonate:diethyl carbonate (EC:DEC, 1:1 wt/wt, Sigma Aldrich, 99% purity) in order to check that the expansion was not dependent on the electrolyte solvent. The pouch cells were vacuum sealed inside a glove box under inert atmosphere with less than 2 ppm O₂ and H₂O at ambient temperature. Fig. 1 shows an illustration of the pouch cell setup.

No literature data were found at appropriate current densities for lithium cells, and so separate cycling was conducted in order to obtain these data. Lithium cells were manufactured in the same way as the potassium cells, with the exceptions of the metal foil (lithium metal in place of potassium metal) and the electrolyte (1 M LiPF₆ in EC:DEC, 1:1 wt/wt). Data for sodium cells were taken from literature [11].

2.3. Electrochemical cycling

Electrochemical measurements were performed using a Biologic VSP potentiostat. Cycling was carried out between 2.5 V and 0.01 V vs. K/K⁺, with the latter voltage considered as the CFs being fully potassiated, and the former as being fully depotassiated. A maximum reversible capacity of 170 mAh/g for the CFs was established by cycling at a low current density (12 mA/g) (see

Table 2

Summary of main differences in the experimental setup between potassium, lithium, and sodium cells.

	K	Li [16]	Na [11]
Approx. fibre count	≈ 1600	< 2000	≈ 1600
Tabbing material	DeltaPreg W105P/DT806W	Gurit SA80	DeltaPreg W105P/DT806W
Tabbing adhesive film	DeltaPreg AX003 epoxy	Gurit SE 84 L V epoxy	DeltaPreg AX003 epoxy
Current collectors (Anode/Cathode)	Al/Al	Cu/Ni	Al/Al
Counter-electrode	K metal	Li metal	Na metal
Electrolyte	0.5 M KPF ₆ in PC	1 M LiPF ₆ in EC:DEC (1:1 wt/wt)	0.6 M NaPF ₆ in diglyme
Cycling upper voltage cut-off	2.5 V vs. K/K ⁺	1.5 V vs. Li/Li ⁺	2.5 V vs. Na/Na ⁺
Cycling lower voltage cut-off	0.01 V vs. K/K ⁺	0.002 V vs. Li/Li ⁺	0.01 V vs. Na/Na ⁺
Voltage-strain coupling applied Strain	0.28%	0.37%	0.36%

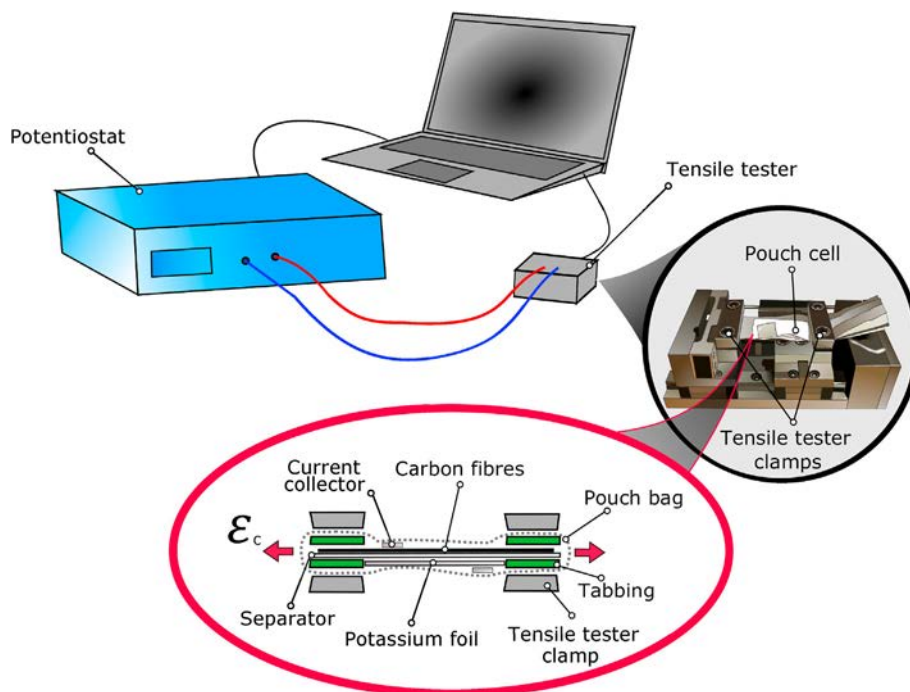


Fig. 1. Illustration of experimental setup for expansion and voltage-strain coupling measurements.

Fig. 2b).

2.4. Axial expansion measurements

Axial expansion/contraction of the CFs during ion-insertion/extraction was carried out using the same operando measurement method described previously [11,24]. The axial direction runs along the lengthwise direction of the CFs. For each test, a pouch cell containing a CF specimen was mounted in a *Deben UK* micro-tensile tester, while connected to the potentiostat (Fig. 1). The sample was then loaded in tension by applying an axial strain ϵ_c , which was held constant under the entire duration of the following electrochemical cycling.

The underlying assumption that the axial stiffness of the CFs remains approximately constant throughout the duration of the electrochemical cycling was found by ex-situ tests to be true for potassium, as previously shown for lithium [24] and sodium [11]. This means that force drops/rises, ΔF , observed during potassiation/depotassiation of the CFs can be equated to axial expansions/contractions ϵ respectively using the CF specimens' axial stiffness S , and the specimen gauge length l_g , through equation (1).

$$\epsilon = \frac{\Delta F}{S \cdot l_g} \quad (1)$$

The stiffness of the CF samples used for the expansion tests was measured to be 727.5 N/mm, and the gauge length was 22 mm.

The force drops/rises and corresponding galvanostatic cycling curves are shown in Supplementary Fig. S1.

Two of the key metrics for measuring actuation performance are the specific actuation energy U and the specific actuation power P [25]. Here these are calculated using equations (2) and (3) respectively.

$$U = \frac{E\epsilon^2}{2\rho} \quad (2)$$

$$P = \frac{U}{t} \quad (3)$$

In equations (2) and (3), E is the Young's modulus of the CFs taken from the manufacturer's data sheet [26], ϵ is the strain in the CFs caused by the ion-insertion, ρ is the CF tow density, and t is the time for one full charge cycle.

2.5. Voltage-strain coupling measurements

Measurements of the voltage-strain coupling were carried out using the same method as described previously [11,12]. CFs were electrochemically cycled through 2 full potassiation/depotassiation cycles in order to establish corresponding cell potentials for 0%, 20%, 40%, 60%, 80% and 100% states of charge (SOC). Here, the term SOC is used to indicate the degree of potassiation of the CFs. For these measurements 100% SOC corresponds to a capacity of 170 mAh/g. On the third cycle the current was stopped at potentials established for the appropriate SOC in order to measure the voltage-strain response. After stopping the current the cell was left to rest for 60 min in order to let the potential stabilise. A cyclic axial strain of 0.28% was applied using the same micro-tensile tester as used for the expansion measurements, while the voltage response was monitored using a potentiostat. The CF sample gauge length was 22 mm, and the cyclic strain was applied at a rate of 0.1 mm/min, with a rest time between cycles of 15 s. Five cycles were measured for each SOC. The value of the cyclic voltage change was then found using a Fast-Fourier Transform function on the voltage response and the mean value of the response was taken. Measurements were carried out and compared on both the potassiation and depotassiation cycles.

In order to quantify the voltage-strain coupling, a coupling factor is defined in equation (4), where ΔV is the change in

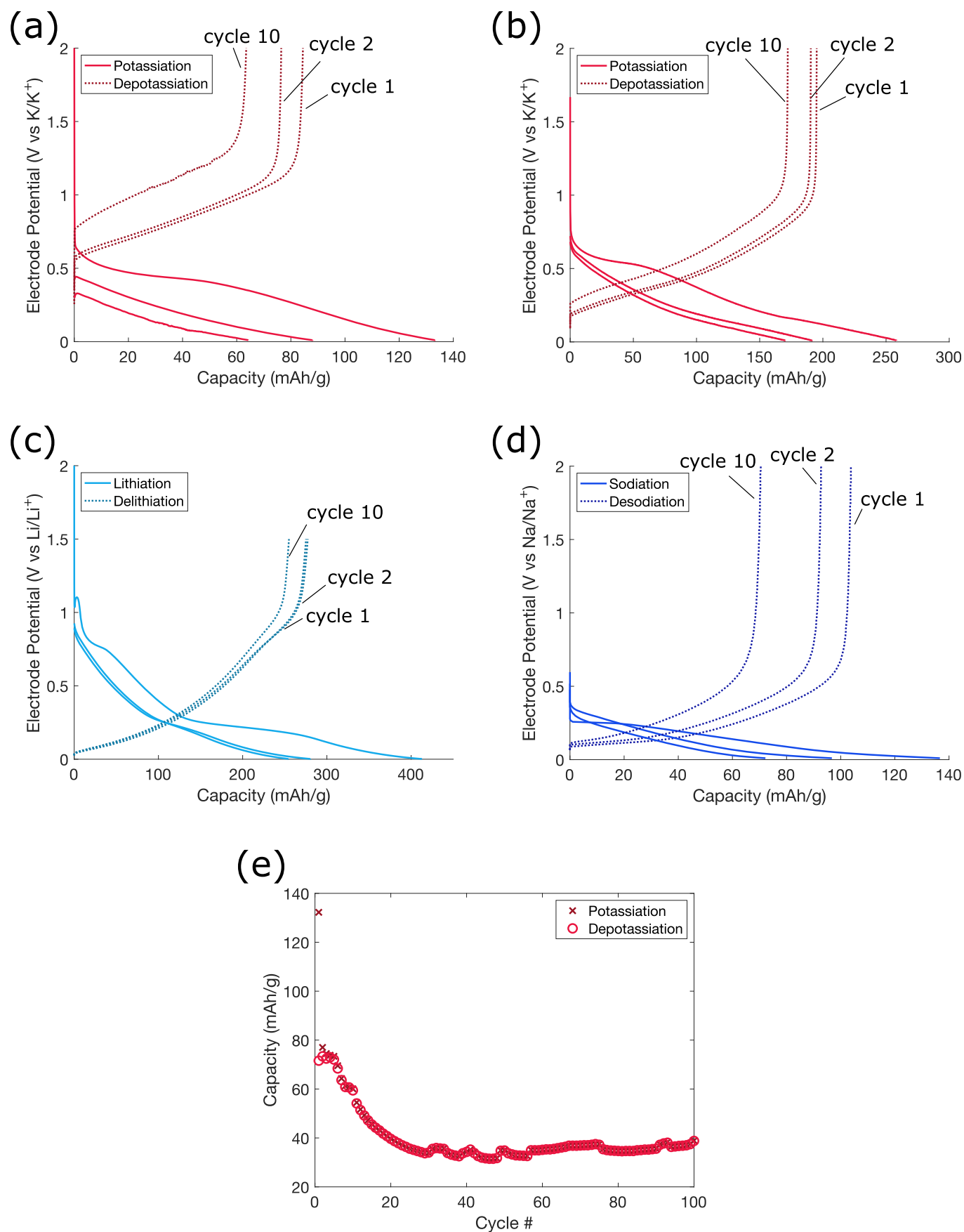


Fig. 2. 1st, 2nd and 10th cycle galvanostatic cycling curves for PAN-based CFs cycling against (a) potassium metal at a current density of 30 mA/g (b) potassium metal at a current density of 12 mA/g (c) lithium metal at a current density of 37 mA/g (d) Sodium metal at a current density of 34 mA/g, and (e) Longer term cycling against potassium metal at a current density of 24 mA/g.

electrical potential versus K/K^+ and $\Delta\epsilon$ is the change in mechanically applied axial strain on the CFs calculated using equation (1). The stiffness of the CF samples used for the voltage-strain coupling tests was measured to be 862.8 N/mm.

$$\text{coupling factor} = \frac{\Delta V}{\Delta \epsilon} \quad (4)$$

A larger coupling factor is favourable for sensing as it allows more sensitive strain measurements to be obtained.

3. Results

3.1. Electrochemical cycling and effect on mechanical performance

Galvanostatic curves for PAN-based CFs cycling against potassium metal at a current density of 30 mA/g are shown in Fig. 2a. The first-cycle capacity is 133 mAh/g, dropping to 89 mAh/g for the second cycle. First-cycle coulombic efficiency — a measure of the irreversibility of the ion-insertion process — is around 67%, which is similar to that measured for graphite [27] and considerably higher than the 41% of carbon nano-fibres [28]. In practice it is desirable to have a high first cycle coulombic efficiency as it results in higher reversible capacities on subsequent cycles. The capacity here continues to drop after the first cycle with the tenth cycle reaching a capacity of around 65 mAh/g. The steady drop in capacity was observed for all potassium cells cycled, with longer term cycling at a current density of 25 mA/g revealing that this decline in capacity continues until around the 20th cycle, where it plateaus around 40 mAh/g and remains relatively stable for the proceeding 80 cycles (Fig. 2e). This is similar to hard carbon electrodes cycled against potassium metal, with other studies finding substantial capacity losses in the first 20 cycles before a stable plateau is reached [23,29,30].

The high overpotentials observed are not encouraging for multifunctional structures and are most likely due to the sub-optimal electrolyte system used. It is possible that increasing the salt concentration of the electrolyte, or using a different solvent such as EC:PC or EC:DEC could help to alleviate the high overpotentials observed [27,31]. At lower current densities the overpotential was found to decrease (Fig. 2b).

For comparison, CFs cycling against lithium and sodium metal are shown at similar current densities in Fig. 2c and d respectively. Cycling against lithium results in considerably higher capacities, and better cycling stability. Cycling against sodium shows similar electrochemical performance to that of potassium.

Table 3 shows the effect of potassium-insertion on the axial stiffness of the charged and discharged CFs. Cells were cycled at a current density of 25 mA/g resulting in a capacity of 59 mAh/g. The subsequent ex-situ tensile tests showed that the CF axial stiffness remains within $\pm 6\%$ of the uncycled CFs when charged, and subsequently discharged. The axial strength drops by 12% when fully charged, recovering by 6% when discharged. Example force-extension curves from this testing are given in Supplementary Fig. S2.

In order to assess longer term effects of potassium-insertion on the mechanical performance of the CFs, new cells were cycled at a current density of 25 mA/g for 100 cycles (Fig. 2e). Ex-situ tensile testing performed on these CF specimens revealed no significant changes in axial stiffness or strength (see Supplementary Fig. S3 and Table S1), suggesting that despite the capacity loss in the first 20 cycles, no significant mechanical damage is being caused to the CFs by potassium-insertion. This is promising for use in multifunctional structures, since it shows that the mechanical stiffness is not significantly affected by the electrochemical processes.

Table 3

The effect of electrochemical cycling on mechanical performance of potassiated, lithiated [32], and sodiated [11] CFs. Percentages are given relative to uncycled CFs.

	K	Li [32]	Na [11]
Current density (mA/g)	25	136	42
Charged capacity (mAh/g)	59	140	120
Charged axial stiffness change (%)	-6 ± 3.3	$+3 \pm 5.9$	$+5 \pm 2.9$
Discharged axial stiffness change (%)	-1 ± 6.5	$+1 \pm 3.6$	$+2 \pm 3.5$
Charged axial strength change (%)	-12 ± 6.5	-19 ± 3.5	-28 ± 3.3
Discharged axial strength change (%)	-6 ± 5.6	-7 ± 2.3	-6 ± 13.5

For comparison, the mechanical performance of both sodiated and lithiated CFs is also given in Table 3, albeit at different charged capacities. The axial stiffness rises marginally with charging for both sodium and lithium, whereas for potassium it seems to fall slightly. Considering the margin of error, the stiffness can be assumed to remain approximately constant during the course of charge and discharge of the CFs. The axial strength drops in all cases, with lithiated and sodiated CFs showing a drop of 19% and 28% respectively when charged, and recovering by 12% and 22% respectively when discharged. This strength drop is greater than for the potassiated CFs, although it should be noted that the lower capacity will have influenced this. It is likely that at a higher capacity the potassiated CFs would show a larger drop in axial strength.

3.2. Linear actuation performance

Fig. 3a–c shows the axial expansion of CFs during potassiation for decreasing current densities, corresponding to slower charge times. For a current density of 32 mA/g a capacity of 51 mAh/g is reached in a charge time of 1.7 h (Fig. 3a and Table 4). This gives a maximum axial expansion of 0.12%. Lower current densities result in higher capacities and hence higher axial expansions, with 15 mA/g giving a capacity of 89 mAh/g, corresponding to an axial expansion of 0.19% (Fig. 3a). Similarly, 8 mA/g gives a capacity of 136 mAh/g, and a resulting axial expansion of 0.24% (Fig. 3a). The axial expansion of the CFs during potassiation is relatively linear, with no pronounced staging in the expansion curves particularly at higher current densities. At lower current densities a slight staging appears in the axial expansion for potassiation (Fig. 3a), suggesting that there is an ion-insertion mechanism that is exploited more at lower current densities. Higher current densities result in a higher cell overpotential, meaning that the full potential range is not exploited, which could explain the lack of pronounced staging.

For comparison Fig. 3b shows the axial expansion of CFs subjected to potassiation, lithiation, and sodiation at various current densities. Lithiation results in a substantially higher expansion due to a higher achievable capacity. However, it is interesting to observe that at around 50 mAh/g potassiation results in a higher axial expansion than lithiation, suggesting that the expansion per charge for potassiation is slightly higher. Sodiation results in a very clear staging, unlike potassiation or lithiation, which has been attributed to different ion-insertion mechanisms in the CF microstructure [11].

To verify that the small change in axial stiffness observed for the potassiated CFs did not significantly affect the axial strain measurements a sensitivity analysis was carried out. A linear decrease of the CF stiffness was assumed during a potassiation cycle down to a minimum of 6% less than the original measured stiffness at full potassiation. Since the axial strain is inversely proportional to the axial stiffness it was found that the maximum measured axial strain would increase by 6% at full potassiation (see Supplementary Fig. S4), which does not significantly impact the comparison

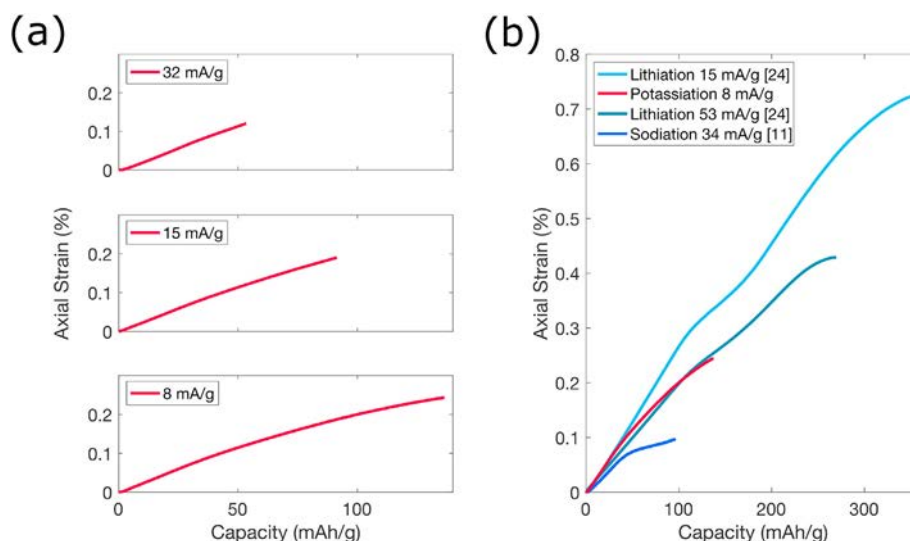


Fig. 3. (a) Axial expansion of PAN-based CFs with potassiation with decreasing current densities. (b) Comparison of axial expansions for potassiation, lithiation and sodiation. (A colour version of this figure can be viewed online.)

Table 4

Summary of actuation potential between potassium, lithium, and sodium functionalised CFs.

Insertion ion	Current Density (mA/g)	Capacity (mAh/g)	Max. Axial Strain (%)	β (g/mAh)	Time to full charge (h)	Actuation Energy (J/kg)	Actuation Power (mW/kg)
K	32	51	0.12	2.35×10^{-5}	1.7	117	19
K	15	89	0.19	2.14×10^{-5}	5.7	293	14
K	8	136	0.24	1.84×10^{-5}	17.0	507	8
Li [24]	53	269	0.44	1.64×10^{-5}	5.1	1572	85
Li [24]	15	354	0.72	2.03×10^{-5}	24.4	4210	47
Na [11]	34	90	0.09	1.01×10^{-5}	3.1	65	5

carried out here.

It has been shown previously that PC-based electrolytes can co-intercalate into graphitic materials [33–36]. To ensure that the expansion results were not affected by the solvent used, a number of expansion tests were carried out using EC:DEC-based electrolyte. It was found that the expansion per capacity for PC- and EC:DEC-based electrolytes were similar, suggesting that the degree of expansion is not solvent-dependent.

The actuation energy and power can be calculated for the axial expansion of the CFs using equations (2) and (3) respectively. These values are shown in Table 4 for varying current densities. Potassiation of CFs at the highest current rate — corresponding to a charge time of 1.7 h — gives a linear actuation energy of 117 J/kg, which is similar to the actuation energy of a typical piezo-ceramic material [25], and more than that of sodiated CFs at a similar current density. At a lower current density of 8 mA/g, a linear actuation energy of 507 J/kg is obtained. Considerably more linear actuation energy is available from lithiated CFs, with lithiation at a current density of 15 mA/g resulting in an actuation energy of 4210 J/kg. The linear actuation power is also relatively low for potassiated CFs, with a maximum of 19 mW/kg being produced at a current density of 32 mA/g.

Overall, potassiated CFs perform better than sodiated CFs but not as well as lithiated CFs in terms of axial strain, linear actuation energy and power.

3.3. Morphing cantilever model

A solid-state morphing structure actuated using the transfer of lithium-ions between two CF layers has previously been shown by

Johannisson et al. [10]. This concept operates when one layer expands during charge, while the other contracts, creating a bending motion. The structure relies on a multifunctional structural battery electrolyte (SBE) which simultaneously bears load and enables ion transfer between the CF layers. A schematic of the setup for such a morphing structure in a cantilever setup is shown in Fig. 4a, where the two CF layers are separated by a non-active separator layer.

Since an SBE does not yet exist for sodium- or potassium-based chemistries, it was not possible to test this setup experimentally. However using a simple analytical model it was possible to simulate the deflections that would be possible based on the measured axial expansions. The same model as used and validated in Johannisson et al. [10] is used here, whereby the structure is modelled analogously to a bi-metal thermostat. A thermal expansion analogy is used as in Dionisi et al. [37], whereby an expansion coefficient β is assigned to each CF layer, and the corresponding expansions are calculated using equation (5), where ΔC is the change in specific capacity in the CF layer in [mAh/g].

$$\varepsilon = \beta \cdot \Delta C \quad (5)$$

Input data for the model can be found in Table 4, where the β value is taken as the maximum axial expansion value divided by the corresponding capacity shown in Fig. 3d, and the ΔC is half of the capacity achieved. The geometrical and mechanical inputs were kept constant for the analyses (summarised in Supplementary Table S2).

Fig. 4b shows the predicted deflections for the morphing structure for potassium, lithium, and sodium activation. Lithium-insertion gives the most deformation — in fact bending back on

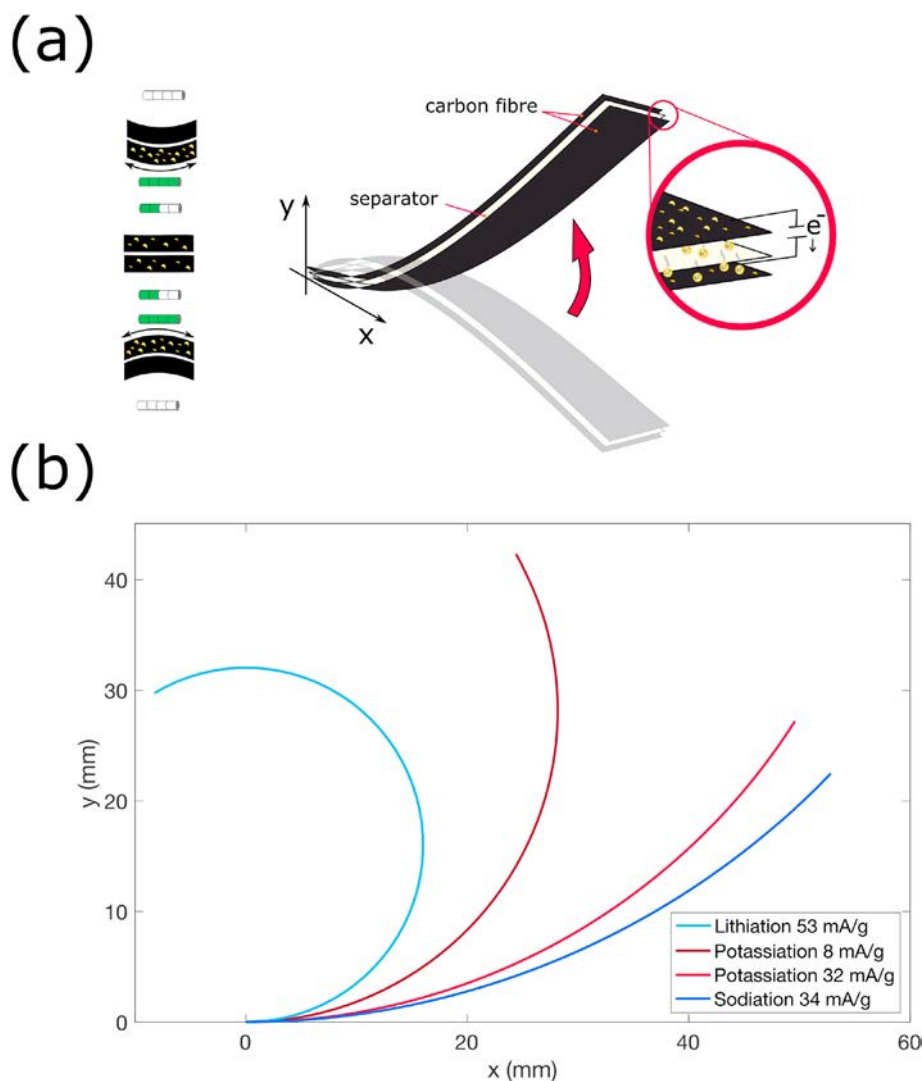


Fig. 4. (a) Concept of a morphing structure using PAN-based CFs and Li-ion insertion presented in Johannisson et al. [10] (b) Modelled morphing displacements at maximum capacity for different current densities using experimentally measured expansion data for potassium-, lithium- [24], and sodium-insertion [11]. (A colour version of this figure can be viewed online.)

itself — similar to the experimentally observed deflections [10]. Potassium-insertion results in slightly more deformation than for sodium, particularly at a lower current density, although it is interesting to note that both give significant deformations, despite lower axial strain values.

3.4. Strain sensing performance

Fig. 5a shows the voltage-strain coupling factor at various SOC for potassiation and depotassiation. The voltage-strain coupling follows a similar trend for both potassiation and depotassiation, reaching a peak around 0.26 on potassiation at 40% SOC, and 0.25 on depotassiation at a 60% SOC. Fig. 5b shows the coupling factor comparison at various SOC for lithiation, sodiation and potassiation. Note that 100% SOC corresponds to 170 mAh/g, 350 mAh/g and 100 mAh/g for potassiation, lithiation and sodiation respectively. The peak coupling factor for potassiation is slightly higher than the 0.15 for sodium, although considerably less than the 1.46 for lithium (Table 5). Despite this, the coupling factor is relatively insensitive to the SOC of the CFs for potassium with a flat response between 0 – 100 % SOC.

It has previously been shown that it is possible to use this voltage-strain coupling to harvest energy from lithiated CFs. This is done by straining the CFs during discharge, meaning that the discharge occurs at a higher potential than the charge, hence converting mechanical energy to electrical potential [16]. This can only work if the cell overpotential can be overcome by applying mechanical strain, and therefore a combination of a large voltage-strain coupling and a low overpotential are required. For potassiated CFs the overpotentials are relatively high and the voltage-strain coupling is relatively low, meaning that the electrochemical system would need to be improved before energy harvesting would be feasible.

4. Discussion

It has been shown using XRD that the d_{002} spacing in graphite increases by around 13% when intercalated with lithium [38] and around 60% with potassium [39]. Sodium does not readily intercalate in graphite [40] without the help of co-intercalation using glyme-based electrolytes, which causes a d_{002} spacing expansion of 15% [41]. This points to a correlation between cation atomic radius,

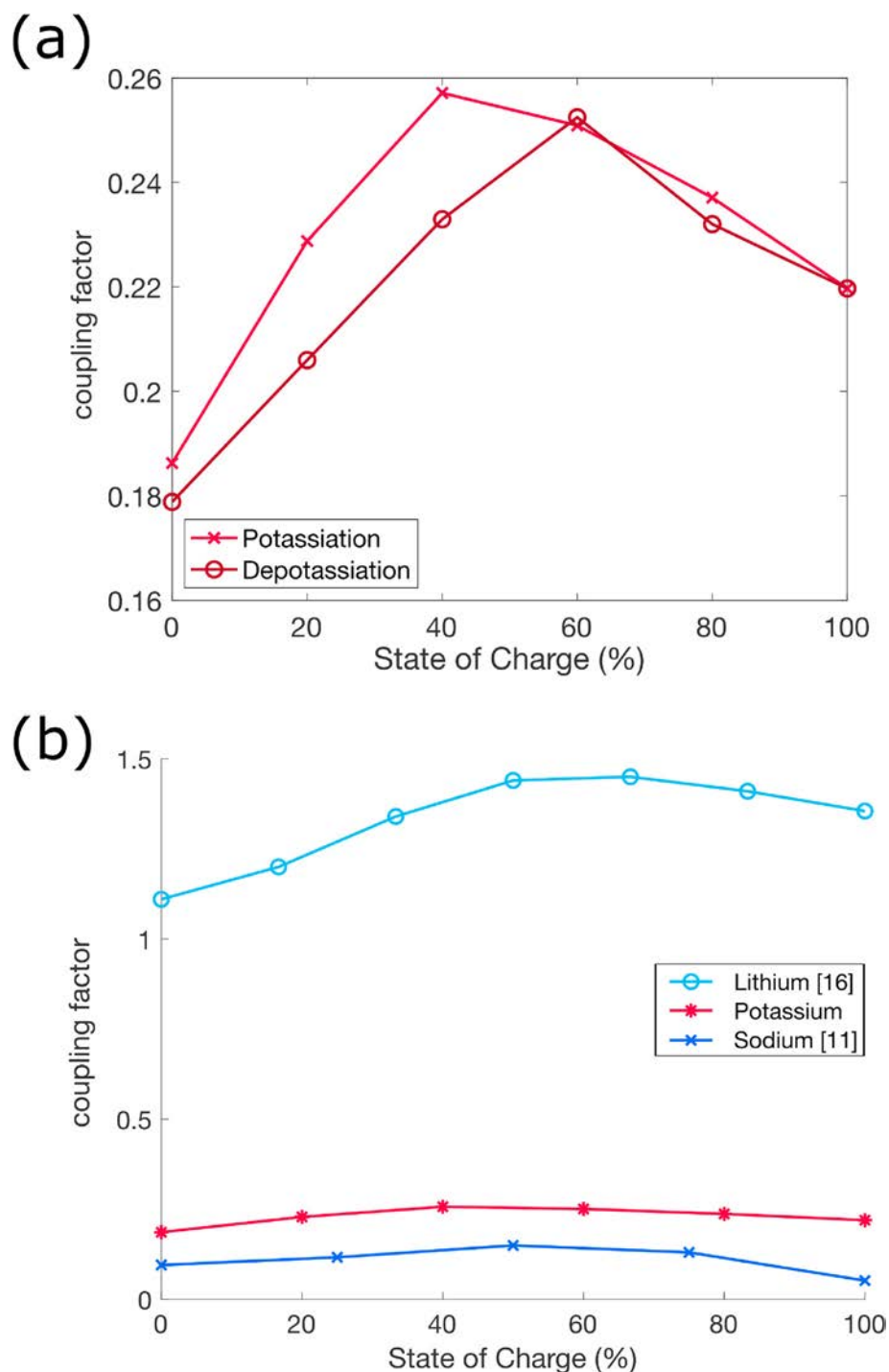


Fig. 5. (a) k factor measuring voltage-strain coupling in CFs for potassiation and depotassiation (b) Comparison of k factor for potassiation, lithiation, and sodiation of PAN-based CFs at various SOC. Note that 100% SOC corresponds to 170 mAh/g, 350 mAh/g and 100 mAh/g for potassiation, lithiation and sodiation respectively. (A colour version of this figure can be viewed online.)

Table 5

Summary of voltage-strain coupling for potassium, lithium, and sodium functionalised CFs.

	K	Li [16]	Na [11]
Max. coupling factor (V/unit strain)	0.26	1.46	0.15
SOC for max. k factor	50%	60%	45%

and the increase in d_{002} spacing, as found elsewhere [29]. However, for the PAN-based CFs used here, there is no clear correlation between the atomic radius and resulting axial expansions. The T800 CF is less dense than graphite, with a microstructure consisting of crystalline graphite-like domains with a d_{002} spacing of 3.7 Å as well as amorphous hard carbon like domains [22].

The most commonly proposed ion-insertion mechanisms for alkali metals include intercalation between graphite sheets and

insertion into micropores and edge-defects [42]. It is often assumed that ion-insertion into micropores and edge-defects causes less expansion than intercalation [42,43]. Our results show that sodium produces the lowest expansion per capacity in the CF. Both lithium and potassium seem to produce similar expansions per capacity, despite XRD analysis showing that potassium intercalation creates around 5 times more expansion than lithium in graphite. It therefore seems likely that there are different ratios of capacity associated with different ion-insertion mechanisms during charging. Our results indicate that more of the potassium and sodium capacities come from insertion in micropores and edge-defects, while little comes from intercalation — although the little that is intercalated may cause a relatively large expansion. In contrast, lithium may intercalate more readily, while also filling micropores and edge-defects.

The insertion mechanisms for sodium and potassium in the CF therefore may be quite similar, with the majority of capacity coming from ion uptake in micropores and edge-defects. Lithium then would be the odd one out; both intercalating and inserting into micropores and edge-defects with considerable capacity.

It is still unknown what causes the voltage-strain coupling in ion-functionalised CFs. One possibility is that, on application of mechanical strain, reversible changes in the CF microstructure cause a local redistribution of ions. In this case, the ability of ions to move and diffuse in the CF microstructure would be key to the magnitude of the voltage-strain coupling. Conventional thinking points towards larger ions having lower ionic mobility [44]. However, in this case, potassium — with a larger ionic radius than sodium — appears to give a larger voltage-strain coupling than sodium. It has, however, been observed previously that potassium has a slightly higher ionic diffusion coefficient than sodium in hard carbon [45]. This could explain the stronger voltage-strain coupling seen in potassiated CFs compared to sodiated CFs. However, further investigation is needed to explain this effect.

5. Conclusions

Potassium-insertion in commercial PAN-based CFs provides a way of augmenting the CFs with further functionality such as energy storage, morphing, and strain-sensing. Potassium-insertion appears slightly more promising than sodium-insertion for creating multifunctionality, although lithium-insertion seems to be the more promising route for high performance structures so far. Further work is required on potassium-based positive electrodes, and solid battery electrolytes in order to progress this work further. Nonetheless, given the fast pace of development in the potassium-ion battery field, potassium-insertion in PAN-based CFs remains an interesting and viable alternative to lithium-insertion for multifunctional structures.

Declaration of competing interest

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

Acknowledgements

This work was supported by the Swedish Research Council project no. 2017-03898, the strategic innovation program LIGHTer (funding provided by Vinnova, the Swedish Energy Agency and Formas), H2020 Clean Sky II project no. 738085 and by the Air Force Office of Scientific Research under award number FA9550-17-1-0244. The Swedish research group Kombatt is acknowledged for its synergism throughout this work.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.carbon.2020.09.042>.

References

- [1] A. Lendlein, R.S. Trask, Multifunctional materials: concepts, function-structure relationships, knowledge-based design, translational materials research, *Multifunct. Mater.* 1 (2018), 010201, <https://doi.org/10.1088/2399-7532/aada7b>.
- [2] P. Thomas, D. Billaud, Sodium electrochemical insertion mechanisms in various carbon fibres, *Electrochim. Acta* 46 (22) (2001) 3359–3366, [https://doi.org/10.1016/S0013-4686\(01\)00536-9](https://doi.org/10.1016/S0013-4686(01)00536-9).
- [3] N. Ihrner, M. Johansson, Improved performance of solid polymer electrolytes for structural batteries utilizing plasticizing co-solvents, *J. Appl. Polym. Sci.* 134 (23) (2017) 1–6, <https://doi.org/10.1002/app.44917>.
- [4] L.M. Schneider, N. Ihrner, D. Zenkert, M. Johansson, Bicontinuous electrolytes via thermally initiated polymerization for structural lithium ion batteries, *ACS Appl. Energy Mater.* 2 (6) (2019) 4362–4369, <https://doi.org/10.1021/acsaem.9b00563>.
- [5] J. Hagberg, H.A. Maples, K.S. Alvim, J. Xu, W. Johansson, A. Bismarck, D. Zenkert, G. Lindbergh, Lithium iron phosphate coated carbon fiber electrodes for structural lithium ion batteries, *Compos. Sci. Technol.* 162 (April) (2018) 235–243, <https://doi.org/10.1016/j.compscitech.2018.04.041>.
- [6] K. Moyer, N. A. Boucherbil, M. Zohair, J. Eaves-Rathert, C. L. Pint, Polymer reinforced carbon fiber interfaces for high energy density structural lithium-ion batteries, *Sustain. Energy Fuels* doi:10.1039/d0se00263a.
- [7] J.F. Snyder, R.H. Carter, K. Xu, E.I. Wong, P.A. Nguyen, E.H. Hgo, E.D. Wetzel, Multifunctional structural composite batteries for U.S. Army applications, in: *Proc. 2006 Army Sci. Conf.*, no. December, Orlando, FL, 2006, pp. 1–11.
- [8] W. Johansson, D. Zenkert, G. Lindbergh, Model of a structural battery and its potential for system level mass savings, *Multifunct. Mater.* 2 (2019), <https://doi.org/10.1088/2399-7532/ab3bdd>.
- [9] L.E. Asp, M. Johansson, G. Lindbergh, J. Xu, D. Zenkert, Structural battery composites: a review, *Funct. Compos. Struct.* 1 (4) (2019), 042001, <https://doi.org/10.1088/2631-6331/ab5571>.
- [10] W. Johansson, R. Harnden, D. Zenkert, G. Lindbergh, Shape-morphing carbon fiber composite using electrochemical actuation, *Proc. Natl. Acad. Sci. Unit. States Am.* 117 (14) (2020) 7658–7664, <https://doi.org/10.1073/pnas.1921132117>.
- [11] R. Harnden, K. Peuvot, D. Zenkert, G. Lindbergh, Multifunctional performance of sodiated carbon fibers, *J. Electrochem. Soc.* 165 (13) (2018), <https://doi.org/10.1149/2.0971813jes>. B616–B622.
- [12] E. Jacques, M.H. Kjell, D. Zenkert, G. Lindbergh, Piezo-electrochemical effect in lithium-intercalated carbon fibres, *Electrochem. Commun.* 35 (2013) 65–67, <https://doi.org/10.1016/j.elecom.2013.07.040>.
- [13] H.P. Konka, M.A. Wahab, K. Lian, Piezoelectric fiber composite transducers for health monitoring in composite structures, *Sensors Actuators, A Phys.* 194 (2013) 84–94, <https://doi.org/10.1016/j.sna.2012.12.039>.
- [14] H. Murayama, D. Wada, H. Igawa, Structural health monitoring by using fiber-optic distributed strain sensors with high spatial resolution, *Photonics Sensors* 3 (4) (2013) 355–376, <https://doi.org/10.1007/s13320-013-0140-5>.
- [15] F. Kopsaftopoulos, R. Nardari, Y.-h. Li, P. Wang, F.-K. Chang, State sensing and awareness for a bio-inspired intelligent composite wing, *20th International Conference on Composite Materials*, 2015. Copenhagen.
- [16] E. Jacques, G. Lindbergh, D. Zenkert, S. Leijonmarck, M.H. Kjell, Piezo-electrochemical energy harvesting with lithium-intercalating carbon fibers, *ACS Appl. Mater. Interfaces* 7 (25) (2015) 13898–13904, <https://doi.org/10.1021/acsaami.5b02585>.
- [17] J.-M. Tarascon, Is lithium the new gold? *Nat. Chem.* 2 (6) (2010) 510, <https://doi.org/10.1038/nchem.680>.
- [18] S.E. Kesler, P.W. Gruber, P.A. Medina, G.A. Keoleian, M.P. Everson, T.J. Wallington, Global lithium resources: relative importance of pegmatite, brine and other deposits, *Ore Geol. Rev.* 48 (2012) 55–69, <https://doi.org/10.1016/j.oregeorev.2012.05.006>.
- [19] Z. Jian, W. Luo, X. Ji, Carbon electrodes for K-ion batteries, *J. Am. Chem. Soc.* 137 (36) (2015) 11566–11569, <https://doi.org/10.1021/jacs.5b06809>.
- [20] S.A. Matlin, G. Mehta, H. Hopf, A. Krief, The periodic table of the chemical elements and sustainable development, *Eur. J. Inorg. Chem.* 39–40 (2019) 4170–4173, <https://doi.org/10.1002/ejic.201801409>, 2019.
- [21] G. Fredi, S. Jeschke, A. Boulaoued, J. Wallenstein, F. Liu, R. Harnden, D. Zenkert, J. Hagberg, P. Johansson, L. Stievano, L.E. Asp, Graphitic microstructure and performance of carbon fibre Li-ion structural battery electrodes, *IOP Multifunct. Mater.* 1 (1) (2018), 015003, <https://doi.org/10.1088/2399-7532/aab707>.
- [22] J. Hagberg, S. Leijonmarck, G. Lindbergh, High precision coulometry of commercial PAN-based carbon fibers as electrodes in structural batteries, *J. Electrochem. Soc.* 163 (8) (2016) A1790–A1797, <https://doi.org/10.1149/2.0041609jes>.
- [23] J.C. Pramudita, D. Sehrawat, D. Goonetilleke, N. Sharma, An initial review of the status of electrode materials for potassium-ion batteries, *Adv. Energy Mater.* 7 (24) (2017) 1–21, <https://doi.org/10.1002/aenm.201602911>.

- [24] E. Jacques, M. Hellqvist Kjell, D. Zenkert, G. Lindbergh, M. Behm, Expansion of carbon fibres induced by lithium intercalation for structural electrode applications, *Carbon* 59 (2013) 246–254, <https://doi.org/10.1016/j.carbon.2013.03.015>.
- [25] J.E. Huber, N.A. Fleck, M.F. Ashby, The selection of mechanical actuators based on performance indices, *Proc. R. Soc. A Math. Phys. Eng. Sci.* 453 (1965) 2185–2205, <https://doi.org/10.1098/rspa.1997.0117>, 1997.
- [26] Toray Carbon Fibres America Inc., T800H Data Sheet, Tech. rep., Santa Ana, CA.
- [27] J. Zhao, X. Zou, Y. Zhu, Y. Xu, C. Wang, Electrochemical intercalation of potassium into graphite, *Adv. Funct. Mater.* 26 (44) (2016) 8103–8110, <https://doi.org/10.1002/adfm.201602248>.
- [28] R.A. Adams, J.M. Syu, Y. Zhao, C.T. Lo, A. Varma, V.G. Pol, Binder-free N- and O-rich carbon nanofiber anodes for long cycle life K-ion batteries, *ACS Appl. Mater. Interfaces* 9 (21) (2017) 17872–17881, <https://doi.org/10.1021/acsami.7b02476>.
- [29] Y. Liu, F. Fan, J. Wang, Y. Liu, H. Chen, K.L. Jungjohann, Y. Xu, Y. Zhu, D. Bigio, T. Zhu, C. Wang, In situ transmission electron microscopy study of electrochemical sodiation and potassiation of carbon nanofibers, *Nano Lett.* 14 (6) (2014) 3445–3452, <https://doi.org/10.1021/nl500970a>.
- [30] Z. Ju, S. Zhang, Z. Xing, Q. Zhuang, Y. Qiang, Y. Qian, Direct synthesis of few-layer F-doped graphene foam and its lithium/potassium storage properties, *ACS Appl. Mater. Interfaces* 8 (32) (2016) 20682–20690, <https://doi.org/10.1021/acsami.6b04763>.
- [31] J. Zhang, X. Yao, R.K. Misra, Q. Cai, Y. Zhao, Progress in electrolytes for beyond-lithium-ion batteries, *J. Mater. Sci. Technol.* 44 (2020) 237–257, <https://doi.org/10.1016/j.jmst.2020.01.017>.
- [32] E. Jacques, M.H. Kjell, D. Zenkert, G. Lindbergh, M. Behm, M. Willgert, Impact of electrochemical cycling on the tensile properties of carbon fibres for structural lithium-ion composite batteries, *Compos. Sci. Technol.* 72 (7) (2012) 792–798, <https://doi.org/10.1016/j.compscitech.2012.02.006>.
- [33] D. Aurbach, Y. Ein-Eli, The study of Li-graphite intercalation processes in several electrolyte systems using in situ X-ray diffraction, *J. Electrochem. Soc.* 142 (6) (1995) 1746–1752, <https://doi.org/10.1149/1.2044188>.
- [34] M. Inaba, Z. Siroma, Y. Kawatate, A. Funabiki, Z. Ogumi, Electrochemical scanning tunneling microscopy analysis of the surface reactions on graphite basal plane in ethylene carbonate-based solvents and propylene carbonate, *J. Power Sources* 68 (2) (1997) 221–226, [https://doi.org/10.1016/S0378-7753\(96\)02555-4](https://doi.org/10.1016/S0378-7753(96)02555-4).
- [35] D. Aurbach, B. Markovsky, I. Weissman, E. Levi, Y. Ein-Eli, On the correlation between surface chemistry and performance of graphite negative electrodes for Li ion batteries, *Electrochim. Acta* 45 (1) (1999) 67–86, [https://doi.org/10.1016/S0013-4686\(99\)00194-2](https://doi.org/10.1016/S0013-4686(99)00194-2).
- [36] D. Aurbach, M. Koltypin, H. Teller, In situ AFM imaging of surface phenomena on composite graphite electrodes during lithium insertion, *Langmuir* 18 (23) (2002) 9000, <https://doi.org/10.1021/la020306e>.
- [37] F. Dionisi, R. Harnden, D. Zenkert, A model to analyse deformations and stresses in structural batteries due to electrode expansions, *Compos. Struct.* 179 (2017) 580–589, <https://doi.org/10.1016/j.compstruct.2017.07.029>.
- [38] Y. Koyama, T.E. Chin, U. Rhyner, R.K. Holman, S.R. Hall, Y.M. Chiang, Harnessing the actuation potential of solid-state intercalation compounds, *Adv. Funct. Mater.* 16 (4) (2006) 492–498, <https://doi.org/10.1002/adfm.200500633>.
- [39] X. Zhao, S.A. Vail, Y. Lu, J. Song, W. Pan, D.R. Evans, J.J. Lee, Antimony/graphitic carbon composite anode for high-performance sodium-ion batteries, *ACS Appl. Mater. Interfaces* 8 (22) (2016) 13871–13878, <https://doi.org/10.1021/acsami.6b01761>.
- [40] D.A. Stevens, J.R. Dahn, The mechanisms of lithium and sodium insertion in carbon materials, *J. Electrochem. Soc.* 148 (8) (2001) A803–A811, <https://doi.org/10.1149/1.1379565>.
- [41] B. Jache, P. Adelhelm, Use of graphite as a highly reversible electrode with superior cycle life for sodium-ion batteries by making use of co-intercalation phenomena, *Angew. Chem. Int. Ed.* 53 (38) (2014) 10169–10173, <https://doi.org/10.1002/anie.201403734>.
- [42] H. Euchner, B.P. Vinayan, M.A. Reddy, M. Fichtner, A. Groß, Alkali metal insertion into hard carbon — the full picture, *J. Mater. Chem.* 8 (28) (2020) 14205–14213, <https://doi.org/10.1039/d0ta04868b>.
- [43] X. Lin, J. Huang, B. Zhang, Correlation between the microstructure of carbon materials and their potassium ion storage performance, *Carbon* 143 (2019) 138–146, <https://doi.org/10.1016/j.carbon.2018.11.001>.
- [44] Z. Wang, A.P. Ratvik, T. Grande, S.M. Selbach, Diffusion of alkali metals in the first stage graphite intercalation compounds by vdW-DFT calculations, *RSC Adv.* 5 (2015) 15985–15992, <https://doi.org/10.1039/c4ra15529g>.
- [45] Z. Jian, Z. Xing, C. Bommier, Z. Li, X. Ji, Hard carbon microspheres: potassium-ion anode versus sodium-ion anode, *Adv. Energy Mater.* 6 (3) (2015), <https://doi.org/10.1002/aenm.201501874>, 1501874.



Bicontinuous Electrolytes via Thermally Initiated Polymerization for Structural Lithium Ion Batteries

Lynn M. Schneider,^{†,‡} Niklas Ihrner,[‡] Dan Zenkert,[†] and Mats Johansson^{*,‡,§}

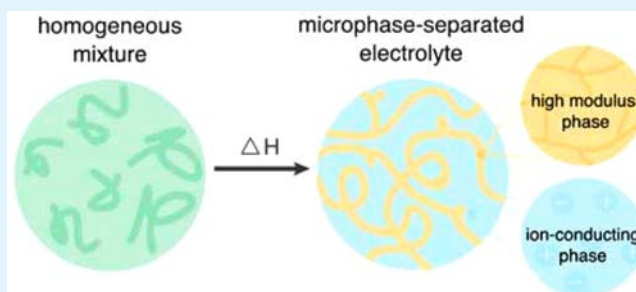
[†]Department of Aeronautical and Vehicle Engineering, KTH Royal Institute of Technology, SE-100 44 Stockholm, Sweden

[‡]Department of Fibre and Polymer Technology, KTH Royal Institute of Technology, SE-100 44 Stockholm, Sweden

[§] Supporting Information

ABSTRACT: Structural batteries (SBs) are a growing research subject worldwide. The idea is to provide massless energy by using a multifunctional material. This technology can provide a new pathway in electrification and offer different design opportunities and significant weight savings in vehicle applications. The type of SB discussed here is a multifunctional material that can carry mechanical loads and simultaneously provide an energy storage function. It is a composite material that utilizes carbon fibers (CFs) as electrodes and structural reinforcement which are embedded in a multifunctional polymer matrix (i.e., structural battery electrolyte). A feasible composite manufacturing method still needs to be developed to realize a full-cell SB. UV initiated polymerization induced phase separation (PIPS) has previously been used to make bicontinuous structural battery electrolytes (SBE) with good ionic conductivity and mechanical performance. However, UV-curing cannot be used for fabrication of a full-cell SB since a full-cell is made of multiple layers of nontransparent CFs. The present paper investigates thermally initiated PIPS to prepare a bicontinuous SBE and an SB half-cell. In addition, the effect of curing temperature was examined with respect to curing performance, morphology, ionic conductivity, and mechanical and electrochemical performance. The study revealed that thermally initiated PIPS provides a robust and scalable process route to fabricate SBs. The results of this study are an important milestone in the development of SB technology as they allow for the SB fabrication for an actual application. However, other challenges still remain to be solved before this technology can be introduced into an application.

KEYWORDS: thermal polymerization, lithium ion conductivity, polymerization induced microphase separation, bicontinuous morphology, polymer electrolyte matrices



INTRODUCTION

Multifunctional structures present an innovative concept to increase system efficiency as two or more functions are combined in one material.^{1,2} An SB is one example for a multifunctional lightweight material that enables energy storage and structural integrity simultaneously.³

An SB is a technological concept that resembles a standard fiber composite laminate. CF composites are lightweight materials with high structural performance. In an SB, this structural composite can simultaneously function as a battery, creating a multifunctional material. In this technology, multifunctionality is introduced by using multifunctional battery constituents such as CFs embedded in an electrolyte/matrix (i.e., structural battery electrolyte). CFs are used as high-performance structural backbone and as electrodes. In an SB concept, fibers and separator are laid up in the sequence: negative electrodes/separator/positive electrodes. For the negative electrode, commercial CFs can be used since Li ions can be intercalated, similar to a state-of-the-art Li-ion battery. The capacity also depends on the type of CF used, and for most intermediate modulus polyacrylonitrile-based CFs, the capacity stabilizes around 200–250 mAh g^{−1} in

commercial liquid electrolyte.^{4,5} The separator could be a thin glass fiber weave or veil. The positive electrode can be made of carbon fibers coated with an electrochemically active material, e.g., LiFePO₄.⁶ The fiber stack is embedded in an SBE, which is a key component to achieve multifunctionality since it has to transfer mechanical loads between the fibers and provide ionic conductivity.

The SB technology is particularly interesting for applications in the vehicle sector as it allows for significant weight savings on a system level. Substantial weight savings could be realized by using SBs in loadbearing structures,⁷ e.g., in the body panel of a car, in the interior of an airplane, or for electric ferries. Weight reduction, e.g., in an airplane, would improve fuel economy and thus reduce carbon dioxide emissions. For electric vehicles, SBs could increase driving range and also open up new design opportunities. The SB technology is still in an early development stage, and before a full-cell SB can be established into an application some challenges have to be

Received: March 15, 2019

Accepted: May 14, 2019

Published: May 14, 2019

solved.⁸ One of the major engineering challenges to realize a full-cell SB is to develop a feasible composite manufacturing process. The manufacturing process should be robust and scalable, provide high system performance, and should be suitable for curing a multilayer structure (full-cell SB). A feasible process allowing the fabrication of a multiple layer stack of full-cells while maintaining electrochemical and mechanical properties of the SB has not been developed yet. Liquid composite molding (LCM) is a well-established composite processing method for thermosets that is suitable for a large variety of geometrical shapes and sizes and requires low financial investment.⁹ Important aspects of LCM include the infusion and consolidation stages. Hence, the flow of the uncured resin must be controlled as well as the subsequent curing steps in order to manufacture an SB (i.e., multifunctional composite material) with desired performance. These aspects are both related to the properties and processing of the polymer matrix. The SBE is a crucial component in the SB since it needs to conduct Li-ions and transfer mechanical loads between the CFs.

Previous work has investigated homogeneous (i.e., uniform) electrolyte systems such as liquid electrolytes, gel polymer electrolytes (GPEs), and solid polymer electrolytes (SPEs). Liquid electrolytes are most commonly used due to their high ionic conductivity around 10^{-2} S cm⁻¹ at ambient temperature.¹⁰ However, they do not provide any mechanical performance and also give rise to safety issues such as leakage, flammability, and thermal instability. SPEs and GPEs are being researched as alternative electrolytes mainly to address the safety issues but also to offer multifunctionality.^{1,11} GPEs can achieve higher conductivities but lack mechanical performance^{12,13} for utilization in an SB concept. SPEs show better mechanical performance and are safer to use, but the ionic conductivity is lower than 10^{-4} S cm⁻¹.^{12,14,15} A common correlation for SPEs is that, as the mechanical performance of the electrolyte increases, the ionic conductivity decreases.¹⁶

Advantageous alternatives for SBEs are heterogeneous electrolytes. Heterogeneous electrolytes are systems that combine at least two different material phases to form at least two percolating structures on a submicron scale. A type of heterogeneous electrolyte is, for example, a liquid–solid system. The liquid phase provides adequate ionic conductivity while a polymer network provides mechanical integrity. These systems can be made using different routes involving, for example, vinyl ester or epoxy chemistries (chain or stepwise polymerization, respectively) combined with commercial liquid electrolytes or ionic liquids.^{17–20} Lodge and co-workers presented different combinations of systems containing ionic liquids providing high ionic conductivity and high mechanical performance simultaneously.^{21–24} However, the use of ionic liquids can be problematic for battery applications due to low Li-ion transfer numbers.^{25,26} Ihrner et al.²⁷ established a phase-separated methacrylate-based SBE involving organic electrolyte for SBs. This system shows an elastic modulus around 360 MPa and an ionic conductivity around 2×10^{-4} S cm⁻¹ at ambient temperature. The utilized monomers are close in resemblance to conventional vinyl ester composite matrices. Therefore, a comparison with respect to mechanical performance with conventional vinyl ester matrices is feasible.

Heterogeneous electrolytes can be prepared using PIPS (i.e., reaction induced phase separation) based on a UV initiated radical chain polymerization. Lodge and co-workers introduced PIPS as a concept to make heterogeneous electrolytes on

stepwise polymerizing systems in combination with ionic liquids.^{21,22} PIPS is a one-pot reaction that is based on solubility differences between the polymer and the monomer used to build it. The phase separation is influenced by a number of factors including the following: relative solubility parameters between ingoing components, reaction mechanism (stepwise vs chain-wise polymerization), temperature, and kinetics. These parameters also change when changing the processing method, e.g., from UV-curing to thermal curing. The concept of PIPS has previously been investigated in other multifunctional material concepts such as extended wear contact lenses²⁸ and dental composite materials.²⁹

Ihrner et al.²⁷ used a UV initiated PIPS with a free radical chain-wise polymerization mechanism. A chain-wise polymerization differs fundamentally from the stepwise polymerizing system³⁰ used by Lodge and co-workers.^{21,22} Chain-wise polymerizing systems for example often produce a significant amount of reaction heat that will determine the thermal history of the system, which will affect the materials properties and the process design.³¹ Composites made of multiple layers of nontransparent CF (e.g., a full-cell SB) cannot be manufactured using UV-curing because the UV light will just penetrate the surface, and thus, curing of a full-cell SB would be incomplete and inhomogeneous. Therefore, UV initiated PIPS cannot be used to fabricate a full-cell SB.

An alternative process route is to use thermal curing which is a well-known technique in the composite industry.³² Thermally initiated PIPS is likely to affect the final properties of the SBE system since reaction kinetics and thermal history of the sample during cure are inherently different compared to UV-curing. In thermal curing, the curing temperature is increased by additional heat of the exothermic reaction which influences the thermal history of the sample. Glauser et al.³¹ showed that thermo-mechanical properties of the systems are affected by the thermal history of the sample during cure. Thermal curing of thermosets also makes it more unlikely for vitrification to occur in an early stage of the reaction. Sample geometry, molds, and packaging as well as other components in the system will also influence the curing behavior. By way of example, CFs can act as heat sinks that reduce the heat in the system caused by the exothermic reaction.³¹ A lower temperature in the specimen during cure can be beneficial to avoid thermal degradation of the material, particularly for thick specimens that do not allow for sufficient heat dissipation.³³

The present work demonstrates a suitable process to fabricate multilayer stacks of full-cell SBs using thermal curing. This process allows the use of an ordinary composite manufacturing that is scalable; and it complies with limitations set by the battery constituents to form a multifunctional CF electrode. The phase separation of the bicontinuous SBE and multifunctional performance was studied on pure SBE films and on a uni-directional (UD) laminae negative electrode. The multifunctionality was evaluated with respect to morphology, curing kinetics, mechanical properties, and electrochemical performance, both as a freestanding film and on a composite level.

■ EXPERIMENTAL SECTION

Materials. Bisphenol A ethoxylate dimethacrylate (M_n : 540 g mol⁻¹) was supplied by Sartomer Company, Europe. Dimethyl methylphosphonate (97%) (DMMP), ethylene carbonate (99% anhydrous) (EC), lithium trifluoromethanesulfonate (LiTFS) (96%), and 2,2'-azobis(2-methylpropionitrile) (AIBN) were pur-

chased from Sigma-Aldrich. CFs of the type T800S from Toray were provided as 10 mm spread tows from Oxeon AB. The linear weight of the fibers was 0.52 g m⁻¹. Before use, DMMP, EC, and LiTFS were heated to remove residual moisture. All other materials were used as received.

Techniques and Procedures. Structural Battery Electrolyte Preparation. SBE mixtures were prepared in argon atmosphere and dry conditions (<1 ppm of H₂O, <1 ppm of O₂). A stock solution of liquid electrolyte was prepared and used for all samples. The liquid electrolyte contained EC and DMMP (50:50 wt %) where LiTFS was dissolved until a concentration of 1 M was reached. The same SBE composition was used for all samples. The SBE solution was obtained by mixing the liquid electrolyte with the monomer bisphenol A ethoxylate dimethacrylate and the thermal initiator, AIBN (1 wt % of the monomer weight). The amount of liquid electrolyte in the SBE solution corresponded to 39 wt % of the total weight. Once a homogeneous mixture was obtained, the solution was transferred to an aluminum mold (30 × 6 × 0.5 mm³) and covered with a glass slide. The mold was clamped on both sides and vacuum-sealed in the glovebox. The samples were then transferred to a preheated oven outside the glovebox and directly thermally cured at 70, 80, and 90 °C for 105, 75, and 45 min, respectively. SBE films were also made using UV-curing as described by Ihrner et al.²⁷

Real Time Fourier-Transform Infrared Spectroscopy and Fourier-Transform Infrared Spectroscopy. Real time Fourier-Transform Infrared Spectroscopy (RT-FTIR) and Fourier-Transform Infrared Spectroscopy (FTIR) were performed to study the reaction rate and the final double bond conversion, respectively. A PerkinElmer Spectrum 100 equipped with a triglycine sulfate (TGS) detector was used in both cases. The instrument was equipped with a single reflection attenuated total reflection (ATR) accessory unit, with a diamond ATR crystal (Golden gate) from Graseby Specac Ltd. The Golden Gate had a temperature control (Specac, Heated Golden Gate Controller). The data was analyzed using Spectrum software v. 10.5.1 from PerkinElmer.

The RT-FTIR data was recorded at 1 scan per 5.7 s with a resolution of 4.0 cm⁻¹. The software used for RT-FTIR was TimeBase from PerkinElmer.

For RT-FTIR, a droplet of uncured resin including liquid electrolyte was put on the heated ATR crystal for each curing temperature and covered with a glass plate. For the samples containing CFs, a 6K CF tow (T800) was placed on the heated ATR crystal and directly after a droplet of uncured resin with electrolyte was put on top of the CFs and covered with a glass plate. In all cases, the recording of the spectra was started before the droplet was put onto the ATR crystal to record all events in the curing. The measurements were stopped when spectral changes no longer occurred. Experiments were executed for curing at 70, 80, and 90 °C.

The samples for FTIR were analyzed both before and after curing, i.e., as SBE solution and as cured SBE films. There were 16 scans with a resolution of 4 cm⁻¹ performed for each spectrum. The conversion of the acrylate groups was determined by comparing the area under the vinyl peak at 1637 cm⁻¹ of uncured resin and cured films. The carbonyl peak of the ester group at 1715 cm⁻¹ was used as the internal reference peak for all spectra.

Scanning Electron Microscopy. Scanning Electron Microscopy (SEM) was used to investigate the microstructure of the SBEs, by analyzing the cross-sections of cured SBE films. For the SEM analysis a Hitachi S-4800 equipped with a cold field-emission electron source was used. Before analysis, the samples were immersed in water for 24 h to extract the liquid electrolyte (LiTFS, EC, and DMMP). The samples were then dried in a vacuum oven overnight at 60 °C. All samples were weighed before immersion in water and after drying to determine the mass loss. The samples were then cooled with liquid nitrogen and fractured. The samples were mounted into a split mold, and the fractured cross-section was coated with Pt/Pd using an Agar HR sputter coater. A sputtered layer thickness of 3 nm was chosen for sufficient conductivity of the sample.

Dynamic Mechanical Analysis. The mechanical properties of SBE films were investigated using Dynamic Mechanical Analysis (DMA)

with a TA Instruments DMA Q800 in tensile mode. The thermally cured or UV-cured (as described by Ihrner et al.²⁷) SBE films were clamped into the sample holder with a length of 10–15 mm between the clamps. The samples were kept isothermally at 25 °C for 10 min to allow them to equilibrate. Next, the sample was heated at a rate of 3 °C min⁻¹ to 200 °C. An amplitude of 8–13 μm was applied (<0.1% of the sample length).

Electrochemical Impedance Spectroscopy. Electrochemical Impedance Spectroscopy (EIS) was used to estimate the ionic conductivity of the sample at ambient temperature. The samples were measured directly after curing inside a glovebox to avoid any evaporation of the electrolyte from the films. The samples were measured using a Gamry Series G 750 potentiostat/galvanostat/ZRA interface with a four-point electrode cell. Gold wires were used as electrodes, with two working electrodes (20 mm apart), and, in between them, two reference electrodes (5 mm apart). The impedance was measured in the frequency range 120 kHz to 1 Hz, with an amplitude of 10 mV. The bulk resistance (*R_b*) was determined from the Nyquist plot by using the low-frequency intercept with the real axis. The ionic conductivity was calculated using the equation below

$$\sigma = \frac{l}{R_b \times A}$$

Here, σ is the ionic conductivity, l the length between the reference electrodes (5 mm), and R_b the bulk resistance determined from the Nyquist plot. A is the cross-sectional area of the sample. The thickness of each sample was measured using a digital slide caliper.

Structural Battery Half-Cell Preparation. Composite CF electrodes were prepared using vacuum infusion, and then, half-cells were assembled in a pouch cell. Spread fibers with a width of 10 mm were taped onto a glass plate (150 mm × 70 mm). Copper foil current collectors were glued to one end of the spread CFs using Electrolube silver conductive paint. The CFs were covered with a release film (perforated polyethylene film) and breather fabric (distribution medium of coarse polyester felt cloth). The assembly was then sealed using a vacuum bag and rubber tape and dried in a vacuum oven at 60 °C for 12 h. The SBE resin was prepared in the glovebox in dry argon atmosphere (<1 ppm of H₂O, <1 ppm of O₂) in the same way as described in the [Structural Battery Electrolyte Preparation](#) section. The resin container was sealed with a septum, and vacuum infusion of the prepared glass plate with CFs was executed outside the glovebox. The samples were then thermally or UV-cured (as described by Ihrner et al.²⁷). The thermal curing of the CF composites was done at 70, 80, and 90 °C for 105, 75, and 45 min, respectively. After curing, the CF lamina (10 mm × 31 mm) was removed from the vacuum bag in the glovebox and directly inserted into a two-electrode pouch cell (70 mm × 70 mm). Lithium metal foil was used as counter electrode with a nickel current collector, and a Whatman glass-microfiber filter was used as a separator between electrodes. Small amounts (around 200 μL) of additional liquid electrolyte were used to wet the separator film to ensure ionic conduction.

Testing of a Half-Cell/Unidirectional Lamina. The half-cell cured at 80 °C was galvanostatically cycled between 0.002 and 1.5 V vs Li/Li⁺ over 40 cycles at ambient temperature. A stepping of current densities was applied. The applied current densities were 18.6 mA g⁻¹ over 10 cycles corresponding to approximately 0.17 C, 37.2 mA g⁻¹ over 5 cycles corresponding to approximately 0.33 C, 74.4 mA g⁻¹ over 20 cycles corresponding to approximately 0.67 C, and 18.6 mA g⁻¹ over 10 cycles corresponding to approximately 0.17 C. The capacities were calculated on the basis of a linear weight of the CFs (0.52 g m⁻¹).

The elastic modulus of the composite electrode in the transverse direction was evaluated using a three-point bending setup as described in previous work by Johannisson et al.⁷ The same experimental procedure was applied where the thin composite electrode (i.e., UD lamina) was bonded to a PET substrate and the bending stiffness of the entire assembly was measured. Then, the modulus of the

composite electrode was calculated from the measured bending stiffness using standard laminate theory.³⁴ The sample cured at 80 °C for 75 min and cycled for 40 cycles was used to estimate the transverse elastic modulus. Six specimens of the UD lamina were tested and evaluated (Figure S3).

RESULTS AND DISCUSSION

Curing Performance. The polymerization of the SBE was monitored in situ utilizing RT-FTIR on specimens that consisted of the monomer, initiator, and liquid electrolyte, with and without the presence of CFs.

The samples cured at 80 and 90 °C show the highest conversion and the fastest curing times. Figure 1 shows the

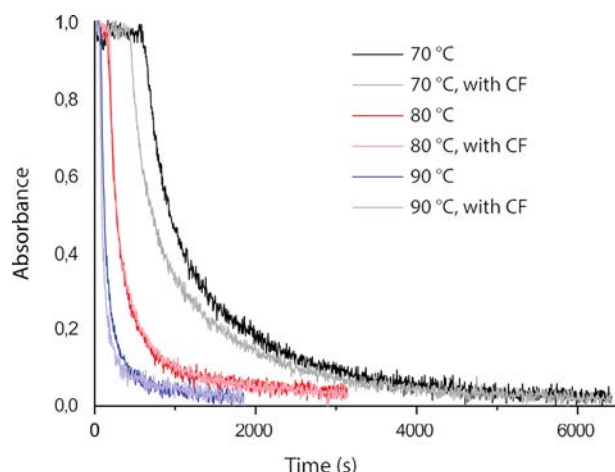


Figure 1. RT-FTIR data show absorbance vs. time. The disappearance of the vinyl stretch peak at 1637 cm^{-1} was observed over time. The data is normalized with respect to the vinyl peak at 1637 cm^{-1} .

RT-FTIR data of different samples as the absorption of the vinyl peak (1637 cm^{-1}) versus time. The resins cured at different temperatures reach an equilibrium state without further reaction after approximately 90, 60, and 30 min for 70, 80, and 90 °C, respectively. The difference in curing times for different temperatures can be related to the half-time of the heat initiator AIBN at different temperatures. Higher temperatures lead to more initiator molecules decomposing and thus a faster reaction. When curing the SBE films and composite electrodes, 15 min were added to compensate for heating up the molds and the vacuum bag.

The samples with and without CFs do not show any significant difference in terms of curing behavior and time. Only the samples cured at 70 °C show a shorter induction time (2–3 min) for the sample containing CFs. The shorter induction time with CFs can be attributed to the fact that CFs improve the heat conduction in the sample, and since induction times are generally longer for 70 °C, this effect becomes apparent when compared to the samples cured at higher temperatures. For higher curing temperatures, this effect is not observed. In fact, the sample at 80 °C shows a higher induction time for the sample containing CFs. However, the difference is only a few seconds and is not conclusive; thus, it can be attributed to experimental scatter.

The FTIR results show that the double bond conversion of the SBE specimens was high (Table 1). The difference compared to the RT-FTIR study is that the FTIR sample geometry is larger and hence heat transfer mechanisms will be

Table 1. Results from FTIR, EIS, and Weight Loss during Solvent Exchange for Samples Cured at Different Temperatures (70, 80, 90 °C) and a UV-Cured Sample

curing [°C/UV]	conversion [%]	ionic conductivity at 25 °C [S cm^{-1}]	weight loss in SEM sample preparation [%]
70	87	$1.95 \times 10^{-4} \pm 4.3\%$	39.5
80	95	$2.00 \times 10^{-4} \pm 7.0\%$	38.6
90	96	$1.96 \times 10^{-4} \pm 1.5\%$	38.1
UV	85	$2.02 \times 10^{-4} \pm 3.4\%$	38.5

different. The increase in sample geometry results in two different effects compared to the RT-FTIR measurements. First, the initiation step of the samples is delayed since the heat transfer from the oven to the specimen is slower in a convection oven compared to the direct contact between the heating source and the specimen as in the RT-FTIR setup. Second, the heat dissipation of the reaction heat is less since the specimen is larger and internal heat transfer rates in a polymer are slow compared to direct heat transfer to a good heat conductor such as the diamond crystal in the ATR-device. In short, this means that the initiation step of SBE films is delayed at lower temperatures but also that when it commences the temperature increase in the specimen might be less which can be beneficial when using more thermally unstable Li-salts in the battery electrolyte. A higher curing temperature will consequently give a quicker initiation but at the same time add a risk of thermal overshoot. The conversion for the 80 and 90 °C cured films was determined to be above 95%, indicating that this is a suitable curing temperature for this specimen geometry, Figure S1. The 70 °C cured film shows a slightly lower conversion of 87% which is comparable with the conversion of the UV-cured specimen (Table 1). The lower conversion of 70 °C cured films is related to the fact that the system reaches vitrification at an earlier stage. Therefore, the system is locked (vitrified) earlier than if films are cured at higher temperatures; i.e., the balance of formed heat and heat dissipation is such that full cure is not completely established. The lower conversion thus leads to a decrease in thermo-mechanical performance of the UV and 70 °C cured films. However, the degrees of conversion are still fairly high for both curing methods (>80%). The results imply that a processing window between the 80 and 90 °C is suitable for the present system and that it is relatively robust against minor changes in curing conditions and sample geometries.

Microstructure of Cured SBEs. Images of the UV and thermally cured SBE films are shown in Figure 2. It can be seen that all thermally cured films have a comparable opaque appearance when cured at different temperatures. This already indicates the presence of a two-phase system that scatters light in the visible light wavelength range ($0.3\text{--}0.9\text{ }\mu\text{m}$). However, the surface of the film cured at 70 °C appears smoother and slightly more transparent indicating a slight difference in phase



Figure 2. Images of SBE films for different curing temperatures and processing methods: 70, 80, and 90 °C and UV-cured (left to right).

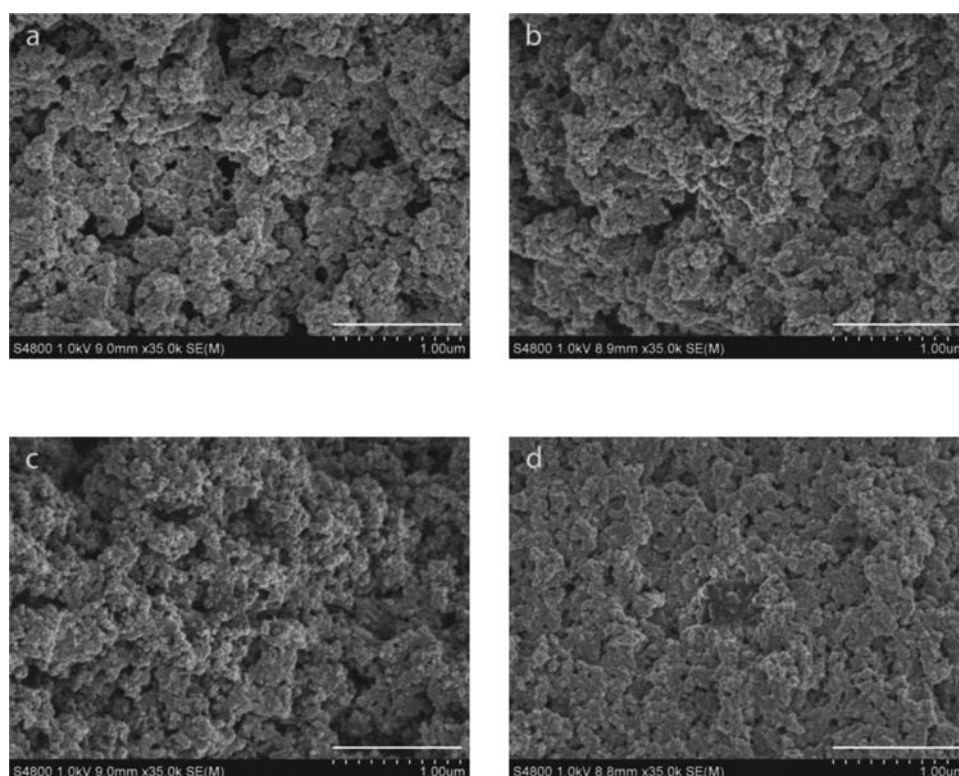


Figure 3. SEM images of samples cured at different temperatures and with a different processing method: (a) 70 °C, (b) 80 °C, (c) 90 °C, (d) UV at 35k magnification. In all samples, the liquid electrolyte has been extracted beforehand.

morphology with smaller domains. The formed domain sizes depend on the polymerization rate and solubility of different molecular weights which both depend on the temperature and their inter-relationship. Differences in surface properties might result from lower thermal stresses in the 70 °C sample. Thus, cure shrinkage that can create voids at the surface³⁵ could be reduced compared to samples cured at higher temperatures.

Another visible feature is that the thermally cured samples are less transparent than the UV-cured film (Figure 2). The increase in opacity indicates a phase separation in a larger domain size on a microlevel as explained in previous work.²⁷ This is also supported by the SEM pictures of the thermally cured samples as shown in Figure 3.

The samples cured at different temperatures all indicate the presence of a phase-separated system. In addition, the curing temperature does not seem to significantly affect the morphology as indicated by the similarity of the different SEM images. The similarity in morphology can be attributed to the stronger influence of the reaction exotherm than a 10–20 °C difference in curing temperature.

The morphology of the UV-cured sample (Figure 3d) is comparable to the thermally cured samples but on a smaller length scale. The UV-cured sample shows a smaller pore size distribution in the range 50–100 nm compared to the thermally cured samples with pore sizes ranging from 50 to 200 nm. This difference can be caused by several different factors related either to the initiation and polymerization rate or to the phase separation rate, which are all dependent on the temperature profile within the specimens. The UV-curing commences at ambient temperature with a high concentration of radicals formed as soon as the initiator is exposed to UV-light. The specimen temperature will mainly depend on the reaction heat and how fast it dissipates. The thermally cured

samples are initiated more gradually with increasing temperature to which the reaction heat is added. The overall thermal profile inside the specimen during curing will thus differ significantly.

The gravimetric analysis of the samples (Table 1) further supports that a bicontinuous structure of a liquid and a solid phase has been formed. The weight loss after washing and drying is close to 39 wt % which is equivalent with the total amount of liquid electrolyte used in each sample. Hence little or no liquid electrolyte is trapped in closed cells inside the thermoset polymer.

Mechanical and Electrochemical Properties of the SBE. All samples could form solid specimens with a good mechanical integrity which demonstrate that a percolating thermoset structure has been formed on a macroscopic level. The DMA results presented in Figure 4 show the storage modulus and $\tan \delta$ data versus temperature for all samples. The data suggest that samples cured at 80 and 90 °C show a comparable thermo-mechanical behavior while the 70 °C sample shows a slightly poorer performance above T_g . The thermally cured samples all exhibit a broad T_g -transition where the modulus gradually decreases with increasing temperature. This trend is typical for a highly cross-linked rigid thermoset network.³⁶ The modulus of the sample cured at 70 °C decreases more drastically at higher temperatures than for samples cured at 80 and 90 °C which is consistent with a slightly lower double bond conversion. The onset of the T_g -transition is also earlier for the specimen cured at 70 °C while the specimens cured at 80 and 90 °C behave comparably.

The UV-cured samples were reproduced for DMA and SEM since a monomer solution from a different supplier was used in the previous study.²⁷ The UV-cured sample showed a significantly lower onset of the T_g -transition compared to the

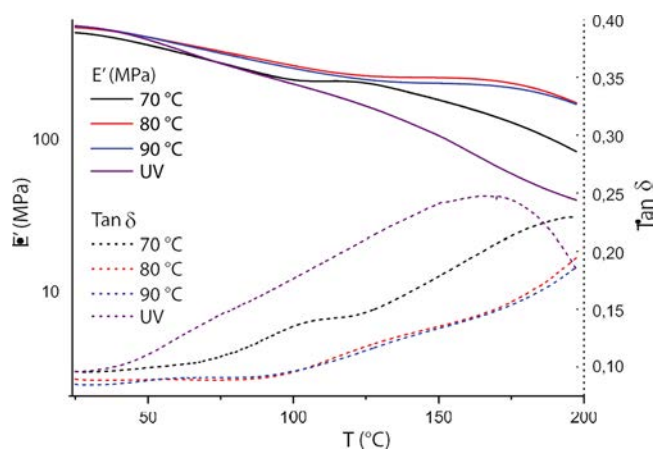


Figure 4. DMA data depicting storage modulus (E') and $\tan \delta$ vs temperature for samples cured at different temperatures (70, 80, 90 °C) and UV-cured.

thermally cured samples which emphasizes that a suitable specimen temperature is needed to avoid vitrification effects during curing. The modulus of the UV and 80 and 90 °C cured SBE specimen is 530–540 MPa at ambient temperature. The 70 °C cured sample shows a slightly lower modulus of 440 MPa at ambient temperature. However, generally speaking the thermally cured samples provide better mechanical properties at higher temperatures compared to the UV-cured sample. Consequently, the thermal curing process is even more beneficial for the assembly of a full-cell SB.

The ionic conductivities for different curing temperatures are presented in Table 1. The ionic conductivity of all thermally cured samples is around $2 \times 10^{-4} \text{ S cm}^{-1}$ at ambient temperature and is in the same range as UV-cured samples from previous work.²⁷ The data indicates that curing temperature and method has no influence on ionic conductivity. In addition, the lower modulus of the 70 °C sample did not influence the ionic conductivity. This observation can be attributed to the heterogeneity of the solid–liquid network where the liquid phase is mainly responsible for the Li-ion transfer. These findings are consistent with previous studies.²⁷ However, it should be noted that higher curing temperatures increase the risk of side reactions and the decomposition of LiTFS, which is not favorable for battery applications. The combined mechanical and electrochemical results also strengthen the fact that there is a complete phase separation in all cases.

Performance of the UD Lamina Half-Cell. The results of the electrochemical cycling of the UD lamina half-cell support the findings that thermal curing is a suitable method to use for SB manufacturing. The combined results from the SEM, gravimetric analysis, mechanical measurements, and electrochemical cycling demonstrate that the SBE matrix consists of two percolating phases, a liquid and a polymer phase. The CF-SBE composite half-cell would show limited or no electrochemical performance if the liquid phase is not percolating through the structure.

The manufacturing process of the composite electrode was conducted without difficulties due to a low-viscosity resin which provides good wetting of the CFs. This is highly beneficial for the composite manufacturing process and facilitates the formation of a strong CF-SBE interface. The CF-SBE interface is also electrochemically important since Li-

ions need to be transferred via this interface. SEM images of uncycled and cycled structural electrodes are shown in Figure S2. They confirm that CFs are embedded in a bicontinuous SBE.

The electrochemical performance of the SBE and the formation of an electrochemically performing interface was further confirmed by the results of the galvanostatic cycling of a CF-SBE composite half-cell. Figure 5 shows the capacity vs

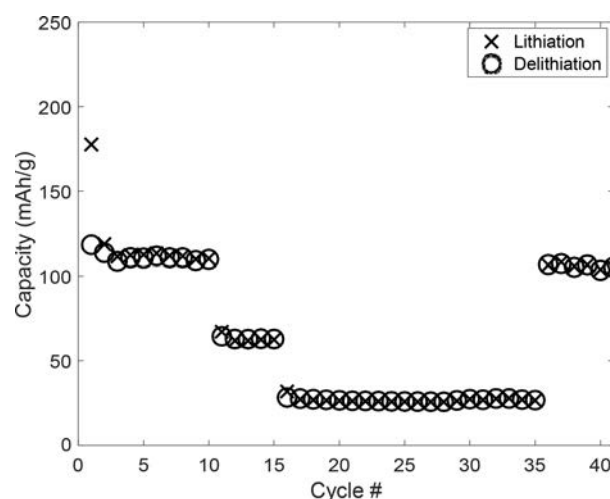


Figure 5. Capacity vs cycle number of a CF-SBE half-cell thermally cured at 80 °C for 75 min. Different current densities were applied corresponding to 18.6 mA g^{-1} (approximately 0.17 C) over 10 cycles, 37.2 mA g^{-1} (approximately 0.33 C) over 5 cycles, 74.4 mA g^{-1} (approximately 0.67 C) over 20 cycles, and 18.6 mA g^{-1} (approximately 0.17 C).

cycle number at different current densities while Figure 6 shows the potential profiles for cycles 1, 2, and 40 (after different current densities have been applied) for a CF-SBE composite half-cell cured at 80 °C. The reproducible potential

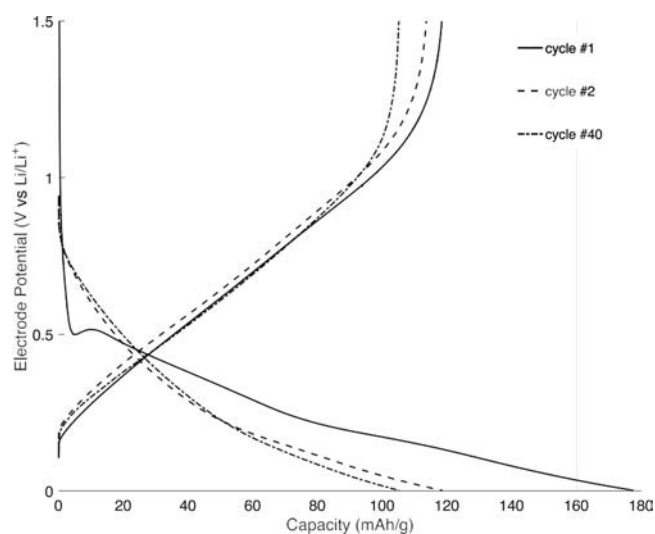


Figure 6. Potential profiles for the 1st, 2nd and 40th cycle of a CF-SBE composite half-cell, thermally cured at 80 °C for 75 min. Different current densities were applied corresponding to 18.6 mA g^{-1} (approximately 0.17 C) over 10 cycles, 37.2 mA g^{-1} (approximately 0.33 C) over 5 cycles, 74.4 mA g^{-1} (approximately 0.67 C) over 20 cycles, and 18.6 mA g^{-1} (approximately 0.17 C).

profiles are comparable with those obtained in previous work with UV-cured composite electrodes.²⁷ The similarity of the profiles indicates the absence of major side reactions and that elevated temperatures during cure did not decrease the electrochemical performance of the SBE electrolyte.

The specific capacity of the fifth cycle was around 110 mAh g⁻¹ at a current density of 18.6 mA g⁻¹ corresponding to approximately 0.17 C. The drop in capacity after the first cycle can be attributed to the formation of an solid electrolyte interphase (SEI) layer on the CF^{37,38} and trapped lithium in the CFs.⁵ The lower specific capacity compared to UV-cured composite electrodes previously reported²⁷ is attributed to difference in fiber type used in this study, which led to a much thicker CF-SBE composite half-cell (90 μm). It has also been shown that different CF types provide different capacities.⁵ The main reason for the high overpotential and large drop in capacity is the thickness of the half-cell; it is roughly twice as thick compared to earlier work.⁷ However, the capacity is still higher compared to an epoxy-based structural electrode investigated by Yu et al.³⁹ which was stable around 10 mAh g⁻¹ at 0.1 C.

A satisfactory capacity retention and a stable cycling behavior at different current densities were obtained (see Figure 5). After prolonged cycling at different current densities, the capacity remained around 105 mAh g⁻¹ at a current density of 18.6 mA g⁻¹ with a loss of around 5% after 40 cycles. However, a large drop in capacities for higher current densities occurs, which can be attributed to mass transport limitations at high current densities which is also influenced by the type of fibers used.

The transverse modulus, a matrix dominated property, of the electrochemically cycled composite electrode was calculated to be 1.3 ± 0.1 GPa. The bending measurement data depicted as load–displacement curves for six samples is shown in Figure S2 in the Supporting Information. This modulus of the composite electrode is twice as high as the modulus of the SBE without fibers although this film was measured in tensile mode using DMA. This supports the structural functionality of the composite electrode (i.e., UD lamina) and an adhesion between matrix and fibers. However, the elastic modulus is lower than the moduli reported in previous studies^{7,27} which can be related to the different polymer systems used. The fiber volume fraction of the UD lamina was evaluated to be 27% on average.

The evaluation of the negative CF-SBE electrode confirmed its multifunctional performance and thus the possibility to use thermal curing for a full-cell SB. In contrast to conventional electrodes, this SBE-CF electrode is a lightweight material that offers electrochemical and mechanical performance simultaneously. Future studies will address performance optimization of the composite electrode, development of a positive electrode, and the assembly of a full-cell SB with adequate performance.

CONCLUSION

This work provides an important contribution to the development of the SB technology since it allows fabrication of a multifunctional SB device while ensuring its multifunctionality. Thermal curing is demonstrated as a feasible and robust processing route to make phase-separated methacrylate-based SBE films and structural electrodes. In addition, this process improves thermo-mechanical properties of the SBE films compared to UV-cured films. A multifunctional negative

electrode (CF-SBE) cured at 80 °C also showed satisfactory multifunctional properties with respect to the structural and electrochemical performance of a UD lamina electrode and half-cell, respectively. The overall results imply that a processing window between 80 and 90 °C is suitable for the present system. The process is also relatively robust against minor changes in curing conditions and sample geometries. Consequently, thermal curing is a suitable processing method for a full-cell SB.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.aem.9b00563.

FTIR spectra for thermally cured SBE films at different temperatures compared with uncured resin used to calculate chemical conversions, SEM images of the composite electrodes cycled and uncycled, and load–displacement curves obtained from the bending measurements of all six samples measured used to calculate elastic modulus of the composite structural battery half-cell (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: matskg@kth.se.

ORCID

Mats Johansson: 0000-0003-3201-5138

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This study was funded by US Air Force Office of Scientific Research (261001). Furthermore, Wilhelm Johansson is acknowledged for providing help with mechanical testing methods. The authors also thank the entire research group for valuable discussions.

ABBREVIATIONS

- AIBN = 2,2'-azobis(2-methylpropionitrile)
- CFs = carbon fibers
- DMA = dynamic mechanical analysis
- DMMP = dimethyl methylphosphonate
- EC = ethylene carbonate
- EIS = electric impedance spectroscopy
- FTIR = Fourier-transform infrared spectroscopy
- LiTFS = lithium trifluoromethanesulfonate
- PIPS = polymerization induced phase separation
- RT-FTIR = real time Fourier-transform spectroscopy
- SB = structural battery
- SBE = structural battery electrolyte
- SEI = solid electrolyte interphase
- SEM = scanning electron microscopy
- UD = unidirectional
- UV = ultraviolet light.

REFERENCES

- (1) Wetzel, E. D. Multifunctional Composites Integrate Power, Communications, and Structure. *AMPTIAC Q* **2004**, 8 (4), 91–95.
- (2) Christodoulou, L.; Venables, J. D. Multifunctional Material Systems: The First Generation. *JOM* **2003**, 55 (12), 39–45.

- (3) Asp, L. E.; Greenhalgh, E. S. Structural Power Composites. *Compos. Sci. Technol.* **2014**, *101*, 41–61.
- (4) Kjell, M. H.; Jacques, E.; Zenkert, D.; Behm, M.; Lindbergh, G. PAN-Based Carbon Fiber Negative Electrodes for Structural Lithium-Ion Batteries. *J. Electrochem. Soc.* **2011**, *158* (12), A1455–A1460.
- (5) Hagberg, J.; Leijonmarck, S.; Lindbergh, G. High Precision Coulometry of Commercial PAN-Based Carbon Fibers as Electrodes in Structural Batteries. *J. Electrochem. Soc.* **2016**, *163* (8), A1790–A1797.
- (6) Hagberg, J.; Maples, H. A.; Alvim, K. S.P.; Xu, J.; Johannisson, W.; Bismarck, A.; Zenkert, D.; Lindbergh, G. Lithium iron phosphate coated carbon fiber electrodes for structural lithium ion batteries. *Compos. Sci. Technol.* **2018**, *162*, 235–243.
- (7) Johannisson, W.; Ihrner, N.; Zenkert, D.; Johansson, M.; Carlstedt, D.; Asp, L. E.; Sieland, F. Multifunctional Performance of a Carbon Fiber UD Lamina Electrode for Structural Batteries. *Compos. Sci. Technol.* **2018**, *168*, 81–87.
- (8) Snyder, J. F.; O'Brien, D. J.; Baechle, D. M.; Mattson, D. E.; Wetzel, E. D. Structural Composite Capacitors, Supercapacitors, and Batteries for U. S. Army Applications. In *Smart Materials, Adaptive Structures and Intelligent Systems, Proceedings of the ASME Conference*; Ellicott City, Maryland, October 28–30, 2008; pp 1–8. DOI: 10.1115/SMASIS2008-315
- (9) Schuster, J.; Duhovic, M.; Bhattacharyya, B. Manufacturing and Processing of Polymer Composites. In *Synthetic Polymer–Polymer Composites*; Bhattacharyya, D., Fakirov, S., Eds.; Hanser Publishers: Munich, 2012; pp 1–38.
- (10) Xu, K. Nonaqueous Liquid Electrolytes for Lithium-Based Rechargeable Batteries. *Chem. Rev.* **2004**, *104* (10), 4303–4418.
- (11) Fergus, J. W. Ceramic and Polymeric Solid Electrolytes for Lithium-Ion Batteries. *J. Power Sources* **2010**, *195* (15), 4554–4569.
- (12) Wang, Y.; Zhong, W.-H. Development of Electrolytes towards Achieving Safe and High-Performance Energy-Storage Devices: A Review. *ChemElectroChem* **2015**, *2* (1), 22–36.
- (13) Stephan, A. M. Review on Gel Polymer Electrolytes for Lithium Batteries. *Eur. Polym. J.* **2006**, *42* (1), 21–42.
- (14) Willgert, M.; Kjell, M. H.; Jacques, E.; Behm, M.; Lindbergh, G.; Johansson, M. Photoinduced Free Radical Polymerization of Thermoset Lithium Battery Electrolytes. *Eur. Polym. J.* **2011**, *47* (12), 2372–2378.
- (15) Ihrner, N.; Johansson, M. Improved Performance of Solid Polymer Electrolytes for Structural Batteries Utilizing Plasticizing Co-Solvents. *J. Appl. Polym. Sci.* **2017**, *134* (23), 44917.
- (16) Snyder, J. F.; Carter, R. H.; Wetzel, E. D. Electrochemical and Mechanical Behavior in Mechanically Robust Solid Polymer Electrolytes for Use in Multifunctional Structural Batteries. *Chem. Mater.* **2007**, *19* (15), 3793–3801.
- (17) Shirshova, N.; Bismarck, A.; Carreyette, S.; Fontana, Q. P. V.; Greenhalgh, E. S.; Jacobsson, P.; Johansson, P.; Marczewski, M. J.; Kalinka, G.; Kucernak, A. R. J.; Scheers, J.; Shaffer, M. S. P.; Steinke, J. H. G.; Wienrich, M. Structural Supercapacitor Electrolytes Based on Bicontinuous Ionic Liquid-Epoxy Resin Systems. *J. Mater. Chem. A* **2013**, *1* (48), 15300–15309.
- (18) Shirshova, N.; Qian, H.; Houle, M.; Steinke, J. H. G.; Kucernak, A. R. J.; Fontana, Q. P. V.; Greenhalgh, E. S.; Bismarck, A.; Shaffer, M. S. P. Multifunctional Structural Energy Storage Composite Supercapacitors. *Faraday Discuss.* **2014**, *172* (0), 81–103.
- (19) Gienger, E. B.; Nguyen, P.-A. T.; Chin, W.; Behler, K. D.; Snyder, J. F.; Wetzel, E. D. Microstructure and Multifunctional Properties of Liquid + Polymer Bicomponent Structural Electrolytes: Epoxy Gels and Porous Monoliths. *J. Appl. Polym. Sci.* **2015**, *132* (42), 42681.
- (20) Bae, S.-H.; Jeon, C.; Oh, S.; Kim, C.-G.; Seo, M.; Oh, I.-K. Load-bearing Supercapacitor Based on Bicontinuous PEO-b-P(S-co-DVB) Structural Electrolyte Integrated with Conductive Nanowire-Carbon Fiber Electrodes. *Carbon* **2018**, *139*, 10–20.
- (21) McIntosh, L. D.; Schulze, M. W.; Irwin, M. T.; Hillmyer, M. A.; Lodge, T. P. Evolution of Morphology, Modulus, and Conductivity in Polymer Electrolytes Prepared via Polymerization-Induced Phase Separation. *Macromolecules* **2015**, *48* (5), 1418–1428.
- (22) Chopade, S. A.; Au, J.; Li, Z.; Schmidt, P. W.; Hillmyer, M. A.; Lodge, T. P. Robust Polymer Electrolyte Membranes with High Ambient-Temperature Lithium-Ion Conductivity via Polymerization-Induced Microphase Separation. *ACS Appl. Mater. Interfaces* **2017**, *9* (17), 14561–14565.
- (23) Schulze, M. W.; McIntosh, L. D.; Hillmyer, M. A.; Lodge, T. P. High-Modulus, High-Conductivity Nanostructured Polymer Electrolyte Membranes via Polymerization-Induced Phase Separation. *Nano Lett.* **2014**, *14* (1), 122–126.
- (24) Chopade, S. A.; So, S.; Hillmyer, M. A.; Lodge, T. P. Anhydrous Proton Conducting Polymer Electrolyte Membranes via Polymerization-Induced Microphase Separation. *ACS Appl. Mater. Interfaces* **2016**, *8* (9), 6200–6210.
- (25) Lewandowski, A.; Świdarska-Mocek, A. Ionic Liquids as Electrolytes for Li-Ion Batteries - An Overview of Electrochemical Studies. *J. Power Sources* **2009**, *194* (2), 601–609.
- (26) Lindbergh, J.; Lundgren, H.; Lindbergh, G.; Behm, M. Benchmarking of Electrolyte Mass Transport in Next Generation Lithium Batteries. *J. Electrochem. Sci. Eng.* **2015**, *7* (4), 213–221.
- (27) Ihrner, N.; Johannisson, W.; Sieland, F.; Zenkert, D.; Johansson, M. Structural Lithium Ion Battery Electrolytes via Reaction Induced Phase-Separation. *J. Mater. Chem. A* **2017**, *5* (48), 25652–25659.
- (28) Nicolson, P. C.; Vogt, J. Soft Contact Lens Polymers: An Evolution. *Biomaterials* **2001**, *22* (24), 3273–3283.
- (29) Szczepanski, C. R.; Pfeifer, C. S.; Stansbury, J. W. A New Approach to Network Heterogeneity: Polymerization Induced Phase Separation in Photo-Initiated, Free-Radical Methacrylic Systems. *Polymer* **2012**, *53* (21), 4694–4701.
- (30) Odian, G. *Principles of Polymerization*, 4th ed.; John Wiley & Sons: Hoboken, NJ, 2004.
- (31) Glauser, T.; Johansson, M.; Hult, A. A Comparison of Radiation and Thermal Curing of Thick Composites. *Macromol. Mater. Eng.* **2000**, *274* (1), 25–30.
- (32) Åström, B. T. *Manufacturing of Polymer Composites*; CRC Press, 1997.
- (33) Bogetti, T. A.; Gillespie, J. W. Process-Induced Stress and Deformation in Thick-Section Thermoset Composite Laminates. *J. Compos. Mater.* **1992**, *26* (5), 626–660.
- (34) Agarwal, B. D.; Broutman, L. J.; Chandrashekhara, K. *Analysis and Performance of Fiber Composites*, 4th ed.; John Wiley & Sons, 2017.
- (35) Ratna, D. General Introduction to Thermoset Networks. *Handbook of Thermoset Resins*; Smithers Rapra Technology: Shrewsbury, UK, 2009; pp 1–59.
- (36) Menard, K. P. *Dynamic Mechanical Analysis: A Practical Introduction*; CRC Press, 2008.
- (37) Peled, E. The Electrochemical Behavior of Alkali and Alkaline Earth Metals in Nonaqueous Battery Systems - The Solid Electrolyte Interphase Model. *J. Electrochem. Soc.* **1979**, *126* (12), 2047–2051.
- (38) Aurbach, D.; Markovsky, B.; Levi, M. D.; Levi, E.; Schechter, A.; Moshkovich, M.; Cohen, Y. New Insights into the Interactions between Electrode Materials and Electrolyte Solutions for Advanced Nonaqueous Batteries. *J. Power Sources* **1999**, *81*, 95–111.
- (39) Yu, Y.; Zhang, B.; Feng, M.; Qi, G.; Tian, F.; Feng, Q.; Yang, J.; Wang, S. Multifunctional Structural Lithium Ion Batteries based on Carbon Fiber Reinforced Plastic Composites. *Compos. Sci. Technol.* **2017**, *147*, 62–70.