



## **Multifunctional performance of a carbon fiber UD lamina electrode for structural batteries**

Downloaded from: <https://research.chalmers.se>, 2021-08-31 20:13 UTC

Citation for the original published paper (version of record):

Ihrner, N., Johansson, M., Johannisson, W. et al (2018)

Multifunctional performance of a carbon fiber UD lamina electrode for structural batteries

Composites Science and Technology, 168: 81-87

<http://dx.doi.org/10.1016/j.compscitech.2018.08.044>

N.B. When citing this work, cite the original published paper.



## Multifunctional performance of a carbon fiber UD lamina electrode for structural batteries

Wilhelm Johannisson<sup>a,\*</sup>, Niklas Ihrner<sup>b</sup>, Dan Zenkert<sup>a</sup>, Mats Johansson<sup>b</sup>, David Carlstedt<sup>c</sup>, Leif E. Asp<sup>c</sup>, Fabian Sieland<sup>d</sup>

<sup>a</sup> Department of Aeronautical and Vehicle Engineering, KTH Royal Institute of Technology, SE-100 44 Stockholm, Sweden

<sup>b</sup> Department of Fibre and Polymer Technology, KTH Royal Institute of Technology, SE-100 44 Stockholm, Sweden

<sup>c</sup> Department of Industrial and Materials Science, Chalmers University of Technology, SE-412 96 Gothenburg, Sweden

<sup>d</sup> Department of Chemistry, University of Paderborn, Warburger Straße 100, 33098 Paderborn, Germany

### ABSTRACT

In electric transportation there is an inherent need to store electrical energy while maintaining a low vehicle weight. One way to decrease the weight of the structure is to use composite materials. However, the electrical energy storage in today's systems contributes to a large portion of the total weight of a vehicle. Structural batteries have been suggested as a possible route to reduce this weight. A structural battery is a material that carries mechanical loads and simultaneously stores electrical energy and can be realized using carbon fibers both as a primary load carrying material and as an active battery electrode. However, as yet, no proof of a system-wide improvement by using such structural batteries has been demonstrated. In this study we make a structural battery composite lamina from carbon fibers with a structural battery electrolyte matrix, and we show that this material provides system weight benefits. The results show that it is possible to make weight reductions in electric vehicles by using structural batteries.

### 1. Introduction

With a growing demand for electric transportation, there is a need for lighter and thus more energy-efficient vehicles [1]. Electric transportation requires the storage of electrical energy onboard the vehicle. Today, the balance between weight and energy storage is a compromise between the conflicting requirements of making the vehicle more energy efficient and having a longer range. One path towards reducing the weight of electrical vehicles while storing the same amount of energy is to exchange the vehicle structure with structural batteries. Structural batteries are materials that intrinsically store electrical energy while being part of the load carrying structure itself. The concept has been investigated in different ways [2–7] but has not yet been shown to provide a systems level improvement over the separate structure and battery constituents.

In order to fulfill requirements of low weight and energy storage at the same time all different parts of the structural battery must work together. It has previously been found that carbon fibers are a good candidate as a main component, since the fibers perform very well at carrying load and at the same time can intercalate lithium ions in the same way as the negative electrode in a commercial lithium ion battery [8,9]. Lithium intercalation is one of the major factors for a lithium ion battery to function, which means that one possible route for structural

batteries is to use carbon fibers as both reinforcement and battery electrode. Another equally important property of a lithium ion battery is the ion conductivity between the electrodes of the battery. The conductivity of ions is generally obtained by a liquid electrolyte. However, for carbon fibers to have any structural use, they need to be combined with a solid electrolyte matrix that can transfer mechanical loads [10]. In order to achieve both ion conductivity and good structural properties, a new structural battery electrolyte (SBE) has recently been developed [11]. This SBE is a two-phase percolating network, with a bicontinuous phase of liquid electrolyte intermingled with a cross-linked polymer. The initial mixture of the SBE components before curing is fully homogeneous which allows the SBE to be used with conventional vacuum infusion techniques used in composite manufacturing. The two phases are then formed during the curing step via a reaction induced phase separation process. The solid phase provides a structural backbone designed to transfer load in the composite as an ordinary composite matrix material, while the liquid phase provides a path for ion transport. A similar approach was taken by Shirshova *et al.* [12] using epoxy resin and an ionic liquid with the aim to develop structural supercapacitors. Reaction induced phase separation (or polymerization induced phase separation (PIPS)), has also been used by Schulze *et al.* [13] and McIntosh *et al.* [14] in making membranes with good ion conductivity and mechanical integrity. A similar type of

\* Corresponding author.

E-mail address: [wjoh@kth.se](mailto:wjoh@kth.se) (W. Johannisson).

<https://doi.org/10.1016/j.compscitech.2018.08.044>

Received 14 March 2018; Received in revised form 27 August 2018; Accepted 29 August 2018

Available online 30 August 2018

0266-3538/© 2018 The Authors. 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/>).

matrix system was also used by Yu *et al.* [7] with aim of making a structural negative electrode combined with carbon fibers. They obtained a unidirectional (UD) carbon fiber lamina with high fiber volume fraction and high longitudinal modulus ( $E_1$ ) but with low electrochemical capacity.

In this study we investigate the mechanical and electrochemical properties of a composite lamina made from carbon fibers and an SBE matrix that can act as a negative electrode in a lithium ion half-cell battery, and at the same time provide mechanical load transfer. An improved version of the SBE recently reported by Ihrner *et al.* [11] is prepared and its mechanical and electrochemical properties are investigated. The lamina is manufactured by vacuum infusion of the SBE into the carbon fibers. The lamina is then electrochemically cycled (charged and discharged). Mechanical characterization is performed on both cycled laminae and laminae that have not been cycled, providing the orthotropic composite engineering constants of the UD lamina and estimates of all five lamina strength properties. The morphology of the laminae is also investigated using scanning electron microscopy (SEM) in order to verify the SBE's bicontinuous and percolating network, and the impact of electrochemical cycling on the SBE and SBE-to-fiber interface characteristics.

Potential for system weight-reduction offered by the structural battery lamina is evaluated by comparing multifunctional performance to the specific performances of the monofunctional materials.

## 2. Material and methods

### 2.1. Materials

For the SBE preparation the following in-going materials were used: Bisphenol A dimethacrylate,  $M = 364.43 \text{ g mol}^{-1}$ , Dimethyl methylphosphonate (DMMP), ethylene carbonate (99% anhydrous) (EC), Lithium trifluoromethanesulfonate (LiTFS) (96%), 2,2'-(Ethylenedioxy) diethanethiol (DODT) and Tris(N-nitroso-N-phenylhydroxylaminato) aluminum (NPAL) were purchased from Sigma-Aldrich. 2,2-dimethoxy-2-phenylaceto-phenone (DMPA) was obtained from BASF. Carbon fiber tows (6k) of the type T800HB-6000-40B were purchased from Toray Industries Inc. All materials were used as received.

### 2.2. Structural battery electrolyte (SBE)

A liquid formulation of the SBE was prepared by mixing Bisphenol A dimethacrylate (56.35% w/w), a 1 M LiTFS solution of EC:DMMP (1:1 w/w) (39.5% w/w), DODT (3.5% w/w), NPAL (0.05% w/w) and DMPA (0.6% w/w) while stirring and heating to 80 °C to form a homogeneous low viscous solution. The mixture was prepared in a glovebox, under argon atmosphere with dry conditions ( $< 1 \text{ ppm H}_2\text{O}$ ,  $< 1 \text{ ppm O}_2$ ). During manufacturing all the components were miscible with each other, while upon cross-linking the solubility parameters of the polymer change, inducing a phase separation between the polymer and the remaining components.

### 2.3. SBE curing

The SBE system reported by Ref. [11] has been modified by an addition of a small amount of a dithiol monomer (DODT). The addition of a dithiol to a free radically polymerizing dimethacrylate monomer system affects several aspects of the system [15,16]. The thiol-methacrylate (thiol-ene) reaction is more rapid than the methacrylate homopolymerization, meaning that the thiol-ene reaction will dominate at early stages of the reaction [17,18]. Furthermore, the thiol-ene reaction furthermore follows a step-wise polymerization mechanism which delays the gelation point to a higher level of overall conversion, which provides a longer period for the phase separation to occur before the system is locked (with respect to conversion, not necessarily time). Using a dithiol as a co-monomer will also lead to a more homogeneous

as well as a slightly looser network structure. The flexible thio-ether linkages will also decrease the stiffness of the SBE to some extent [19]. One drawback with thiol-ene systems is the high reactivity that gives the SBE formulation a very short pot-life. This was addressed by adding small amounts of inhibitor (NPAL) resulting in an induction time before the polymerization commenced [20]. For UV initiation of the polymerization DMPA is added. It should be noted that the amount of dithiol in the present study is very small, while the effect on the properties compared to the previously reported SBE [11] can be considered as fine-tuning.

### 2.4. Manufacturing of the lamina

The SBE formulation was cured both as a film by itself to determine the SBE's intrinsic properties, and as laminae where the SBE was combined with unidirectional carbon fiber tows using the same curing procedure. The carbon fiber tows were spread in order to achieve a thin and uniform composite UD lamina and copper current collectors were attached to the carbon fibers with Electrolube silver conductive paint. Carbon fibers with copper current collectors were enclosed with a vacuum bag, a peel-ply and a distribution medium on a glass plate. The samples were then dried for 12 h in a vacuum at 60 °C before being infused with the SBE in a dry Argon atmosphere ( $< 1 \text{ ppm H}_2\text{O}$ ) with a vacuum assisted infusion (no external pressure used). The SBE was then cured under UV-light (100 W Blak-Ray B-100AP 365 nm) for 3.5 min, providing an intensity of 5.2 mW/cm<sup>2</sup> on the sample. The cured UD composite laminae had approximate dimensions of 30 mm  $\times$  60 mm, with a thickness of  $0.044 \pm 0.007 \text{ mm}$  for different laminae manufactured. Within a single lamina there was also some thickness variations due to imperfect spreading of the carbon fiber tows. This was measured with a micrometer to be in the order of  $\pm 0.004 \text{ mm}$ . The composite is a single lamina and since it is very thin there are two relatively thick resin rich layers on both sides. More even spreading of the tow and the use of external pressure in addition to vacuum could increase the fiber volume fraction somewhat. Making multiple layer composites, as is expected when making structural batteries, the fiber volume fraction is expected to increase by more than a factor of 2.

The fiber volume fraction is calculated by measuring the outer dimensions of the lamina and calculating the volume of the carbon fibers in the lamina. The volume of the carbon fibers in the sample is calculated by the tow length, with known tow linear density and carbon fiber density from the manufacturer.

Control samples made from the same carbon fibers and only the structural polymer constituent of the SBE were manufactured and cured using an identical method. This was done without liquid electrolyte and thus provided a homogeneous polymer matrix material to be tested mechanically as a reference.

### 2.5. Electrochemical testing

Electrochemical impedance spectroscopy (EIS) was used to measure the ionic conductivity of the SBE. A Gamry Series G 750 Potentiostat/Galvanostat/ZRA interface was used together with a four-point electrode type cell with gold wires as electrodes, EIS testing was performed as in Ref. [11] with the frequency range 1 Hz–120 kHz.

For electrochemical testing, the lamina was combined with a positive lithium metal electrode, thus completing an electrochemical battery cell. A glass microfiber filter separator (Whatman 260  $\mu\text{m}$  glass microfiber filter), saturated with electrolyte (1.0 M LiTFS in EC:DMMP 1:1 w/w), was used to ensure electrical insulation and ion conduction between the electrodes. The pouch cell made were similar to those in Ref. [6], with samples enclosed in a pouch bag with a nickel collector for the lithium metal electrode. All work with lithium and the manufacturing of electrochemical cells were carried out in a dry argon atmosphere. To measure the electrochemical capacity, galvanostatic charge and discharge was performed between 0.002 and 1.5 V vs. Li/

$\text{Li}^+$  for 10 cycles. The applied current was 18.6 mA per gram of carbon fibers, resulting in a charging time of approximately 12 h. All samples were cycled at a temperature of  $25 \pm 1$  °C.

## 2.6. Mechanical testing

Dynamic mechanical analysis (DMA) measurements were performed to characterize the mechanical properties of the pure SBE using a TA Instruments DMA Q800 in tensile mode, at a frequency of 1 Hz with a ramping temperature of 3 °C/min between 25 and 150 °C.

In order to investigate the mechanical performance of the laminae, all mechanical properties need to be determined. They include the full lamina elastic properties (4 elastic constants  $E_1$ ,  $E_2$ ,  $G_{12}$  and  $\nu_{12}$ ) and 5 strength properties ( $\sigma_1$  tension,  $\sigma_1$  compression,  $\sigma_2$  tension,  $\sigma_2$  compression and shear strength  $\tau_{12}$ ). The mechanical testing of the laminae was performed on three types of samples; never-charged laminae (non-cycled), electrochemically cycled laminae (cycled), and control samples (control). The aim is to compare non-cycled to cycled samples in order to investigate potential degradation in mechanical properties due to electrochemical cycling. Also, the SBE is a phase separated matrix with a stiff phase and a liquid phase. In order to investigate the mechanical properties of the SBE, it is compared to control samples with homogenous matrix made from the same monomer without electrolyte. Due to the size and thickness of the laminae, measuring mechanical properties of the laminae raises certain challenges, especially in the transverse direction of the UD lamina where the failure load was found to be about 1.5 N. Thus, conventional mechanical testing of composites such as the testing standard ASTM D3039 [21], was found not to work for the transverse properties of this material. Instead, an unconventional method had to be adapted in order to measure the properties of the lamina. This method consists of adhering the lamina to a substrate material (0.13 mm PET film adhered with Reichhold Dion 9102) and then bending this layered specimen in a Deben 300 N micro tester in a three-point bending set-up, see Fig. 1. The size of the bending specimens was approximately 10 mm × 5 mm.

The flexural properties of the substrate were first measured. Subsequent tests were then done on the two-layer assembly to measure the flexural stiffness. The unknown lamina properties of the carbon fiber composite were then back-calculated using standard laminate theory [22]. Furthermore, this method provides the opportunity to measure the compressive material properties by turning the specimen upside down so the bending translates to compression in the lamina. The laminae were tested in longitudinal, transverse, and off-axis direction (about 10°), to produce the orthotropic stiffness properties of each set of laminae. The stiffness of the 10° off-axis specimens were

used to calculate the in-plane shear modulus ( $G_{12}$ ) [22].

The ultimate tensile and compressive strengths were calculated from the data load-displacement curve, by identifying the first deviation from linearity in the load-displacement curve. This deviation was taken as the ultimate load, which was transformed to the ultimate stress in the lamina by the specimen's bending stiffness and specimen geometry. The shear strength was obtained from the calculated shear stress at failure of the 10° off-axis specimens.

Testing was also carried out in pure tension for longitudinal specimens, in order to verify the bending test method, using an Instron 5567 universal testing machine with a 5 kN load cell. The longitudinal and transverse strains were measured with a Digital Image Correlation (DIC) method (GOM Aramis 5M 2016) to calculate the longitudinal modulus ( $E_1$ ) and the major Poisson's ratio ( $\nu_{12}$ ).

## 2.7. Fiber-matrix interface

Scanning electron microscopy (SEM) was used to investigate the phase separation of the SBE and the failure surfaces at the fiber/matrix interface. The laminae were broken and separated transversally and dried (24 h in 50 °C vacuum) prior to coating with palladium using a Emitech K500X sputter coater for 30 s in an argon atmosphere. The SEM images were then produced with a Zeiss Leo Ultra 55 field emission gun scanning electron microscope with an accelerating voltage of 2 kV.

## 3. Results and discussion

### 3.1. Electrochemical testing

The conductivity of the SBE is measured as  $3.21 \times 10^{-4}$  S/cm  $\pm 5.2\%$  which can be considered as a very good conductivity in the context of structural batteries.

The results for galvanostatic charging and discharging for one lamina are shown in Fig. 2, where the 1<sup>st</sup>, 2<sup>nd</sup> and 10<sup>th</sup> cycles are shown. Average data from all cells result in a capacity of  $232 \pm 26$  mAh/g. There is a capacity loss after the first lithiation, which is a normal behavior for lithium ion batteries [23,24]. This loss results from lithium ions being trapped in the carbon fiber structure and a solid-electrolyte interphase (SEI) layer forming on the carbon fibers [6]. The voltage profiles correlate well with what is expected from a carbon fiber electrode cycled in state of the art liquid electrolyte [8], indicating that there are no additional side reactions present due to the SBE. The cycling demonstrates that the SBE allows for lithium ion transport to and from the carbon fibers through the SBE matrix.

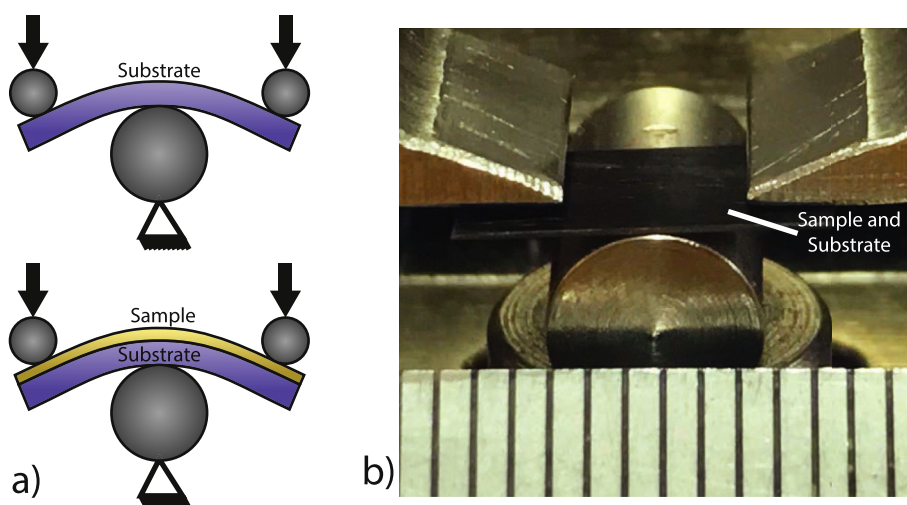


Fig. 1. a): Schematic description of substrate and sample bending testing. b): Deben 300 N micro tester with a three-point bending set-up, scale bars are 1 mm.

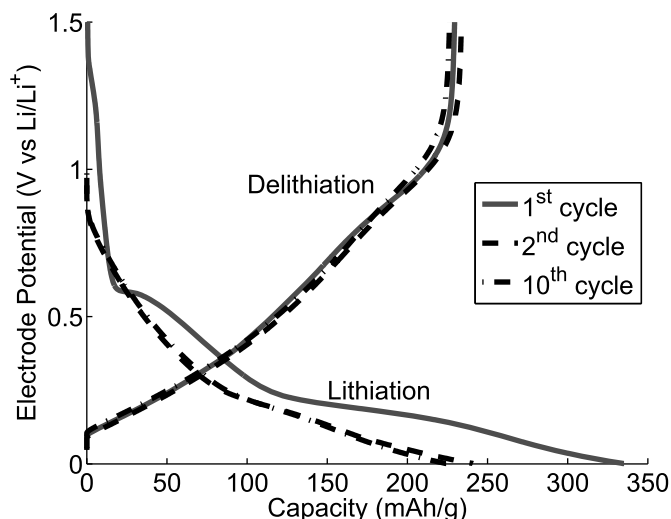


Fig. 2. Electrochemical charge and discharge curves for a multifunctional composite lamina (1<sup>st</sup>, 2<sup>nd</sup> and 10<sup>th</sup> cycle).

### 3.2. Mechanical testing

Measuring the mechanical properties of the SBE with DMA results in an elastic modulus ( $E_m$ ) of 690 MPa at 25 °C, and the samples with only the structural polymer constituent (control) of the SBE have an elastic modulus of 2.5 GPa at 25 °C.

Representative 3-point bending load-displacement curves for three longitudinal and three transverse specimens are shown in Fig. 3, where an asterisk marks the deviation from linearity used for strength calculations. Even though the load-displacement curves are not perfectly linear we chose the point where there is a clear shift in slope.

All results from mechanical testing are presented in Table 1, where it can be seen that there is no statistical difference in mechanical properties between non-cycled and cycled samples. This shows that there are no losses in mechanical properties due to ion transport in the SBE and SBE-to-carbon fiber interface. The moduli and strengths of the control samples are slightly higher than those of the SBE laminae, which is expected since the solid and homogeneous polymer without electrolyte has a higher elastic modulus.

The values for longitudinal modulus ( $E_T$ ) may all seem low for a UD

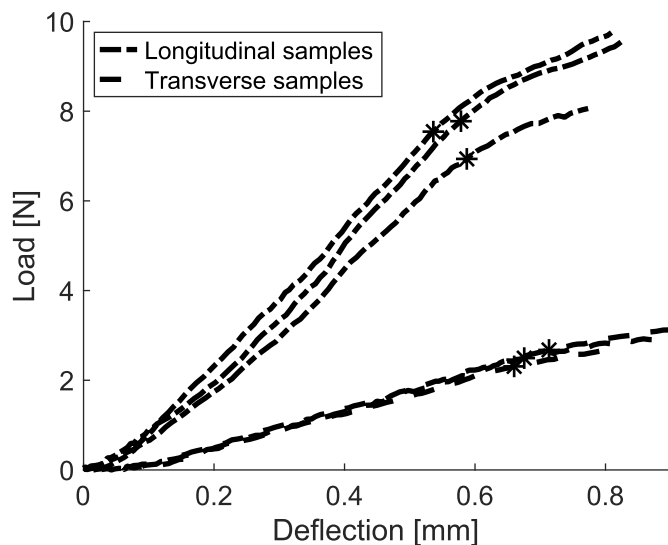


Fig. 3. Load-displacement curves for bending of non-cycled samples, showing results for longitudinal direction and transverse direction. First deviation from linearity is marked by an asterisk (\*).

lamina; however, the volume fractions of fibers are measured to 18% for both the SBE laminae and the control laminae. This volume fraction is very low for a structural composite and are due to the current manufacturing method creating two relatively thick resin rich layers on both sides. Substantial increase in fiber volume fraction (more than a factor 2) can be made by making multiple layer composites, as is expected when making structural batteries. Increasing the volume fraction of fibers will also increase the electrochemical properties due to shorter internal distances in the electrochemical cell. However, the transverse properties of the UD laminae are not expected to change drastically when increasing the fiber volume fraction since they are matrix dominated properties.

Pure tensile testing in the longitudinal direction was also performed (marked with an asterisk in Table 1) resulted in similar modulus  $E_T$ , thus verifying the results from the three-point bending. The shear modulus is calculated using the stiffness of the 10° off-axis specimens, the moduli  $E_1$  and  $E_2$ , and the value of  $\nu_{12}$  obtained from the tensile testing.

The strength values should be interpreted more as estimates rather than quantitative numbers due to the testing setup. The ultimate tensile strength ( $\sigma_T$ ) differs quite a lot between the bending and tensile testing due to intrinsic test limitations. In the bending test, the normal stress is not constant over the thickness of the laminae and in the tensile test there is a difficulty in evenly applying force to this single and very thin longitudinal lamina, thus breaking some fibers before the whole lamina is fully strained. However, the estimated strengths are still reasonable considering the fiber volume fraction. The longitudinal tensile strength is fiber dominated and is expected to increase with increased fiber volume fraction. The tensile strength of carbon fibers has previously been shown to be influenced by lithium intercalation [6], although the effect was limited. Strength in longitudinal compression is assumed to be most affected by SBE matrix stiffness properties. Most importantly, the lamina exhibits relatively good transverse and shear properties, which are both matrix dominated, and they appear to be unaffected by electrochemical cycling.

### 3.3. Fiber-matrix interface

SEM images of a non-cycled lamina are shown in Fig. 4a and b, with comparable images of an electrochemically cycled lamina shown in Fig. 4c and d. SEM images of a control sample are shown in Fig. 4e and f. The bicontinuous network and phase separation is very similar when comparing the morphology of the SBE in bulk [11] and the morphology of the SBE in the laminae (Fig. 4b). Thus, the formation of the SBE does not seem to be influenced by the presence of carbon fibers, since the SBE shows a phase separated network all the way into the carbon fiber surface. It can also be seen that the SBE adheres well to the surface of the carbon fibers by leaving matrix residue in most places for both non-cycled samples (Fig. 4a) and cycled samples (Fig. 4c), confirming that there is mechanical adhesion of the structural phase of the SBE to the carbon fibers. This also confirms that the ability to transfer load between fiber and matrix is not lost due to volume expansions associated with lithiation of carbon fibers as reported by Jacques *et al.* [25]. Furthermore, this confirms that there is no degradation in mechanical properties due to electrochemical cycling. If anything, the adhesion between the fiber and matrix appears to be slightly improved after electrochemically cycling. Additionally, the phase separated network of the SBE at the fiber-matrix interface is present in both non-cycled samples (Fig. 4a and b) and cycled samples (Fig. 4c and d); allowing for ion transport as well mechanical load transfer between the fiber and matrix. The control sample (Fig. 4e) shows polymer matrix residue on the fiber, which further indicate that the polymer matrix adheres to the carbon fibers. Also, the control sample has a different, homogenous morphology in the bulk (Fig. 4f), without a phase separated network as in the SBE samples (b and d).

**Table 1**

Mechanical properties for SBE laminae before electrochemical charging (non-cycled) and after electrochemical cycling (cycled). Compared to properties for a control lamina consisting of the same polymer but without electrolyte (control). Results with asterisk (\*) are measured with pure tensile testing and DIC, all other results are produced with three-point bending.

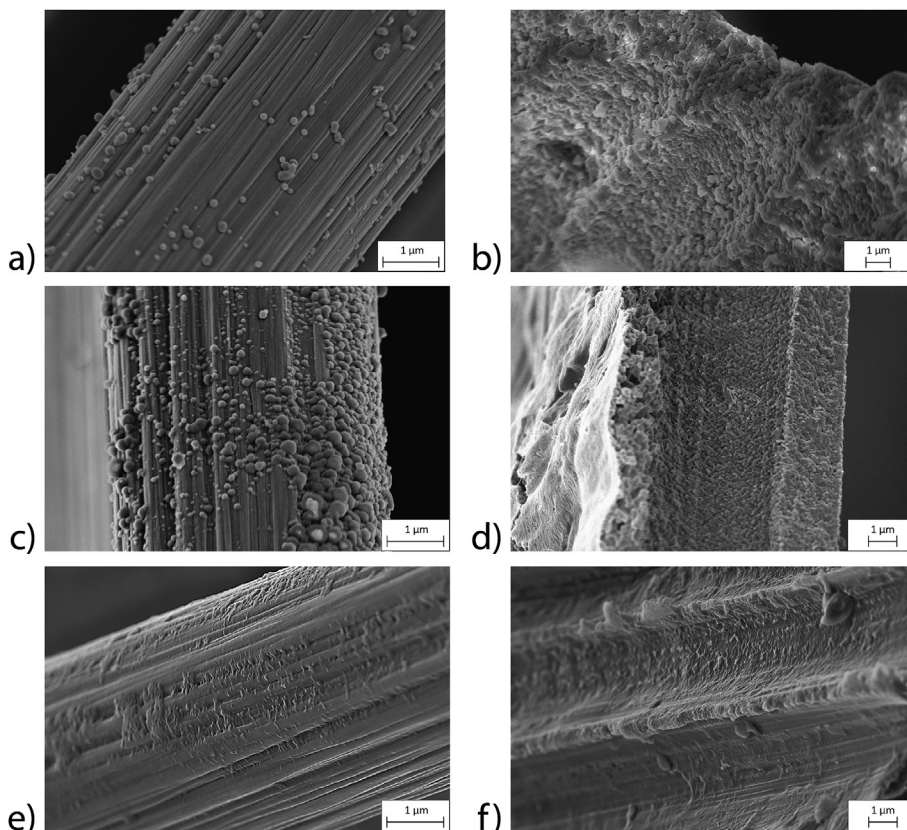
Property and Unit	SBE lamina		Control lamina
	Non-cycled	Cycled	
$E_1$ [GPa]	$52 \pm 3$ ( $47 \pm 5^*$ )	$52 \pm 2$	$57 \pm 3$ ( $51 \pm 6^*$ )
$E_2$ [GPa]	$1.7 \pm 0.3$	$1.9 \pm 0.2$	$3.6 \pm 0.3$
$G_{12}$ [GPa]	$1.5 \pm 0.2$	$1.6 \pm 0.2$	$1.9 \pm 0.2$
$\nu_{12}$ [-]	$0.36 \pm 0.01^*$	–	$0.44 \pm 0.04^*$
$\sigma_1$ tension [MPa]	$982 \pm 65$ ( $680 \pm 88^*$ )	$965 \pm 134$	$1046 \pm 128$ ( $640 \pm 89^*$ )
$\sigma_2$ tension [MPa]	$12.1 \pm 1.6$	$14.7 \pm 3.3$	$20.0 \pm 7.4$
$\sigma_1$ compression [MPa]	$997 \pm 59$	$849 \pm 106$	$1038 \pm 130$
$\sigma_2$ compression [MPa]	$11.7 \pm 5.2$	$11.4 \pm 1.5$	$24.3 \pm 5.5$
$\tau_{12}$ [MPa]	$13.2 \pm 2.4$	$14.6 \pm 3.1$	$16.5 \pm 3.7$

### 3.4. Multifunctional characterization

To compare multifunctional efficiency with the efficiency of separate mono-functional constituents, a multifunctional efficiency graph has been adapted to visualize the relationship, see Fig. 5a. The vertical axis represents the electrochemical capacity of the lamina normalized with the maximum capacity of the carbon fibers (290 mAh/g) when electrochemically cycled in pure liquid electrolyte [8]. The horizontal axis shows the structural efficiency for different elements of the orthotropic material properties, normalized with respective properties of the control samples. Hence, a mono-functional liquid battery would be situated in the top left corner, with maximum battery efficiency and no structural efficiency. A mono-functional composite material on the other hand would have no electrochemical efficiency but maximum structural efficiency, situated in the bottom right corner. The multifunctional material can now be mapped on such a multifunctional efficiency graph, with results above the diagonal representing properties

that outperform those of the separate mono-functional constituents. The results show that the multifunctional efficiency outperforms that of separate mono-functional constituents for all material properties.

To further investigate multifunctional performance, the same type of analysis is made versus the best possible theoretical monofunctional properties, see Fig. 5b. Now the electrochemical efficiency is normalized with the maximum theoretical capacity for graphite (372 mAh/g) and mechanical efficiency is normalized with the corresponding material properties of a high performance UD carbon fiber epoxy prepreg lamina [26]. As can be seen in the figure, the longitudinal ultimate tensile and compressive strength ( $\sigma_l$ ) of the lamina are both above the diagonal, and the longitudinal modulus ( $E_l$ ) is just at its boundary. However, given the very low volume fraction of fibers in the laminae produced in this work, the longitudinal modulus is most penalized, which means that with increased volume fraction of fibers in the lamina the longitudinal modulus structural efficiency will increase significantly. However, all other structural efficiencies of the lamina are



**Fig. 4.** a): Non-cycled sample showing SBE matrix residue sticking to carbon fibers that have been broken off from SBE (40 k magnification). b): Non-cycled sample showing SBE matrix with fiber imprint (17.5 k magnification). c) Cycled sample showing SBE matrix residue sticking to carbon fibers that have been broken off from SBE (40 k magnification). d): Cycled sample showing SBE matrix with fiber imprint (20 k magnification). e): Control sample showing polymer matrix residue sticking to carbon fibers that have been broken off from the matrix (40 k magnification). f): Control sample showing homogeneous polymer matrix with fiber imprint (20 k magnification).

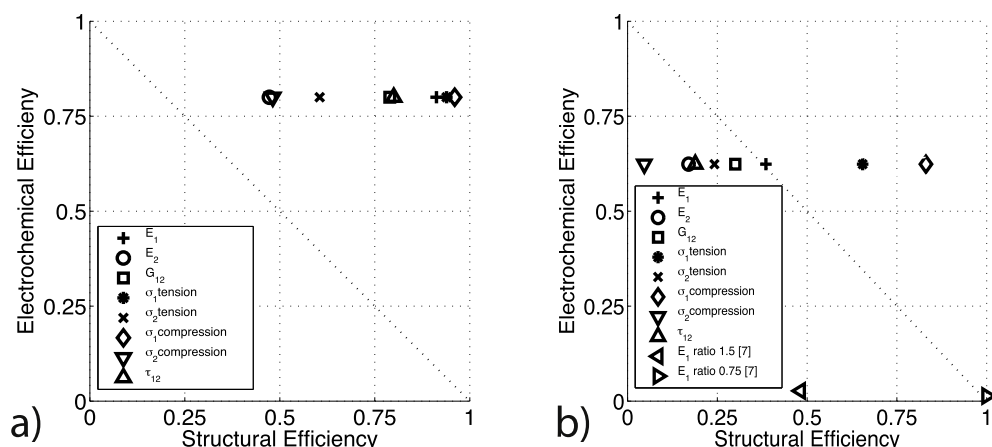


Fig. 5. Efficiency graphs, a) showing electrochemical efficiency normalized with the maximum capacity of the carbon fibers (290 mAh/g [8]) and mechanical performance normalized with respective material properties of the control sample. b) showing electrochemical efficiency normalized with the maximum capacity of graphite (372 mAh/g) and mechanical performance normalized with respective material properties of a standard UD carbon fiber epoxy prepreg [26].  $E_1$  structural efficiency for multifunctional cells from Ref. [7] are included for comparison.

governed by the mechanical properties of the SBE (matrix dominated), which is known to not be comparable with the properties of a standard epoxy matrix used in normal carbon fiber composites (typically  $E_m$  between 2.75 and 4.10 GPa and  $E_2$  in the order of magnitude 10 GPa [22]). On the other hand, in a multi-angle composite laminate the longitudinal lamina properties are more important than the transverse properties for the structural performance of the laminate. The dominating elastic constant for the overall stiffness of a multi angle laminate comes from the longitudinal modulus  $E_1$ , as can be computed using laminate theory [22]. Thus, low matrix dominated properties, like  $E_2$  and  $G_{12}$ , will not be detrimental to the overall properties of a laminated structural battery.

Previous research on a UD composite lamina with multifunctional properties is also added to the efficiency graph for comparison [7]. They report a longitudinal modulus ( $E_1$ ) of about 65 GPa and a stable cycling capacity of about 10 mAh/g, for the liquid phase/epoxy mass ratio of 1.5. Another mixture (0.75 liquid phase/epoxy mass ratio) had  $E_1$  at 146 GPa and a stable cycling capacity of less than 5 mAh/g.

### 3.5. Towards multifunctional batteries

A structural composite battery would combine the negative electrode presented herein with a positive electrode. Generally, positive electrodes are made with  $\text{LiFePO}_4$  or similar lithium-based ceramics. Recent research used a technique to coat  $\text{LiFePO}_4$  particles onto carbon fibers using a low fraction of PVDF as binder and a small amount of carbon black [27]. The carbon black is needed to make the coating electrically conductive. This results in a spread tow of carbon fibers with the active electrochemical material coated to its surface which can then be used as a structural positive electrode. The carbon fibers on this side are not themselves electrochemically active but provide both structural capacity and can be used as current collectors.

Such coated carbon fibers can then be laid up in a dry state together with carbon fibers on the negative side, separated by a separator, to form a 3-layer composite laminate. The assembly can then be infused with the SBE used herein to form a structural battery. However, for these multilayer assemblies UV curing of the SBE is likely not possible to use and another initiation of the polymerization would be required, e.g. heat curing.

## 4. Conclusions

This research builds towards the realization of structural batteries by showing the possibility of system-wide improvement over the separate mono-functional electrochemical and structural constituents. The improvement shows that structural batteries could result in an overall lighter system than having separate systems for structure and energy storage.

A structural battery electrolyte (SBE) matrix has been used to manufacture carbon fiber laminae with a vacuum infusion method producing a carbon fiber UD lamina with multifunctional properties. The lamina can be electrochemically cycled against lithium stably for 10 cycles with a capacity exceeding 200 mAh/g. No decrease has been seen in mechanical properties when comparing non-cycled to a cycled lamina. SEM shows that there is no significant difference in appearance of SBE in bulk compared to SBE in the presence of carbon fiber, and that the structural phase of the SBE adheres well to the surface of the carbon fibers even after electrochemical cycling.

A low longitudinal modulus (52 GPa) is measured for the lamina, which is directly linked to the low volume fraction of fibers (18%) due to the manufacturing of a very thin UD lamina. Increasing the volume fraction of fibers in the lamina would linearly increase the longitudinal modulus. A higher fiber volume fraction would also have a positive effect on the electrochemical properties due to shorter internal distances in the electrochemical cell. A higher volume fraction of fibers could be achieved with further improvements of the manufacturing method and the stacking of laminae into laminates.

## Acknowledgements

This work was supported by the Swedish Energy Agency, project 37712-1, the Swedish Research Council, projects 2017-03898 and 621-2014-4577, and the strategic innovation program LIGHTer (funding provided by Vinnova, the Swedish Energy Agency and Formas). DC, LA and DZ acknowledge financial support from H2020, Clean Sky II project no. 738085. The Swedish research group Kombatt is acknowledged for its synergism throughout this work.

## References

- [1] EPoS ERTRAC, *The Electrification Approach to Urban Mobility and Transport*, (2009).
- [2] J.P. Thomas, M. a. Qidwai, The design and application of multifunctional structure-battery materials systems, *JOM* 57 (2005) 18–24, <https://doi.org/10.1007/s11837-005-0228-5>.
- [3] J.F. Snyder, R.H. Carter, E.L. Wong, P. a. Nguyen, K. Xu, E.H. Ngo, E.D. Wetzel, Multifunctional structural composite batteries, *Proc. Soc. Adv. Mater. Process Eng.* 2006, pp. 6–9 [www.dtic.mil/cgi-bin/GetTRDoc?AD=ADA472085](http://www.dtic.mil/cgi-bin/GetTRDoc?AD=ADA472085).
- [4] M. Wysocki, L.E. Asp, S. Ekstedt, ECCM13, Sweden, *Structural Polymer Electrolyte for Use in Multifunctional Energy Storage Devices* vol. 46, (2008), pp. 7–8.
- [5] P. Liu, E. Sherman, A. Jacobsen, Design and fabrication of multifunctional structural batteries, *J. Power Sources* 189 (2009) 646–650, <https://doi.org/10.1016/j.jpowsour.2008.09.082>.
- [6] 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>.
- [7] 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>.

- [8] 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>.
- [9] E. Jacques, M.H. Kjell, D. Zenkert, G. Lindbergh, The effect of lithium-intercalation on the mechanical properties of carbon fibres, *Carbon* 68 (2014) 725–733, <https://doi.org/10.1016/j.carbon.2013.11.056>.
- [10] L.E. Asp, E.S. Greenhalgh, Structural power composites, *Compos. Sci. Technol.* 101 (2014) 41–61, <https://doi.org/10.1016/j.compscitech.2014.06.020>.
- [11] 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>.
- [12] N. Shirshova, A. Bismarck, S. Carreyette, Q.P.V. Fontana, E.S. Greenhalgh, P. Jacobsson, P. Johansson, M.J. Marczewski, G. Kalinka, A.R.J. Kucernak, J. Scheers, M.S.P. Shaffer, J.H.G. Steinke, M. Wienrich, Structural supercapacitor electrolytes based on bicontinuous ionic liquid–epoxy resin systems, *J. Mater. Chem. A* 1 (2013) 15300, <https://doi.org/10.1039/c3ta13163g>.
- [13] M.W. Schulze, L.D. McIntosh, M.A. Hillmyer, T.P. Lodge, High-modulus, high-conductivity nanostructured polymer electrolyte membranes via polymerization-induced phase separation, *Nano Lett.* 14 (2014) 122–126, <https://doi.org/10.1021/nl4034818>.
- [14] L.D. McIntosh, M.W. Schulze, M.T. Irwin, M.A. Hillmyer, T.P. Lodge, Evolution of morphology, modulus, and conductivity in polymer electrolytes prepared via polymerization-induced phase separation, *Macromolecules* 48 (2015) 1418–1428, <https://doi.org/10.1021/ma502281k>.
- [15] A.F. Jacobine, Thiol–ene photopolymers, *Radiat. Curing Polym. Sci. Technol.* Elsevier, London, 1993, pp. 219–268.
- [16] C.E. Hoyle, C.N. Bowman, Thiol-ene click chemistry, *Angew. Chem. Int. Ed.* 49 (2010) 1540–1573, <https://doi.org/10.1002/anie.200903924>.
- [17] C.E. Hoyle, A.B. Lowe, C.N. Bowman, Thiol-click chemistry: a multifaceted toolbox for small molecule and polymer synthesis, *Chem. Soc. Rev.* 39 (2010) 1355, <https://doi.org/10.1039/b901979k>.
- [18] T.Y. Lee, Z. Smith, S.K. Reddy, N.B. Cramer, C.N. Bowman, Thiol-allyl ether-methacrylate ternary systems. Polymerization mechanism, *Macromolecules* 40 (2007) 1466–1472, <https://doi.org/10.1021/ma062494b>.
- [19] M. Claudino, J.-M. Mathevet, M. Jonsson, M. Johansson, Bringing d-limonene to the scene of bio-based thermoset coatings via free-radical thiol–ene chemistry: macromonomer synthesis, UV-curing and thermo-mechanical characterization, *Polym. Chem.* (2014) 3245–3260, <https://doi.org/10.1039/c3py01302b>.
- [20] C.E. Hoyle, T.Y. Lee, T. Roper, Thiol-enes: chemistry of the past with promise for the future, *J. Polym. Sci. Part A Polym. Chem.* 42 (2004) 5301–5338, <https://doi.org/10.1002/pola.20366>.
- [21] ASTM D3039, Standard Test Method for Tensile Properties of Polymer Matrix Composite Materials vol. 3, (2011), pp. 1–13, <https://doi.org/10.1520/D3039>.
- [22] B.D. Agarwal, L.J. Broutman, Analysis and Performance of Fiber Composites, second ed., A Wiley-Interscience Publications, 1990.
- [23] E. Peled, The electrochemical behavior of alkali and alkaline earth metals in non-aqueous battery systems—the solid electrolyte interphase model, *J. Electrochem. Soc.* 126 (1979) 2047–2051, <https://doi.org/10.1149/1.2128859>.
- [24] D. Aurbach, B. Markovsky, M. Levi, E. Levi, A. Schechter, M. Moshkovich, Y. Cohen, New insights into the interactions between electrode materials and electrolyte solutions for advanced nonaqueous batteries, *J. Power Sources* 81–82 (1999) 95–111, [https://doi.org/10.1016/S0378-7753\(99\)00187-1](https://doi.org/10.1016/S0378-7753(99)00187-1).
- [25] 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>.
- [26] Performance Composites Ltd, Mechanical Properties of Carbon Fibre Composite Materials, Fibre/Epoxy Resin (120°C Cure), (2017) [http://www.performance-composites.com/carbonfibre/mechanicalproperties\\_2.asp](http://www.performance-composites.com/carbonfibre/mechanicalproperties_2.asp).
- [27] 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.* (2018), <https://doi.org/10.1016/j.compscitech.2018.04.041>.