Multifunctional approaches for safe structural batteries[☆]

Sergiy Kalnaus[a,*], Leif E. Asp[b], Jianlin Li[c], Gabriel M Veith[d], Jagjit Nanda[d], Claus Daniel[c], Xi Chelsea Chen[d], Andrew Westover[d], Nancy J Dudney[d]

[a] *Computational Sciences and Engineering Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6085, USA*
[b] *Department of Industrial and Materials Science, Chalmers University of Technology, Gothenburg, Sweden*
[c] *Electrification and Energy Infrastructures Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6479, USA*
[d] *Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6164, USA*

Abstract

Recent advancements in Li and Li-ion based energy storage resulted in development of novel electrode materials for higher energy density which are finding their applications in transportation. There appears to be a limitation in improvement of specific energy of the system based solely on design of material compositions for multivalent intercalation compounds. In addition, higher energy stored by the system implies need for addressing safety concerns especially when it comes to large automotive battery packs. New

[*]Corresponding author
Email address: kalnauss@ornl.gov (Sergiy Kalnaus)

approaches for improvement of both energy density and safety of batteries are emerging, where multifunctionality of the materials and/or architectures is utilized. This article presents a review for such approaches from multifunctional current collectors to design of batteries capable of supporting mechanical loads and thus possessing ability to be used as a structural component.

Keywords: Energy storage, Li-ion, Lithium, Safety, Multifunctional

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Contents

1. Introduction

The concept of an electrochemical energy storage device has been perceived for a long time as a separate system with the sole role of providing electrical current to the external load. Such system would require protective measures in terms of physical barrier against any mechanical impacts as well as cooling and battery management systems (BMS). Such perception dominated the research since the first introduction of Li-ion batteries to the market by SONY [1]. Significant efforts undertaken by the research community have led to development of multiple new materials for electrodes in addition to progress in processing and manufacturing [2]. This resulted in incremental increase of specific energy of cathodes, which are the limiting electrodes in terms of potential and capacity of the cell. A good example is the progress made with the layered transition metal oxide compounds where increase in nickel content $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ (NMC333) [3] - $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$ (NMC532) [4] - $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$ (NMC622) [5]-
$LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ (NMC811) [6] has resulted in the overall increase in usable capacity from 150 mAh/g (NMC333) to 200 mAh/g (NMC811) [5, 7]. Novel materials and processing methods for the negative electrodes have also been developed [7–10]

While materials research and discovery resulted in development of electrodes with increased capacity and fast charging capabilities [11], the cell and system level energy density still needs improvement. The structure of

the typical cell sandwich, a unit block of a cell and battery, involves significant amounts of inactive components in form of metal current collectors (copper on the negative side and aluminum on the positive side of the electrode pair) and separators. This reduces both volumetric and gravimetric energy densities of a single electrode pair. With the addition of cell packaging material (pouch of pouch cells, or cans used for prismatic and cylindrical cells), module enclosures, battery enclosures and protective structures, the useful volumetric energy density decreases even further. Implementation of multifunctional concepts and materials in batteries can eliminate some of the inactive components in battery structure. Developments in this area are expected to provide significant improvement in performance of energy storage systems in addition to discovery of new Li (or other) ion host materials for electrodes.

Multifunctionality has been an actively pursued concept in engineering and covers a wide range of applications [12, 13]. In this regard, it is rather more suitable to utilize the notion of multifunctional materials systems, which covers materials and composites as well as structures [12]. Usually the multifunctional materials applications combine intrinsic material properties of responding to external stimulus with some degree of integration into structures. The response to stimulus can have different forms, which most frequently include: response to temperature (shape memory alloys), response to mechanical stress (piezoelectric), response to electric current (piezoelectric, dielectric elastomers), and response to magnetic field (magnetorheological fluids). These properties are utilized by embedding the devices in structures for sensing, vibration damping, energy harvesting, heating and cooling, etc.

Excellent reviews can be found in [12, 13]. Multifunctional systems can span different length scales, depending on the target properties and application. As a good example, carbon nano-tubes (CNTs) can serve as reinforcement for composites (meso- and macro-scale) utilizing their high strength. Such composites in turn serve as structural components. Other properties of CNTs, such as high electrical and thermal conductivity, allow expansion of multifunctionality and usage of CNT-based composites in applications for heat dissipation [14] and mechanical damage sensing [15].

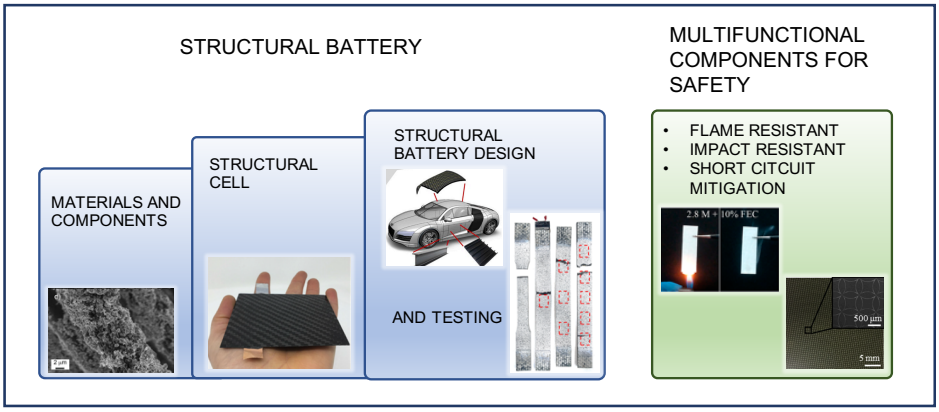

Figure 1: Battery multifunctionality aspects considered in this review: multifunctional structural batteries (materials to cells to batteries integrated into structures) and multifunctional battery components for safety . [16–21]

While multifunctionality in composite structures has been explored relatively well, mostly from the mechanics view point, multifunctionality applied to energy storage is a rather new subject. One of the earlier examples is the structural battery introduced by Liu et al [22] and Ekstedt et al [23]. Most recent reviews can be found in [24, 25]. In addition to load bearing capabilities, multifunctionality, when applied to batteries should result in improved

safety and performance without sacrifice of stored energy per unit mass and volume. In this report we summarize achievements in this area that cover both multifunctional materials and multifunctional structures utilized for energy storage purpose. An overview of multifuntional energy storage approaches is given in Fig. 1. The structure of this review will follow Fig. 1 with the discussion of multifunctional materials and concepts for battery cell components, battery cells, embedded batteries, and finally battery safety.

2. Structural batteries

Following the notion of multifunctional materials systems [12], the structural batteries can be designed based on the two main concepts [26]. The first approach is to make a multifunctional battery material from multifunctional constituents. For example, structural battery composite electrodes can be made from carbon fibers in an matrix electrolyte material [27]. In this case, the electrolyte, typically represented by an ion conducting polymer, is capable of some mechanical load transfer and is termed a structural battery electrolyte (SBE) [28]. Neat carbon fibers (CF) are used in a structural negative electrode, exploiting their high mechanical strength (2-4 GPa tensile strength [29, 30]), excellent lithium insertion capacity (280 mAh/g [31]) and high electrical conductivity (4.9 S/cm). Carbon fibers coated with a cathode active material can be used as the structural positive electrode. Here, the cathode material (for example lithium iron phosphate [27]) is the electrochemically active component and the fibers carry mechanical load and conduct electrons. The surrounding SBE is a lithium ion conductor and transfers mechanical loads between fibers. With these constituents, struc-

tural battery cells intrinsic to the structure can be realized [27].

The second approach is to design a multifunctional component, in which the battery cells are distributed within a load supporting structure. In this case the battery cells are not designed for strength as they do not participate in mechanical load transfer, although they are embedded in the structure [26, 32]. In a recent paper Hopkins et al [33] labeled the multifunctional materials as coupled and the multifunctional components as uncoupled systems and presented an overview of their performance. In what follows we consider both approaches. It should be mentioned however that so far, uncoupled systems, i.e. multifunctional components, demonstrate superior combination of stiffness and specific energy values compared to those of the coupled ones [33].

2.1. Li-ion battery cells with enhanced stiffness and strength

One of the earliest approaches to multifunctionality of energy storage devices is modifying battery structure to re-design it as a structural component. In this way, the load bearing capability of the battery is used in structural elements and therefore mechanical properties (typically flexural stiffness) need to be enhanced by introducing high-strength materials into the cell composition. Each of the battery cell components, electrodes, separator, and electrolyte, can be enhanced to provide higher strength of the cell. Simultaneous enhancement of several components is preferable, especially if such approach eliminates one or several inactive components in a battery cell, as it increases the degree of multifunctionality. The increase in overall cell stiffness should introduce no or minimal decrease in energy and power density in order to justify multifunctionality.

2.1.1. Structural battery electrolytes and separators

The SBE matrix needs to be formulated to simultaneously allow for lithium ion conduction while providing mechanical load transfer and stable interface with other battery cell constituents. Research to realise highly multifunctional SBEs is briefly described below. In majority of cases polymers with lithium salts are used as electrolytes in structural batteries. An ideal polymer electrolyte needs to be strong enough to eliminate the need for the battery separator and yet retain high ionic conductivity. Simultaneous increase in stiffness and in ionic conductivity presents the major roadblock for the development of structural polymer electrolytes as these two properties seem to be inversely correlated. In [34] a new series solid poly(ethylene oxide)-methacrylate lithium ion conducting electrolytes with varying content of thio-ether segments were introduced and the elastic modulus was enhanced via ultraviolet (UV) curing. Ionic conductivity increased with increase in thiol content and was achieved as high as 8×10^{-7} S/cm [34]. Unfortunately, as an associated trade-off, it was determined that an increase in content of thio-ethers decreased the flexural rigidity of the material. With the highest achieved elastic modulus of approximately 2 GPa, the ionic conductivity remained rather modest 1.2×10^{-8} S/cm.

Such a trade off between elastic modulus and ionic conductivity appears typical for polymer electrolytes, as summarized in a comprehensive report by J.F. Snyder *et. al.* [28]. The study investigated effects of different formulation variables, such as salt concentration, concentration of the vinyl ester in solvent-free vinyl ester resins, inclusion of hardening agents, etc. The observed overall trend shows that ionic conductivity decreases with increase

in mechanical stiffness [28]. The correlation between ionic conductivity and modulus in compression is shown in Fig. 2 and the corresponding nomenclature describing different types of vinyl ester derivatives of poly(ethylene glycol) (PEG) is arranged in Table 1. A sharp decrease in ionic conductivity can be observed followed by a plateau at around $2{\cdot}10^{-8}$ S/cm for electrolytes stiff enough to be considered for structural applications (elastic modulus greater than 1 GPa).

Table 1: Nomenclature for vinyl ester PEG derivatives for Fig. 2 [28]

mXn-Y			
m	X	n	Y
number of vinyl ester groups	M → methacrylate A → acrylate	number of glycol units	OH → hydroxyl OMe → methoxy BPA → bisphenol-A TMP → trimethylpropane PE → pentaerythitol

It is therefore likely that the design of electrolytes for structural batteries would involve composites containing polymer and ionic conducting ceramics or glass phases to increase strength, Fig. 3. This area has already attracted a significant amount of research spanning several decades [36–58], in which almost exclusively particulate composites of hard ceramics and soft polymer phase are considered [59]. Composites with non-conductive ceramics (e.g. alumina) [36, 43–45] have been proposed as a means to enhance elastic modulus. In addition, composites in which both phases conduct Li ions

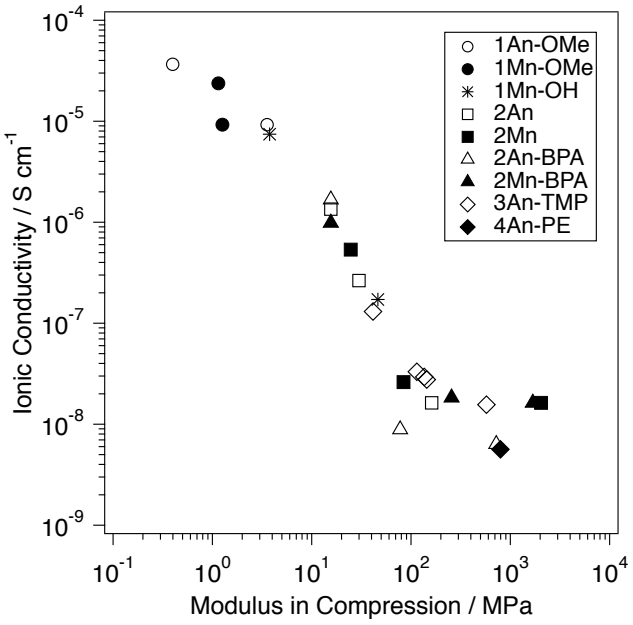

Figure 2: Conductivity as a function of modulus for the materials in Table 1 [28].

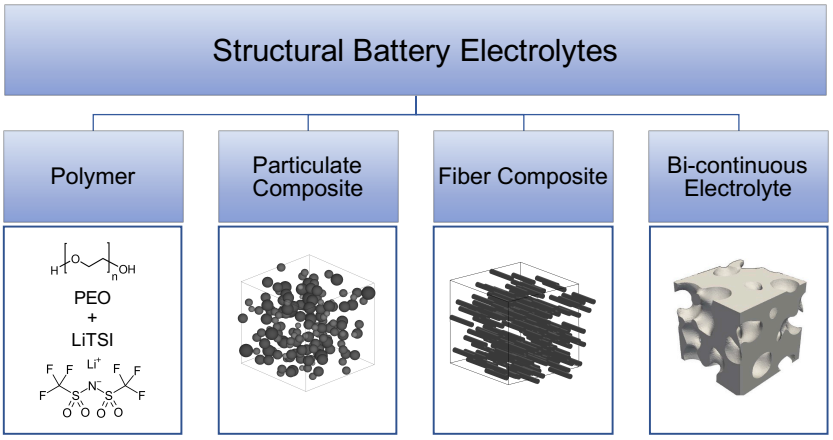

Figure 3: Types of structural battery electrolytes. [35]

[37, 41, 48, 54–56] have been fabricated in order to utilize high ionic conductivity of crystalline garnet-type materials. While generally good mechanical

strength and manufacturability have been achieved [50], such composites suffer from high interfacial impedance between polymer and ceramics or glass phases [52, 53]. This results in ionic transport path which excludes highly conductive ceramics particles, thus lowering the expected effective conductivity. Numerical modeling [49] shows that in order to achieve sufficient improvement in both ionic conductivity and mechanical stiffness, the composite must have very high volumetric fraction of the ceramic phase ($60vol\%$ and higher). Consequently, composites with high ceramics loading, in which the approach of "ceramics in polymer" was shifted towards "polymer in ceramics", have been fabricated [50, 56] and demonstrated good ionic conductivity (1.2×10^{-6} - 6.2×10^{-5} S/cm) together with stable electrochemical cycling. Further improvement has been achieved by partially sintering the network of ceramics particles with subsequent back-filling of such interconnected scaffold with polymer electrolyte [57, 58]. Following this approach, a composite electrolyte membrane was made containing partially sintered lithium aluminum titanium phosphate (LATP) glass-ceramic particles and crosslinked poly(ethylene glycol) diglycidyl ether (PEGDGE) polymer mixed with Jeffamine®and Lithium bis-trifluoromethanesulfonimide (LiTFSI). The resulting composite showed good ionic conductivity (order of magnitude improvement over composite with dispersed particles) as well as good equibiaxial mechanical strength of 20 MPa [58]. The design of the electrolyte is schematically shown in Fig. 4 where the ionic transport is shown to occur through the conductive ceramic particles (numerical simulation in Fig. 4(a)).

In addition to particulate composites, the SBEs with fiber reinforcements have been made [60–62]. In one particular case, the composite was made

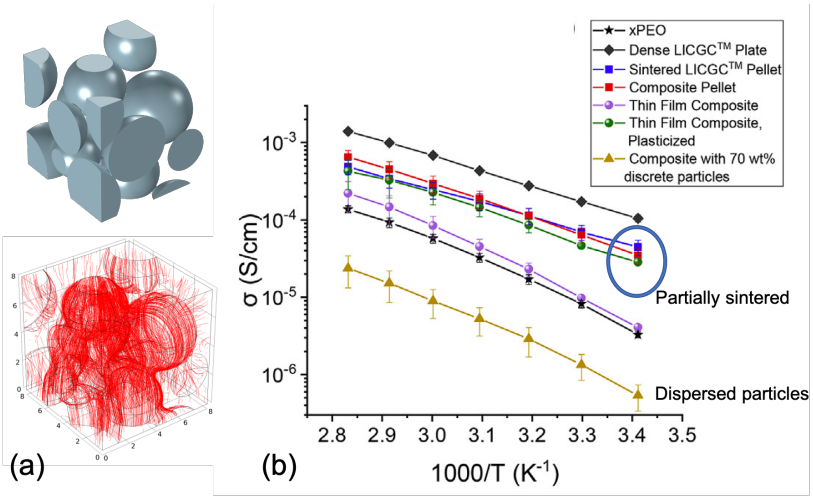

Figure 4: Partially sintered strucural electrolyte [58]. (a) simulation showing ionic current flowing through the ceramics phase; (b) measured ionic conductivity

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by in-situ cross-linking poly(ethylene oxide) (PEO) inside the woven glass fiber mat [61]. Such approach resulted in very high tensile modulus of the composite, above 1 GPa, which was unachievable by any polymer electrolytes, especially if plasticizers were used to improve conductivity. The high modulus was attributed to dynamic hydrogen and ionic bonding interactions between glass fibers and PEO-based electrolyte.

An alternative route to realize highly multifunctional SBE matrices for structural batteries is to make two-phase bi-continuous material systems [63–65]. Here, the two-phase SBE composite material is designed as a porous polymer "sponge" filled with a liquid electrolyte. The role of the polymer phase is to transfer mechanical loads, whereas the liquid electrolyte allows for Li-ion transport to realize the battery functionality [63]. This concept is somewhat similar to the described above approach for partially sintered com-

posite electrolytes, except the liquid electrolyte in this case functions only as ionic conductor while the sintered ceramic scaffold can support external load in addition to providing pathway for ionic current. Ideally, such inhomogeneous SBEs can simultaneously accommodate high ion-conductivity and elastic modulus (or mechanical strength). Ihrner et al. [64] and later Schneider et al. [65] developed highly improved bi-continuous SBEs for structural batteries. Ihrner et al. [64] combined a conventional liquid solvent/Li-salt electrolyte with a bis-phenol-A based methacrylate monomer that resembled a conventional vinyl ester resin often used for advanced composites. Fully phase separated SBE with two percolating intermingled phases was made by photo-induced 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 conductivity in the range $1 - 2 \times 10^{-4}$ S/cm. The presence of two percolating phases was verified since the SBEs showed structural integrity even after liquid electrolyte was fully extracted from the SBE. When applied to structural anodes, the utilized photopolymerization is however of limited use as CF composites are not transparent to UV-light. Therefore, a thermally induced polymerization route was also developed [65].

This thermally induced polymerization process allows for conventional production processes used for composite manufacturing. An optimized curing scheme was $80 - 90^{o}C$ for 30 minutes which yielded a monomer conversion more than 90%. Schneider et al. [65] further demonstrated that the thermal curing could be performed in presence of carbon fibers without any impact on the curing rate. The thermally cured SBEs exhibited a similar morphology with structural features in the submicron range as the UV-cured

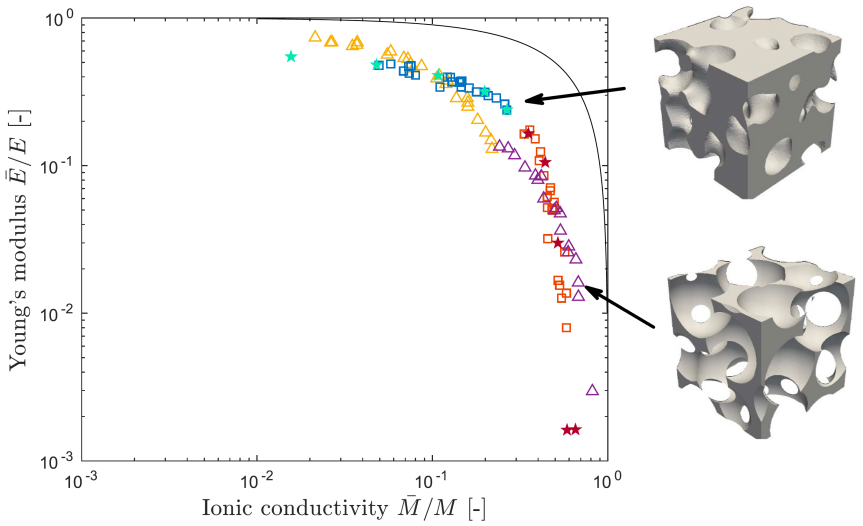

Figure 5: Schematic of the multifunctional performance of different SBE architectures, modelled by Tu et al. [35].

systems, i.e. pore sizes in the range of 50-200 nm. Furthermore, an elastic modulus at ambient temperature around 500 MPa and an ionic conductivity around 2×10^{-4} S/cm were reported for the thermally cured systems [65]. Recently, Tu et al. [35] presented numerical analyses to assess the multifunctional performance of different inhomogeneous SBE systems. In Fig. 5, the multifunctional performance is plotted for different microstructural topologies. From these analyses, it is evident that inhomogeneous SBEs offers an advantage to homogeneous ones, when the comparison to Fig. 2 is made.

2.1.2. Structural battery electrodes

Apart from electrolyte or separator modifications, reinforcement of electrodes has been demonstrated, typically via introduction of CF [22, 66–68] and carbon nanotubes [69]. High tensile strength and high Young's mod-

ulus thick (100 μm) composite electrodes for all solid state batteries [70] have been fabricated using two-phase $Li_4Ti_5O_{12}$−$Li_{0.29}La_{0.57}TiO_3$−Ag composition. The tensile strength and tensile modulus were measured as 90 MPa and 29 GPa respectively. These values are orders of magnitude higher than what has been reported for traditional slurry-processed electrodes: 4.2 MPa and 0.7 GPa for tensile strength and Young's modulus correspondingly [71]. While the ductility of such composite was rather low, the high strength provides an opportunity for using these electrodes in structural, load bearing battery applications.

Carbon fibers represent an ideal anode material which combines both high theoretical capacity for lithium intercalation of 372 mAh/g with high strength. The experimentally measured capacity of CFs certainly differs from the theoretical value and depends on fiber processing. An in-depth review of polyacrylonitrile derived CFs can be found in [72]. Mechanical properties and 1st cycle lithiation capacity of different commercially available carbon fibers are arranged in Table 2. The values in Table 2 are reported for the fibers with coating removed. Such coating is termed sizing in industry and is a polymer layer applied to carbon fibers to protect them during handling and to promote adhesion between fibers and epoxy matrix in carbon fiber structural composites. As can be seen, the IMS65 grade provides the best combination of the highest mechanical strength (6 GPa) and higherst 1st cycle capacity (360 mAh/g). Fredi et al. [73] studied the influence of the carbonaceous structures on the multifunctional performance of carbon fibers. They were able to explain the high electrochemical capacity of the IMS65 and T800 fibers as they were found to insert lithium by a mechanism like that

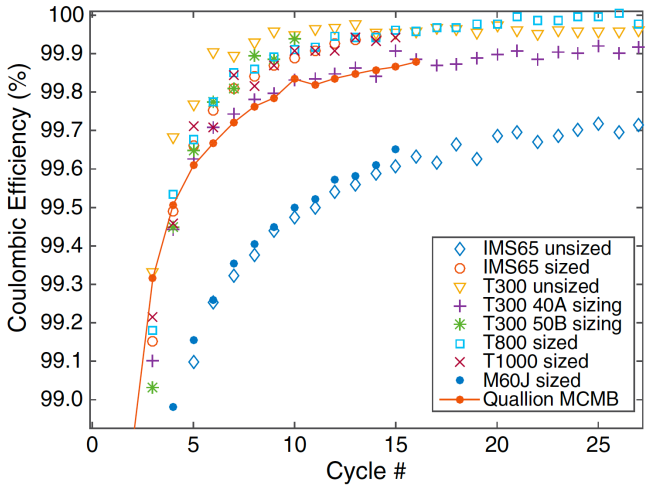

Figure 6: Coulombic efficiency as function of cycle number for various carbon fibre. Solid line is for a commercial MCMB (Quallion) [74]

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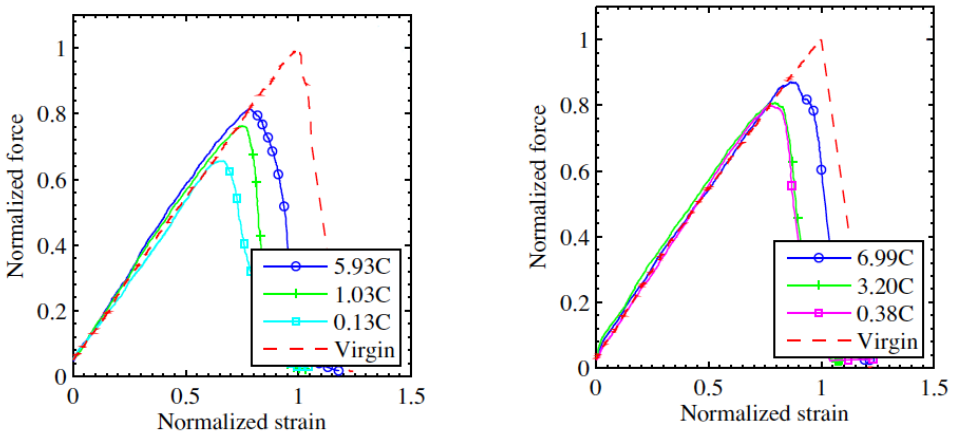
found for disordered carbons. Hagberg et al. [74] measured the coulombic efficiency of several types of CFs and compared with state-of-the-art graphitic battery electrodes from meso-carbon micro beads (MCMB). The results are presented in Fig. 6. For high precision coulometry tests the CF electrodes were sealed in pouch cells with lithium foil serving as counter and reference electrode. A glass microfiber separator was used and the cells were filled with 1.0M $LiPF_6$ in ethylene carbonate (EC): diethyl carbonate (DEC), 1:1 by weight. As can be seen in Fig. 6 the coulombic efficiency is very high for some of the CF tested in this study, some even outperform that of state-of-the-art MCMB.

It should be mentioned however, that the tensile strength of carbon fibers depends on the degree of lithiation, i.e. on the state of charge (SOC) [27, 75, 76] and electrochemical cycling [77]. A rather significant decrease in tensile



(a) (b)

Figure 7: Load-strain curves of (a) IMS65, and (b) T800H CFs lithiated at different C-Rates [76].

strength (up to 40%) can happen upon lithiation [76] and this change is only partially recoverable. Since the tensile strength of CFs is governed by the amount of defects, it is suggested that the loss of strength is related to lithiation of regions with high concentration of defects [76]. The load-strain curves for two types of CFs tested in [76] are shown in Fig. 7. As can be seen, reduction in tensile strength is associated not only with Li concentration, but with lithiation rate as well. It is important to note however that the elastic stiffness of CFs in Fig. 7 is not influenced by the lithium concentration. This indicates that Li intercalation into CF host structure introduces elastic strains that do not result in permanent damage leading to decrease in stiffness (e.g. microcracking).

Sheets made of carbon nano-tubes, nano-foams, and activated carbon-based fabrics have also been researched as possible self-supporting anodes

Table 2: Mechanical properties of commercial carbon fibers (without sizing) [23]

Manufacturer	Grade	Diameter μm	Strength MPa	Modulus GPa	Capacity mAh/g
Toray	T300	7	3530	230	350
Toray	T800	5	5490	294	194
Toray	M40	5	4410	377	87
Toray	M46	5	4210	436	87
Toho Tenax	UTS50	7	4800	240	48
Toho Tenax	IMS65	5	6000	290	360
Toho Tenax	UMS45	4.7	4500	430	49

[31, 78, 79]. Such approach eliminates necessity for the metal current collector of the negative electrode thus increasing the multifunctionality factor of a battery cell. The capability for Li storage in such materials is rather promising, as can be seen in Table 3. However, it is expected that, just as in the case of single CF, the tensile strength of these materials will be a function of state of charge, weakening with lithiation. It also remains unknown how these CNT-based electrodes will perform under compression loading. Finally, it should be noted that apart from carbon nanotube sheets, other carbon-defived fabrics lose up to 50% capacity by 50th cycle (Table 3).

To date, only few studies have addressed the design of structural cathodes. Hagberg et al. [16] described a path to manufacture structural positive electrodes via electrophoretic deposition of $LiFePO_4$ (LFP), carbon black and polyvinylidene fluoride onto CFs. The carbon fibers simultaneously act as re-

Table 3: Li storage capacity of carbon-derived sheets for battery anodes [31]

Manufacturer	Grade	Capacity, mAh/g		
		1st cycle (c)	1st cycle (d)	50th cycle (d)
Activated carbon-based fabrics				
Engineered Fibers Tech	2225	1269	198	90
Sterling Fibers	14/86	844	122	65
Carbon nanotube sheets				
NanoLab	SWNT	553	112	84
NanoLab	MWNT	604	119	110
Nano-foams				
Marketech	I	811	245	135
Marketech	II	872	248	126

inforcement and current collectors. The CF-based structural cathodes were tested in pouch cells containing Li foil as a negative electrode and 1.0M $LiPF_6$ in EC:DEC (1:1 by weight) [16]. Electrochemical characterization demonstrated a specific capacity of up to 110 mAh/g with a 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 of coated and uncoated CFs demonstrated good adhesion between the coating and the fiber. In another recent study, Bouton et al. [80] presented an alternative method to coat the CFs with LFP particles. The method is a repeated dip coating process to generate a layer-by-layer (LbL) assembly of LFP particles. The process results in a few hundred nanometer thick coating layers. The dipped CFs were heated up to 450^oC to carbonize the organic binders used in the solution. The LbL-electrodes showed a specific capacity close to 100 mAh/g.

Polyaniline (PANI) has been integrated into structural cathodes together with aramid nano-fibers (ANF) and CNTs. With theoretical capacity for Li storage of 147 mAh/g PANI can be either grown on ANF pre-fabricated films [81] or polymerized in presence of ANF and CNT to create strong free-standing cathodes [82]. Tensile strength of up to 233 MPa and discharge capacity of 128 mAh/g of PANI-based structural electrodes was measured. It should be mentioned that cycling was done vs lithium metal in half-cell configuration and in cycling performance could be different if these cathodes are paired with carbon anodes with limited supply of lithium ions available for intercalation.

2.1.3. Structural battery composite cells

Finally, approaches involving simultaneous reinforcement of several components of the battery cell have also been demonstrated [23, 67, 83–85]. A cell combining woven anode made of CF, cathode ($LiFePO_4$) deposited on woven aluminum fiber current collector, and a glass weave separator has been built and successfully evaluated for structural battery application [23]. The structural battery, containing lithiated carbon and LFP showed an open cell potential of 3.3 V. The cell was not characterized for its electrochemical capacity or mechanical properties. Johannisson et al. [67] made the laminated half-cell from a thin T800 spread-tow fabric negative electrode versus lithium metal using a standard vacuum infusion technique. The matrix material was the structural battery electrolyte, developed in [64]. After curing, the lamina was tested both electrochemically and mechanically; the latter was done both before and after the electrochemical cycling. Electrochemical testing was performed in a pouch cell format where the negative electrode filled with the SBE was paired with Li foil and the galvanostatic cycling was done with upper cut-off potential equal to 1.5V. The multifunctional performance of the structural battery negative half-cell was very promising. The electrochemical capacity was around 230 mAh/g of carbon fiber after 10 galvanostatic charge/discharge cycles at C/10. Manufacturing of a single-layer very thin lamina resulted in low fiber volume fraction of approximately 20%. Still, the measured mechanical properties were quite good with a longitudinal stiffness of 52 GPa. In addition, it was shown that the matrix-dominated transverse strength increased by approximately 21% after electrochemical cycling [67]. Recent work reported in [83] shows a very promising example of the state

of the art structural battery combining carbon fiber anode, glass fiber separator filled with bi-continuous electrolyte [64], and commercial LFP positive electrode. The battery cells were tested electrochemically and for mechanical strength in tension and it was determined that such structural batteries provide combination of 24 Wh/kg energy density and 25 GPa elastic modulus in tension making them good candidates for structural energy storage [83].

The work in [67] reported the first laminated negative half-cell from a thin T800 spread-tow negative electrode versus lithium metal using an inhomogeneous electrolyte, developed in [64]. To further improve the performance concerning internal resistance, capacity and mechanical strength, the carbon fiber / SBE interface must be optimized. Further studies of the carbon fiber structural battery electrolyte are needed to understand the effects of electrochemical cycling on the multifunctional performance and durability of the interface. While the strength of individual carbon fibers as a function of lithium content has been a subject of several studies [27, 75, 76], to date, only a few attempts to characterize the performance of the carbon fiber / SBE interface have been made. In a recent paper, Xu et al. [86] characterized the interfacial shear strength between carbon fibers and SBE. The SBE acts as the composite matrix material and thus contains the carbon fiber reinforcement / electrodes. Given the porous structure of the matrix, not all fiber surface area is covered by the polymer phase where shear load transfer may occur, as schematically illustrated in Fig. 8. Consequently, the interfacial strength (i.e. load transfer) was expected to be low compared to that in traditional high-performance composites. In [86], the interfaces for two structural battery electrolytes with highly multifunctional carbon fibers

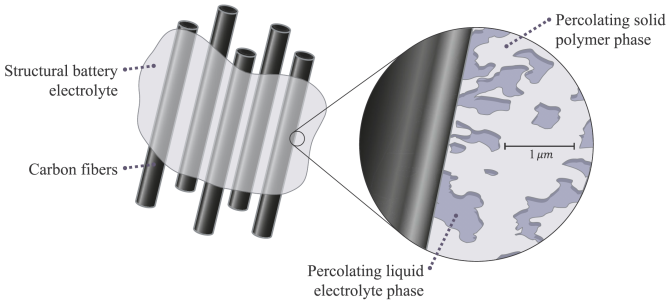


Figure 8: Schematic of carbon fibers in a structural battery electrolyte. Within a structural battery, the carbon fibers are included in a structural battery electrolyte. This matrix material both transfer load between the reinforcing fibers using a solid polymer network and conduct lithium ions through a network of liquid electrolyte. From Xu et al. (2020) [86]

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were investigated for their mechanical integrity. The results show that the mechanical adhesion of the structural battery electrode components is close to that of a comparable vinyl ester matrix composite resulting in transverse tensile strength of approximately 25 MPa.

Successful fabrication of a full structural pouch cell was demonstrated by Moyer et al [17]. In this approach, both electrodes were reinforced with carbon fibers and in addition the cell sandwich was laminated between two CF-epoxy composite sheets. Energy density of 35 Wh/kg at C/10 and a mechanical strength of 213 MPa were reported [17]. Graphite was utilized as anode material in this cell instead of using CFs directly to intercalate lithium ions. Such route was chosen to eliminate additional variables associated with changes in CF properties with electrochemical cycling, as previously described in the present review (Fig. 7). The positive electrode material was LFP, coated on CF which served as current collector. The structural

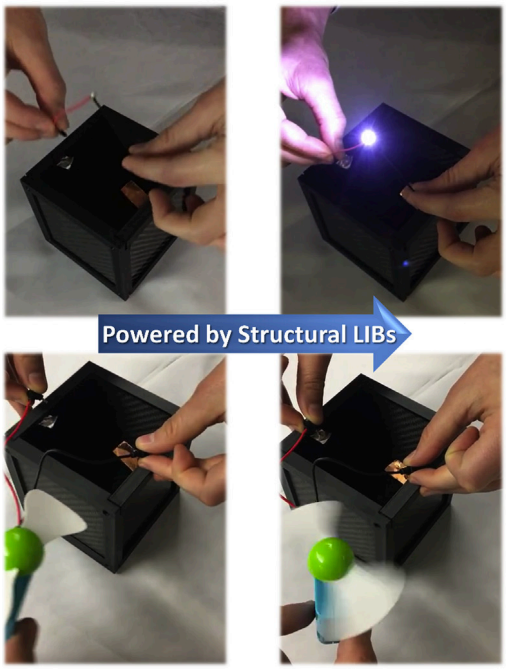

Figure 9: Structural composite cells as CubeSat walls developed in [87].

composite cells were directly integrated as CubeSat [87] structure walls to free the internal space for the electronic components 9.

2.2. Structural components with embedded Li-ion batteries

As an alternative approach to strengthening internal cell components, distribution of commercially available Li-ion cells in load bearing structures has been researched [88–93]. A term "structure-battery" materials has been applied to such designs [88, 94]. This approach targets elimination of inert mass of the battery enclosure by placing the battery cells within the structural components with no, or minimal, modification done to the cells. It is therefore commercially viable approach since it introduces no changes to the battery production line and therefore reduces the cost of the final prod-

uct. In addition, a possibility of sacrifice of electrochemical performance in order to increase mechanical stiffness by modifying battery electrodes and electrolytes is eliminated. In one of the pioneering works in this area, the NiH_2 battery was reconfigured to serve as a structural panel [89] of a space satellite. The effective energy density exceeded 100 Wh/kg. In [90, 95], the multifunctional structure of a spacecraft sandwich panels has been designed so that it would accommodate commercial Li-polymer cells without compromising the required mechanical rigidity. In [96] a similar approach was taken to desigh structural panels with integrated batteries for marine applications.

The early research demonstrated successful combination of Li-polymer cells into the wings of DARPA Wasp miniature Unmanned Aircraft System (UAS) [88, 97]. A 26% increase in flight endurance time was obtained with the multifunctional design where the custom trapezoid-shaped Li-ion pouch cells were embedded in the upper skin of the wings. The components of the cell were not reinforced in any way and therefore the increase in flight endurance was provided solely by savings from eliminating the weight of a standard battery enclosure. It should be mentioned that the later design of Wasp UAS had the prismatic battery cells installed into the wings with easy procedure for their replacement.

Integration of batteries into structures requires knowledge of the mechanical properties of the battery cells in terms of suitability for being a part of structural component. Long term durability and fatigue resistance need to be addressed as well. Therefore, a significant amount of effort went into testing of battery cells, either free standing, or embedded into the structures, under quasi-static shear [98], bending [92, 99], compression [92, 100], ten-

Figure 10: Darpa Wasp UAS with integrated Li-ion cells [88].

sion [19, 92], and vibrational loading [101]. Depending on the application, as apart of structure a battery cell can experience various loading modes. For instance, if a battery becomes a part of a lightweight truss system, it is expected to be subjected to shear. A four-bar linkage system was designed in [98] to test the commercial pouch cells under in-plane shear. The cells demonstrated very high stiffness in shear and failed by de-bonding from the grip sections of the setup. While showing some wrinkling of the pouch material, none of the cells revealed any failures or changes in open circuit potential [98]. Tensile and compression response of composite structures containing commercial Li-polymer pouch cells has been investigated in [19] and [100]. In both cases, the panels containing 0.5 Ah pouch cells were prepared by placing different number of cells in the carbon fiber reinforced epoxy laminates. Typical panel for tensile testing consisted of 24 plies of plain weave T300 carbon fabric [19]. In addition sandwich composites were made, where the cells were placed within the inner thick core consisting of a polyvinyl chloride (PVC) foam with cut-outs to accommodate the battery cells, which was then

laminated between two outer carbon fiber reinforced polymer (CFRP) face sheets. Digital image correlation and acoustic emission techniques were used to monitor strain distribution and internal damage during the tensile tests [19]. The results show significant reduction in both stiffness and strength (when normalized to the density) as a function of the number of integrated Li-ion cells. In case of the CFRP laminate such reduction comes from replacing continuous CFRP composite with lower stiffness and strength areas filled with battery cells. This leads to in-homogeneous strain distribution and concentration of strain at the CFRP-battery interface. However, since the effective density of the battery cell is similar to that of the CFRP there is no trade-off in terms of increase of the mass of the composite panels. When it comes to the sandwich structures with PVC foam core, the overall strength does not change due to placement of batteries, since the stiffness and strength of PVC foam are similar to those of a typical prismatic battery cell. However the density of the cells is much higher, so that when the mechanical properties are normalized with respect to density (or weight), a trade off is still noticeable. This is illustrated in Fig. 11, [19] where ED stands for energy storage density, i.e. is a function of the number of embedded cells. The results underscore the necessity for research and development of batteries with enhanced mechanical properties as discussed in the above sections of the current report.

Similar investigations have been done by subjecting composite CFRP panels with embedded battery cells to compression [100] and by applying 3-point bending to composite sandwich panels with battery cells embedded into the inner PVC foam core [99]. In both cases degradation of mechanical

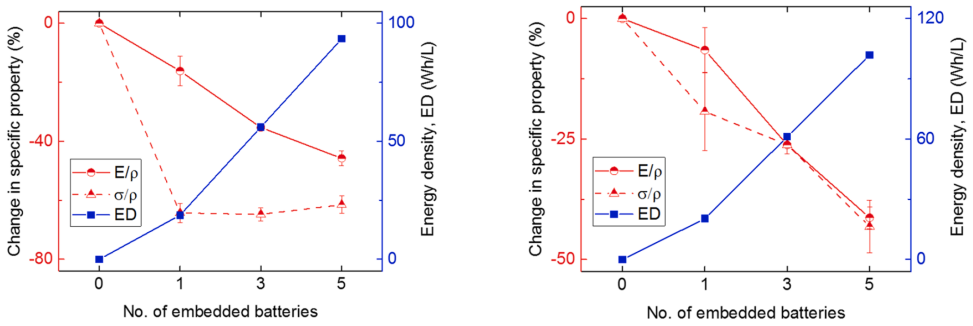

Figure 11: Mechanical and energy storage properties of multifunctional composite panels. a) CFRP laminate, b) PVC foam/CFRP sandwich. [19]

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properties due to introduction of the cells into the structure was observed. This degradation was especially severe in the case of the compression loading mode where the failure stress in compression was reduced up to 80% after two cells were placed in the structure along the line perpendicular to the loading axis. These results again emphasize the need for development of battery cells with enhanced strength and application of different design principles for the structural components, so that the maximum applied loads would be diverted from frame members with batteries. Finally, the compression-compression fatigue was applied to the composites with embedded batteries in [100]. Once again, the integration of Li-ion cells into the structure worsen the mechanical response, which in this case resulted in lower fatigue endurance limit. It should be mentioned however, that the embedded battery cells cycled really well under applied stress and did not show any degradation of the voltage profile up to the loads equal to 60% of the

tensile strength and up to 35% of the compression strength, which is rather encouraging. Under the bending loading mode, the cells embedded into the sandwich structure did not show any changes in cycling characteristics even after the composite itself developed through-thickness cracks [99]. It appears that the unmodified Li-ion cells are very resilient and can be safely cycled under large external loads. The load bearing capability of the battery cells however may need improvement. A simple pathway for such an improvement was demonstrated in [18, 102], where the cells were strengthened in bending without any modifications to the electrode active materials or separators. Increase in flexural rigidity was achieved by connecting the electrode with non-conducting polymer rivets. The rivets are passed through pre-fabricated perforations in electrodes. With such approach, the electrodes in the cell stack become mechanically connected and prevent sliding of the electrodes with respect to each other thus increasing the stiffness in bending. Laminating the "riveted" cells with CFRP sheets results in energy storing composite structures of high stiffness, albeit reduced energy density due to fraction of active material volume being replaced with the interlocking rivets.

2.3. Structural multifunctionality assessment

The ultimate goal of integration of battery cells into structural components is what sometimes is termed a "massless energy storage". In such structure, a single multifunctional component can support mechanical loads and simultaneously store and release electrical energy. In this section we discuss practical approaches to design metrics for multifunctionality and resulting weight savings. Perhaps the most straightforward approach is to use the structural and energy storage coefficients of a system introduced in

[103, 104]. Following [103] each of these coefficients can have a value between 0 and 1. For instance in a typical electric vehicle (EV), a battery pack has an energy storage coefficient of 1, but the structural coefficient of the same pack close to zero. The total mass of the system containing an energy storage component is a sum of the structural mass m_s and the mass of the battery pack m_{batt} reduced by its multifinctionality factor [103, 104].

$$m_{tot} = m_s + (1 - \sigma_s) \times \frac{m_{batt}}{\sigma_e} \tag{1}$$

where σ_s and σ_e are the structural and energy storage coefficients of the battery pack. These coefficients are defined as follows. The structural efficiency coefficient (σ_s) is based on mechanical metrics (i.e. flexural strength or stiffness) and is equal to 1 if the component performs as well as the current state of the art structural composite material designed for the specific application. The energy storage coefficient (σ_e) is based on metrics typical for batteries (i.e. energy or power density) and is equal to 1 if the component performs as well as the current state of the art battery designed for the specific application. It is obvious from Eq. 1 that with fully structurally integrated battery, the total system mass equals to the structural mass (hence the term "massless energy storage"). As an example, the total mass normalized to the structural mass is shown in Fig. 12 as a function of structural coefficient of a battery for a scenario where the mass of the battery is one-tenth of the structural mass of the system (approximating a CubeSat satellite). Complete elimination of the battery dead weight is possible when the battery cells can be integrated into the structural components without compromising the initial performance of the structure.

It is clear that the multifunctionality assessment using the above approach

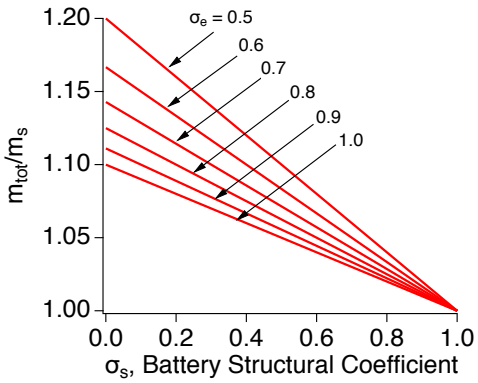


Figure 12: Normalized total mass of the system depending on structural and energy multifunctionality coefficients of a battery pack.

would strongly depend on the choice of benchmark parameters (mechanical and energy storage properties of the state of the art structural and energy storage components correspondingly). In addition the analysis includes neither cost nor the requirements for cooling systems or bussing and wiring. More detailed analyses have been developed in [105–107]. A system-level modeling framework has been introduced to quantify multifunctional performance of EVs with structural batteries in [105]. The approach allows estimation of a vehicle drive range under different drive cycle conditions. The mechanical properties of structural pouch batteries were estimated based on elastic laminate theory and the electrical performance of the batteries was modeled by equivalent circuit models. It should be mentioned that in [105] no protective or additional safety measures were assumed to be needed for the structural batteries. Under these assumptions, an increase of up to 70% in drive range was predicted from the theoretical analysis based on Tesla Model S and BMW i3 chassis.

3. Multifunctionality for safety

Lithium-ion batteries are capable of storing large amounts of energy, which, if released instantaneously, can lead to thermal runaway and fire. The severity of this event depends on the battery SOC and nominal capacity. The rapid release of stored energy in a battery can happen when the electrodes of opposite polarity come into contact; in this case a high current flowing through the area of contact creates significant local heating which can trigger further exothermic reactions and eventually fire. Such short circuit could be internal, or external with respect to the battery cell. The internal short circuit can occur either as a result of the separator failure due to battery damage such as impact or foreign object intrusion. External short circuit occurs via battery cell tabs, cables, or conductive enclosures. Significant amount of work has been published over the years dedicated to battery safety under abusive conditions [108–114]. For large battery cells, in the order of 20 Ah, used in automotive electric drivetrains, additional safety measures need to be implemented to protect the battery back from mechanical and thermal loads, since the fire events resulting from thermal runaway in a 20 - 100 kWh battery pack of EV can be truly catastrophic and hard to control. Additional protective enclosures around battery pack add weight to the vehicle and therefore reduce the specific energy density and consequently available range. Utilizing multifunctional materials within the cells is a promising approach to enhance battery safety so that savings on the requited battery protection can be made. The the approaches have been designed to either prevent the short citcuit or to isolate the area of contact so that all of the energy in the battery is not available for release. In what

follows we discuss such approaches.

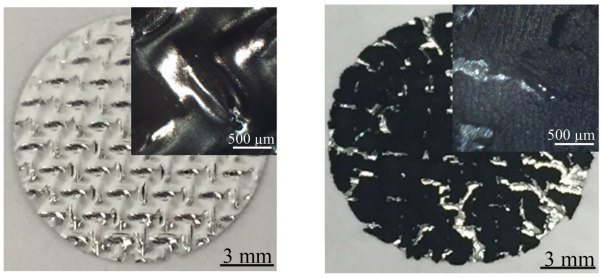
3.1. Multifunctional safe electrodes and separators

Battery safety mainly relies on separator, which is expected to block the pores, stop ionic flow, and shut down the cells upon sudden increase in temperature [2]. Mechanical strength and thermal stability are two crucial properties of separators [115, 116]. A common practice to increase mechanical strength and thermal stability is coating a layer of inert ceramic particles on separator [117]. Separators, however, cannot completely prevent catastrophic failure especially upon mechanical impact. Additional safety components, such as a positive thermal coefficient barrier layer [118], current interruption device, thermal fuses, and vents [119], and enclosure of battery packs are utilized to ensure battery safety, which introduces extra weight, volume and cost to the batteries. Oak Ridge National Laboratory (ORNL) has developed a novel technology to boost battery safety, where slitted patterns were applied to the current collectors [120]. The slitted patterns enable electrodes to break upon impact into electrically isolated pieces before the separator fails and allows contact between the electrodes. Thus, the electric current passing through the internal short(s) is reduced, preventing the onset of exothermic reactions and thermal runaway. Figure 14(a) shows the slit patterns. In order to test the approach, two types of pouch cells were assembled: with standard electrodes (standard cell hereafter), and with the electrodes containing slit patterns (modified cell). The cells were then subjected to an out-of-plane mechanical indentation with spherical indenter and their potential was continuously monitored during the tests. The two cells showed identical capacity before undergoing indentation. When the indenta-

tion exceeded a certain level, the open circuit voltage (OCV) of the standard cell started reducing and eventually dropped to zero indicating short circuit was formed. In comparison, no change in the OCV was observed during the indentation test for the modified cell. Both cells were connected to a battery cycler after the indentation tests. The standard cell could not be cycled electrochemically whereas the modified one not only was still functional but also delivered 93% of the capacity before the indentation test. A very similar approach was reported in [20], where a variety of current collector slit patterns was investigated. The patterning was done by applying photolithography methods, and some of the examples are shown in Fig.15. Based on the finite element analysis and experiments, it was determined that the pattern based on square unit cell with double-curved edges (center image in the bottom row of Fig. 15 was the most efficient in isolating the internal short circuit and reducing the temperature of the cell upon external loading [20]. The technology provides a potential solution to avoid a catastrophic thermal runaway after mechanical abuse.

A slightly different approach was investigated in [121] where forced delamination of the active material coating from the current collector under applied impact loading was explored. For that purpose the current collectors were patterned with sigmoidal ridges (Fig. 13) to promote delamination and cracking of electrodes upon application of external load to the battery and thus reducing the amount of current flowing through internal short circuit. At the same time it was demonstrated that the cells with sigmoidal current collectors cycled just as well as the standard cells and showed the same capacity retention. Battery cells with patterned electrodes also showed capability

of impact energy dissipation by reducing the impact force by about a factor of seven in comparison with standard current collectors.

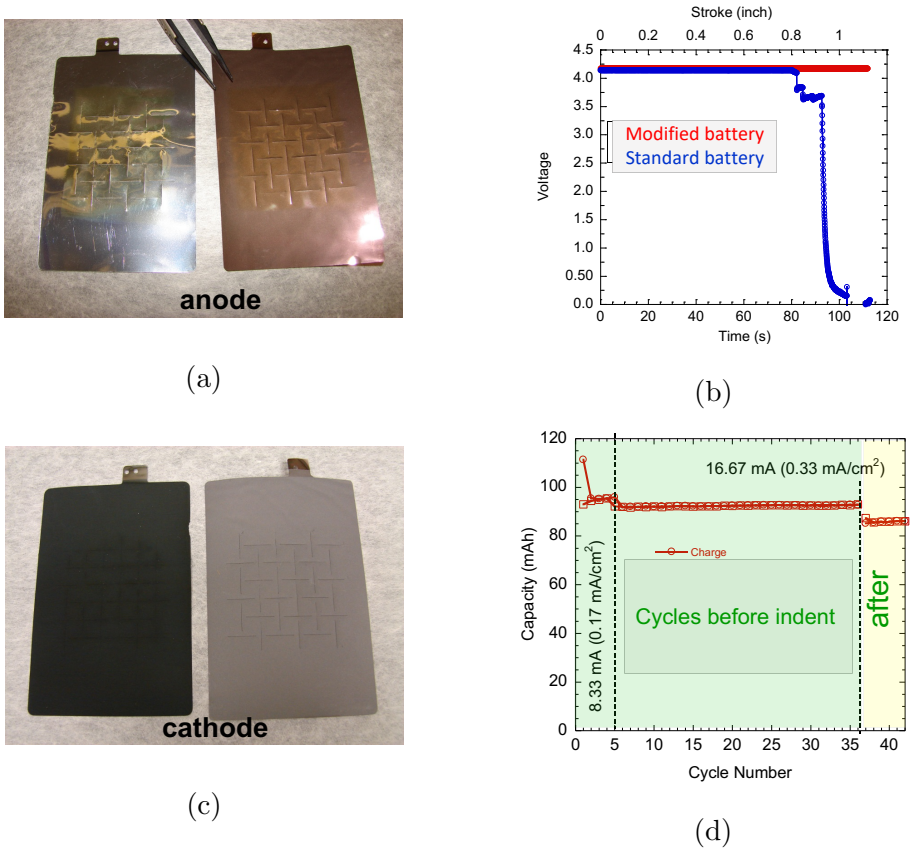


(a) (b)

Figure 13: Performance of current collectors with sigmoid patterning. a) patterned electrode before impact; b) patterned electrode after impact loading showing cracking and delamination of active material [121].

Battery safety can be further improved using metallized film current collectors. The metal layer is optimized to be thick enough to conduct electrons without inducing high electrical resistance yet thin enough to be oxidized and melted with extremely high current densities, such as resulted from short circuit. The metallized film current collectors are thinner and much lighter than the traditional metal foils which increases energy density. The ORNL slitted pattern is to avoid catastrophic failure from mechanical impact and the metallized file is efficient in preventing short circuit. Integrating the slitted pattern design with the metallized film could create a battery with superior safety features, which could further simply cell and pack design.

As an alternative to introducing stiffer polymer and polymer composite electrolytes into the battery cell (Section 2.1.1), approaches focused on cells with traditional liquid electrolytes but containing separators with increased



(a) (b) (c) (d)

Figure 14: Concept of electrodes with slit pattern for safety: a)anode; b) open circuit voltage during the indentation test for both standard and modified cells; c) cathode; d) capacity vs cycle number for the modified cell with pre-slit electrodes before and after the indentation test.

strength and decreased thermal shrinkage and degradation have attracted significant research effort. Several design approaches have been demonstrated with the majority of them utilizing inorganic fiber mats [122–127] or employing glass fiber [128–131] to replace the traditional porous polymer membranes. In this case, the degree of multifunctionality is enhanced even further since the multifunctional separator both increases the stiffness of the

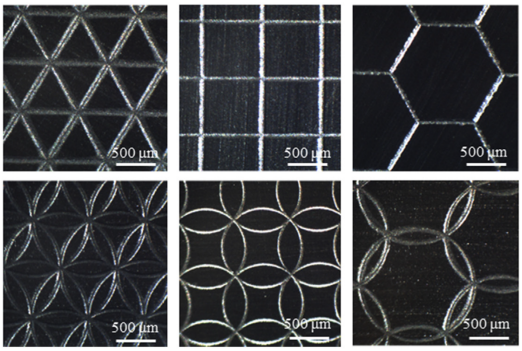


Figure 15: Different patterns of electrode current collectors designed to fail along the etched lines and isolate the area of local short circuit. [20]

battery cell and improves safety. It should be mentioned however that the production of such separators is limited in most cases to a small amount of experimental samples. Nevertheless, these separators show significant advantages over their polymer counterparts due to excellent mechanical and thermal properties. Successful examples of continuous free standing films composed of SiO_2 [123, 125], Al_2O_3 [122, 127], and CeO_2 or ZrO_2 [124] fibers have been demonstrated and revealed outstanding thermal properties and stability during electrochemical cycling. A multifunctional composite separator developed in [122] was designed to improve ionic transport in addition to thermal stability and stiffness, thus demonstrating elevated multifunctionality where one component addresses several aspects of battery operation. The fast ion transport was achieved by aligning alumina nanotubes in the direction perpendicular to the electrode surface and therefore significantly reducing the tortuosity of the separator.

Fibers derived from poly(*p*-phenylene terephthalamide), otherwise known as Kevlar, have been researched for implementation in Li-ion battery separa-

tors for reduction of thermal shrinkage and potential improvement of mechanical strength. Separators made of non-woven para-aramid fibers are available as commercial separators manufactured by Dreamweaver International. They show very good thermal stability up to 500^oC, but have relatively low tensile strength of 12 MPa and very low strain at failure of only 3% [132]. Such low strength is in part induced by the high porosity of the separator (approximately 40%) which is required to maintain sufficient effective ionic conductivity for high power applications. An alternative approach was pursued in [133], where the ANFs were used to create a battery separator with enhanced strength and thermal stability. The ANFs were produced from commercial Kevlar fibers and were wither freeze-dried or oven dried following the filtration to produce separator membranes. These membranes showed high tensile strength of 250 MPa, which is a factor of 20 improvement over Dreamweaver and a factor of 2 improvement over Celgard separators (when compared to the strength of Celgard in machine direction) [132, 133]. In addition the ANF-based separator showed an ability to self-extinguish upon introduction of flame. The self-extinguishing tipe was 3.1 s for a dry separator and 4.7 s for separator soaked in 1:1 EC/DEC [133].

The most common commercially adopted safety mechanism associated with separators is placement of a shutdown separator between the positive and negative electrodes. A typical shutdown separator consists of a meltdown PEO middle layer sandwiched between two outer polypropylene layers. Upon the temperature rise to approximately 130^oC the inner PEO layer starts melting and collapsing its pore structure so that the transport of charge by ions in the solution is interrupted [2]. This safety mechanism is therefore by design

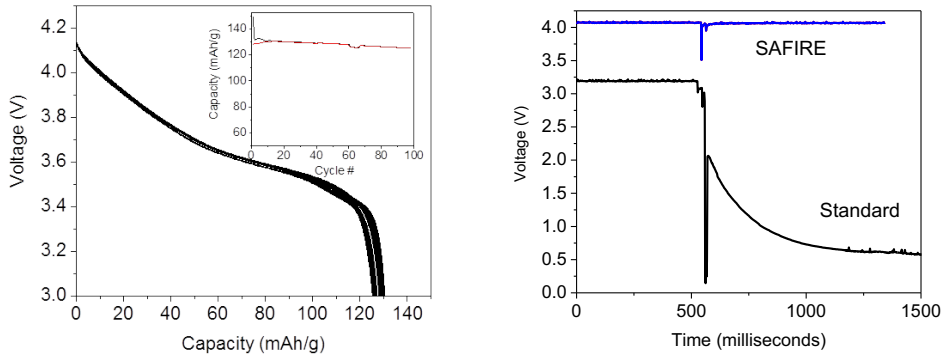
a single-use process since the structure of the separator gets destroyed once the temperature reaches a threshold value and this process is irreversible. To address this drawback, a novel on-off separator was designed in [134]. The separator was a membrane of polyvinylpyrrolidone (PVP)/TiO_2 nanofibers produced by coaxial elecrospinning method. It was observed via temperature dependent cycling of $LiFePO_4$/Li cells that at 60^oC the separator prevents the transport of ions through the electrolyte ($LiPF_6$ in EC/DMC). This process however is reversible and once the cell is cooled down to the room temperature, its performance is restored. The mechanism behind such behavior is not fully understood, however having a reversible shutdown feature would be beneficial in development of long lasting advanced Li-ion batteries.

3.2. Drop-in electrolytes designed for safety

In addition to modifications of separators and current collectors designed to isolate the electrodes in case of battery crush, techniques of enhancing battery safety via electrolyte additives or modifications have been developed [21, 135–140]. The risk of thermal instability of a typical commercial liquid electrolyte comes from the high flammability of the organic solvents and thermal instability of the salt, $LiPF_6$. Based on the requirements of ionic conductivity and viscosity, the electrolyte typically contains a combination of ethylene carbonate (EC), dimethyl carbonate (DMC), methylethyl carbonated (EMC), propylene carbonate (PC), and diethyl carbonate (DEC) all of which are highly flammable. Therefore, in order to decrease the fire hazard, more stable salts and non-flammable solvents need to be introduced into the electrolyte composition. Several alternative salts [137] have been proposed for $LiPF_6$ replacement, such as lithium LiTFSI and lithium

bis(oxalate)borate. Non-flammable electrolyte solvents have been also researched, such as dimethyl methyl phosphonate (DMMP) [135] and hydrofluoro ethers (HFEs) [138] used as a co-solvent. Finally, electrolyte additives serving as fire retardants have been proposed [21, 136, 139]. Initial investigation of phosphate-based flame retardant additive (triphenyl phosphate, TPP) showed very little impact on flammability while increasing viscosity and significantly reducing ionic conductivity [139]. Subsequent research however showed promise for the phosphate flame retardants and successful development of a fluoroethylene carbonate (FEC)/triethyl phosphate (TEP) electrolyte with LiTFSI salt [21].

Apart from chemical modifications, enhancement of safety can also be achieved through changes in physical response of the electrolyte to external stimulus. Several research efforts demonstrated engineering the rheology of the electrolyte to enhance its stiffening in response to external impact load [141–144]. The goal is to use the stantdard liquid electrolyte and impart a non-Newtonian behavior to it. The shear thickening electrolyte, termed SAFIRE (SAFe Impact Resistant Electrolyte) [142, 143, 145] showed instantaneous phase transition from liquid to solid upon high speed impact thus preventing contact between positive and negative electrodes in the cell. A regular liquid electrolyte (1.2M $LiPF_6$ in EC/DMC) was mixed with nano-sized inert silica particles to form a colloidal suspension with shear thickening behavior due to particle hydroclustering [142]. When such electrolyte was introduced into the pores of a porous battery separator, it significantly increased its stiffness upon impact by projectile. At the same time the cells were able to cycle normally, since the electrolyte remains liquid without ap-



(a) (b)

Figure 16: Performance of Safe Impact Resistant Electrolyte (SAFIRE): a)cycling in a coin cell at C/3 current; b) response to the projectile impact at 2.9 m/s of a pouch cell with regular and impact resistant electrolyte SAFIRE [142].

plication of a high strain rate impact (Fig. 16). The performance of SAFIRE was tested in 0.2 Ah pouch cells under galvanostatic cycling before and after being subjected to 3 m/s impact by the 2 kg brass ball. Through rheology experiments and numerical modeling it was determined that the best shear thickening response is obtained at 30 wt% of highly monodisperse silica particles. At such loading there is minimal effect on the ionic conductivity of the electrolyte. Shear thickening electrolytes similar to SAFIRE can provide substantial weight savings for a battery pack due to elimination of protective structure surrounding the cells. In fact, with this concept, the electrolyte itself becomes a protective feature. Due to its instantaneous increase in stiffness by orders of magnitude in the event of impact, this electrolyte can be utilized in battery cells integrated with protective body armor.

4. Critical analysis and research gaps

The notion of employing multifunctionality concepts in energy storage has led to the rapidly growing research field of structural batteries and supercapacitors. While significant progress has been made, there are still remaining challenges which we will briefly review. We also identify promising future directions and research gaps.

Structural batteries rely on multifunctional materials in their internal structure. Ideally all of the structural cell components (cathode, anode, electrolyte and separator) should be capable of participating efficiently in charge transport and storage as well as having increased stiffness and strength compared to the current state of the art cells. The most common approach to solve this challenge is to use composites built with carbon fibers for strength and electron transport and polymers with lithium salt for ionic transport and load transfer among the fibers. This approach is directly derived from the carbon fiber composites, which have been proven to display very high strength to weight ratio [146]. The following bottlenecks can be identified based on the analysis of the published results. This is definitely not an exhaustive list, it rather identifies the most apparent, in our opinion, areas in need of more research and more transformative solutions.

- Insufficient conductivity-to-strength ratio of polymer and composite electrolytes. There appears to be a fundamental trade-off between polymer electrolyte elastic modulus and ionic conductivity which prevents fully realizing multifunctionality for structural applications. In addition, reasonable conductivity in polymer electrolytes can be achieved

at temperatures above T_g, for example one of the most common electrolytes, PEO:LiTFSI reaches ionic conductivity of $4 \pm 2 \times 10^{-4}$ S/cm at 60^oC [147]. Alternative appproach is to use gel electrolytes; so far the most promising transport properties have been reported in organic gel electrolyte based on $LiClO_4$ in EC/PC + poly(acrylonitrile) (PAN): 2×10^{-3} S/cm [147]. Imparting mechanical stiffness has been sought therefore by creating composite electrolytes with the hard filler phase which can be an ionic conductor on its own (for example lithium ion conducting glass-ceramic (LICGC) $Li_2O-Al_2O_3-SiO_2-P_2O_5-TiO_2$ [50]). Activating the ionic transport through the hard phase however faces difficulties due to the resistive interface. Some success has been achieved by partially sintering the LICGC to create the percolative network structure and enhancing the mechanical strength followed by impregnating this structure with polymer electrolyte [58]. Integrating such composite electrolyte with carbon fiber-based electrodes has not been attempted yet and can be rather challenging and costly from the manufacturing perspective. Another promising approach has been demonstrated in [64, 65] where a two-phase polymer-liquid electrolyte was produced by thermal polymerization.

- Degradation in strength with cycling. The load bearing capacity of structural batteries relies primarily on carbon fibers incorporated in the electrode structure. However benchmarking studies [76, 77] have identified degradation of strength in carbon fibers with lithium insertion and removal (up to 30% reduction in strength [76]). Interestingly, the elastic modulus of the fibers remains constant with electrochemical

783 cycling, but their tensile strength suffers degradation [75, 77].

784 • Lack of thorough experimental program connecting electrochemical
785 performance with externally applied loads. Mechanical testing so far
786 has been limited to tensile and flexural strength ignoring more com-
787 plex loading scenarios as well as strain rate effects. These mechanics
788 experiments should be combined with electrochemical testing under
789 different current densities in order to quantify the structural battery
790 performance under different applied load modes (bending, shear, com-
791 pression, uniaxial tension, biaxial tension, torsion). While there are
792 reports on testing the multifunctional structures containing standard
793 batteries under several loading modes [92, 98, 99, 101], the reports
794 describing electrochemical performance of structural batteries under
795 applied load are scarce. The most notable study [85] describes perfor-
796 mance of full structural battery based on CF for current collectors and
797 simultaneous strength enhancement. It was shown that both capac-
798 ity and rate capability of the cell diminished significantly with applied
799 tensile load.

800 • Lack of research on the system level requirements for structural bat-
801 teries (i.e. interconnects, bussing, cooling systems, etc.). This gap is
802 rather understandable considering structural battery research is still in
803 its early stages and is mostly focused on material or cell level studies
804 with few examples of working device prototypes [85]. However as this
805 research area matures, consideration should be given to the passive ele-
806 ments of the structural battery pack, since their design influences both

gravimetric and volumetric energy and power densities.

Despite the above challenges, the field of multifunctional energy storage is growing and promises significant savings in weight as well as improvements in safety of the energy storage systems. Such savings can be especially beneficial for electrified aircraft where the increase in flight endurance is desired. While majority of the research effort involves batteries with either gel or liquid electrolyte, we believe that development of all solid state batteries for structural applications will be a new promising direction. This technology eliminates safety risks associated with flammable solvents involved in a typical binary electrolyte and relies on glassy or ceramic materials for ionic transport between the electrodes. Development of a robust cathode with glass or ceramic electrolyte appears challenging, with some novel processing such as freeze templating being researched [148]. It is not surprising therefore that available examples of structural components with solid state batteries involve cells in a thin-film form [32]. However, inherent high elastic modulus and high strength in compression of glass and ceramic electrolytes indicate that solid state cells can be potentially integrated in load supporting structures while minimizing safety risks of traditional batteries.

5. Conclusions

The concept of multifunctionality, when applied to batteries, shows substantial promise in boosting effective energy and power density, especially when applied to battery powered aircrafts and drones, where the flight endurance is influenced more strongly by the mass savings then by the nominal energy density of a battery pack. The major bottleneck to wide acceptance

of structural batteries seems to be the increased cost of manufacturing custom cells and development of novel sensing and cooling solutions integrated with the BMS. The closest to realization approach is laminating unmodified commercial cells in the structural modules and packs. This way the cell production protocol does not have to be disrupted. Careful design strategy however needs to be undertaken to consider the balance between reduction in specific mechanical properties (stiffness and strength) and achieved savings in volume when cells are integrated into panels. With advancements of structural battery concept, safety aspect of battery performance becomes critical since no additional protective or reinforcing mechanisms or enclosures are implemented when a battery pack is integrated into structural members. While this field of research is relatively young, numerous approaches demonstrated high degree of multifunctionality where mechanical response is combined with enhanced safety; some of these approaches do not require significant retooling of battery production.

6. Acknowledgment

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