



Multifunctional Structural Composite Batteries for U.S. Army Applications

**by J. F. Snyder, R. H. Carter, K. Xu, E. I. Wong, P. A. Nguyen,
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ARL-RP-193

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*A reprint from the Proceedings of the 2006 Army Science Conference,
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MULTIFUNCTIONAL STRUCTURAL COMPOSITE BATTERIES FOR U.S. ARMY APPLICATIONS

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ABSTRACT

We are developing structural polymeric composites with battery functionality. These devices both carry structural loads and store electrochemical energy. If designed with sufficient structural and energy efficiency, these materials could enable significant system-level weight reductions by replacing inert structural components while providing supplementary power for light load applications. To enable this concept, we have designed load-bearing properties directly into the battery electrodes and electrolyte such that each component is itself multifunctional. Carbon fiber fabric anodes, cathode-coated metal meshes, and solvent-free structural polymer electrolytes are each being developed to exhibit a desirable combination of mechanical strength and electrochemical performance. These components are being integrated using moldable, scalable, cost-effective composite processing techniques.

1. INTRODUCTION

The weight and volume of conventional energy storage technologies greatly limits the performance of a range of U.S. Army platforms, including soldier systems, ground vehicles, and unmanned aerial vehicles (UAVs). Significant research efforts are currently underway to reduce battery weight and volume through improvements in battery efficiency. A different approach is to design batteries that are also load-bearing (South et al., 2004). These multifunctional structural batteries could be used to replace conventional structural components, such as vehicle frame elements or a UAV wing structure, with components capable of storing energy. If designed with sufficient structural and energy efficiency, these structural batteries could enable significant system-level weight reductions (Thomas and Qidwai, 2004).

Previous examples of structural batteries have primarily utilized structural packaging. (Qidwai et al., 2005). The current study instead explores a multifunctional composite battery concept that utilizes a fiber-matrix composite platform in which each structural component is designed to function as an electrochemical

battery component. The basic design (Fig 1) consists of a carbon fiber fabric acting as an anode, a fiberglass separator layer, a metal mesh coated with a cathode material, and a structural solid polymer electrolyte binding the components together. The cathode coated mesh and carbon fiber electrodes both carry load and can act as electrically conductive current collectors. The fiberglass separator layer provides additional structural support while ensuring electrical isolation of the electrode layers. The polymer electrolyte transfers load to the other components and simultaneously conducts ions between electrodes. Each component is fulfilling multiple roles in the composite device, allowing for a synergistic weight or volume reduction to be accomplished compared to the individual state-of-the-art (SOA) battery and structure. The challenge of this design, however, is to create components that fulfill their multiple roles simultaneously and cooperatively.

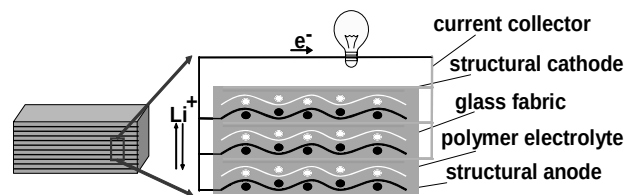


Figure 1. Concept for a structural battery.

This paper will discuss the development and optimization of the each of the components of the multifunctional lithium-ion battery: the anode, cathode, and electrolyte materials. Each component is designed to provide multifunctionality of both structural and electrochemical properties. A lithium-based chemistry has been chosen due to its high energy density and compatibility with polymer-based electrolytes (Xu, 2004). The fabrication approach used to combine these components into an integrated structural battery composite is then described. Special emphasis is placed on selecting scalable composites manufacturing routes. Preliminary data pertaining to the properties of the whole composite battery are also discussed.

2. ELECTRODE DESIGN AND CHARACTERIZATION

2.1 Anode

The current device design employs conventional carbon fiber fabrics as an anode material (Takami et al., 2001). For this application, a carbon fiber-based anode material was chosen due to its inherent multifunctionality. Carbon fibers have a high stiffness and strength which provides mechanical reinforcement for the composite battery, and favorable electrical conductivity that allows for transport of electrons into and out of the cell. In addition, for lithium-ion battery chemistry, carbon fibers can serve as the media for the intercalation of lithium ions.

Several forms of structural carbon have been considered for anode research, including woven carbon fabrics, nonwoven carbon fabrics, and carbon nanofoam papers. The woven fabrics under investigation were all received from Textile Products Inc. and are styles 4375, a 12K IM7 unidirectional fabric; 4163, a 3K T-300 bidirectional plain weave fabric; 4607, a 3K AS4 bidirectional plain weave fabric with interwoven aluminum wire; and 4607-PB, a 3K AS4 bidirectional plain weave fabric with interwoven bronze wire. The nonwoven mats were received from Hollingsworth and Vose in grades 8000015, 8000020, 8000028, 8000030, 8000033, 8000036, 8000037, 8000039, and 8000047, which pertain to thicknesses ranging from 0.05mm to 0.84mm. The carbon papers were received from Marktech as Grade I and Grade II. Elemental graphite has been used as a benchmark anode since it is considered to be the most efficient form of carbon for lithium ion intercalation in an electrochemical cell, and is commonly used in commercial lithium cells. Accordingly, structural forms of carbon with a primarily graphitic composition, such as PAN-based fibers, are most likely to provide efficient anodic properties.

Each of the anode materials were characterized as half cells paired with pure lithium metal foil, immersed in a liquid electrolyte composed of 1.0 M LiPF_6 in EC/DMC at 30:70 by weight. A polypropylene separator was positioned between the electrodes, and the full stack with electrolyte was then placed into a 15 mm coin cell package.

Anodes composed of nonwoven mats and carbon papers were made by directly stamping out 10 mm disks. The unidirectional and bidirectional carbon weaves did not retain their original form when cut into small samples, but cycle tests were still performed on samples with roughly the same form. Elemental graphite anodes were made by combining graphite with a poly(ethylene oxide)

(PEO) binder, solvent cast from acetonitrile onto a nonporous stainless steel 15 mm disk. A loading of approximately 20 wt% PEO binder was found to provide an optimum of mechanical binding and electrochemical activity.

A protocol for half-cell battery cycling was run on a Maccor Series 4000 Automated Test System at a constant current. The first two cycles were run at 1.2×10^{-4} A during formation of the solid electrolyte interface (SEI) layer (Fong et al., 1990), then the current was increased to 4.0×10^{-4} A for the remainder of the test. Tests were run for approximately two weeks, yielding about 50-100 cycles depending on the quantity of material in the film. Each sample was run in duplicate and the results averaged.

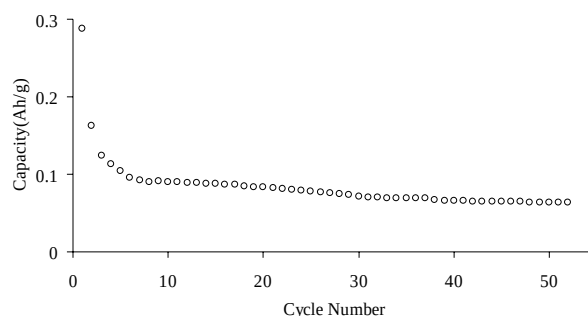


Figure 2. Specific capacity fade for a nonwoven carbon fiber mat in a half cell vs. lithium metal foil.

Figure 2 illustrates the loss in capacity with cycling for a nonwoven mat 0.25mm thick. Specific capacity decreased significantly over the first few cycles and then leveled to less than 1% loss between cycles. Figure 3 is a plot of average specific capacity at the third cycle versus type of anode material and includes error bars where applicable. The measured graphite capacity is lower than the ideal value most likely due to the use of a binder for the former, which may reduce the available anodic active area. The non-woven carbon mats and carbon papers demonstrated good capacity. For the carbon papers, little variation in average capacity was found for both grades; therefore the data point in Figure 3 is an average of grades. For the non-woven carbon mats, the data point in Figure 3 is an average over the seven grades pertaining to mat thicknesses greater than 0.25 mm. Note that, for non-woven mats with a thickness less than 0.2 mm, the specific capacity was found to drop by about 75% by the third cycle, which could be due to partial electrical isolation of fibers in the low thread count mats. The IM7 unidirectional woven carbon fabric showed virtually no capacity. This low performance could be due to the sizing on the fibers put on by the manufacturers for improved strength and handling. Preliminary studies on the bidirectional plain weave fabrics show very good capacity. However, the bidirectional woven fabrics with interwoven metals have

a decent capacity with high error. More studies on bidirectional woven fabrics with and without metals interwoven need to be conducted to verify these preliminary results. Additional testing is underway to understand the impact of fiber density, fiber length, and sizing on capacity. Based on this existing data, carbon papers, nonwoven mats and possibly bidirectional woven fabrics are the strongest candidates for multifunctional anodes.

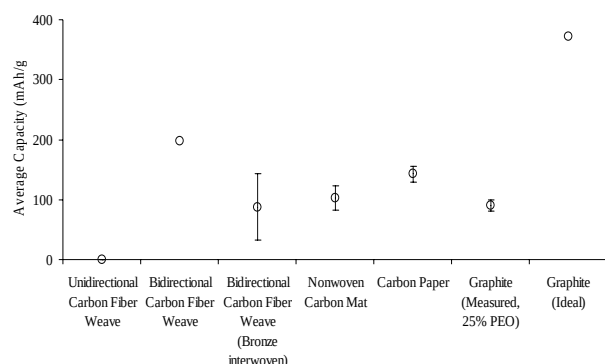


Figure 3. Average specific capacity at third cycle for carbon anode half cells vs. lithium foil.

2.2 Cathode

The multifunctional cathodes must be electrically conductive and structurally robust. Carbon fabric cannot be used as part of the cathode since it can act as an anode and short the battery. Instead, a metal substrate is employed as the primary electrical bus (current collector), which is coated with a thin film of active cathode material and electrically conductive carbon powder. The precise composition and processing route are optimized for high electrochemical capacity, electrical conductivity, rechargeability, and mechanical integrity.

LiCoO_2 and LiFePO_4 are the cathode materials under evaluation. The former is currently used in a large number of off-the-shelf battery systems with benefits of high specific capacity, a multitude of literature describing its properties, and established methods for circumventing or otherwise handling its known limitations. LiFePO_4 , a recent material with less established knowledge, has a potentially greater use for a composite battery with a higher theoretical capacity than LiCoO_2 , greater allowance for deep discharge, and greater tolerance for stainless steel substrates.

Acetylene black, a form of carbon powder with high conductivity, is used to optimize electronic conductivity of the cathode film. This carbon powder is milled together with the cathode material for several days to minimize particle size and to ensure adequate integration of the two materials. The carbon powder is necessary for facilitating electron transport between the cathode

particles and the metal current collector. Use of less than 8% carbon powder in the films yielded too high of an electrical resistance to be useful, and the corresponding measured specific capacities were orders of magnitude lower than the theoretical values. By increasing the volume fraction of carbon powder, it increases the electrical connectivity of the film but in turn reduces the overall capacity by reducing the volume fraction of active cathode material. An optimal acetylene black addition of 10% w/w relative to the weight of cathode material was found to generate the best overall cathodic activity.

A high molecular weight (2×10^5 Da) PEO binder was used to attach the cathode material and carbon powder mixture to the metal current collector substrate. A 20 wt% binder addition (relative to overall cathodic film weight) was found to provide the best mechanical integrity and cathodic activity. Note that traditional lithium-ion batteries utilize a polymer binder with the electrode materials, a polypropylene separator between the electrodes, and a liquid electrolyte saturating the assembly. The polymer binder does not directly transport ions, but absorbs the liquid electrolyte which in turn transports ions between cathodic particles. On the contrary, our PEO binder acts as a solid state ion conductor which does not require the presence of liquid to function, as is required by our solid-state goal and is compatible with our PEO-based resin electrolytes.

The metal substrate provides structural support as well as being a current collector that efficiently transports electrons between the circuit and the cathode film. With the lithium cobalt oxide, aluminum was used due to its high specific strength and stiffness, high electrical conductivity, and favorable inertness to the lithium cobalt oxide under the conditions studied. For lithium iron phosphate, either aluminum or stainless steel can be used in testing since they are both chemically inert to this material, have high strength and stiffness, and have high electrical conductivity. Both woven wire mesh and expanded foil substrates are being tested. These forms of the metal are structurally robust and porous, allowing the polymer matrix to wet out the cathode and mechanically bridge the various material layers together. Analogously, a control set of samples used cathodic thin films deposited on the inside bottom of the aluminum coin cell apparatus (lithium cobalt oxide) or on a nonporous stainless steel disk (lithium iron phosphate). Note that many conventional batteries use nonporous metal substrates for cathodes (e.g. foils) to maximize surface area, which would likely present sources of delamination if used in a structural battery design.

To fabricate the cathode films for initial cycle and capacity tests, the desired quantities of acetylene black

and the active cathode material were either hand mixed or ball-milled to reach homogenization. This mixture was mixed with PEO in acetonitrile, and then dip coated or brushed onto the metal substrate. After the film was allowed to air dry, it was heated under vacuum to ensure complete removal of the solvent. These cathodes were characterized as half cells paired with lithium metal foil using a coin cell configuration similar to the one described in Section 2.1.1.

The cathode half cells were run at a constant current of 9×10^{-5} A for the first two cycles while the SEI layer formed, and at 3×10^{-4} A for the remainder of the test. A capacity fade between the first and third cycles was found to be much less than that of the anodes, and it was about 20% for most configurations. After the third cycle the specific capacity was usually found to plateau until the test was terminated. Tests were run for about two weeks, yielding 20-100 cycles depending on the quantity of material in the film.

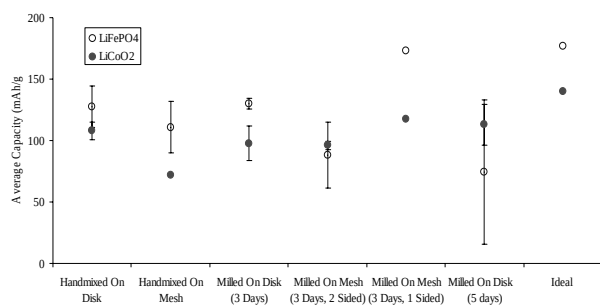


Figure 4. Average capacity at third cycle for LiFePO₄ and LiCoO₂ half cells vs. lithium foil. The cathode films employ 10 wt% acetylene black and 20 wt% PEO binder.

Figure 4 indicates the average specific capacity measured for several cathodic configurations at the third cycle. The film composition for each sample included 10 wt% acetylene black and 20 wt% PEO binder. The results from one to three cells are averaged to yield each data point. The ideal reversible capacity value is also plotted for each of LiCoO₂ and LiFePO₄. For the nonporous current collectors, handmixed and milled cathodic materials produced comparable results. This indicates that our current milling procedure is not providing enhanced mixing of the constituents. A study of the duration of mill was done by comparing 3 day milling to a 5 day milling of the materials. As shown in Figure 4, there is high error in the 5 day milling samples, but even with the error, it is still comparable to the 3 day milling data. This indicates that there is no added advantage to milling the materials for a longer period of time. Alternative mixing techniques are under consideration for improving this process such as attritor milling and high energy milling.

The metal mesh current collectors show performance similar to the nonporous substrates. However, it is interesting that the one-sided coating (brushed coating) exhibits higher specific performance than the two-sided coating (dip coating). This possibly signifies prohibitively slower rates of ion transport to the back side of the mesh or increased electrical resistivity between the mesh and current collector. These obstacles are not expected to have much impact on the final layered composites in which both sides of each cathode will be directly facing an anode and the meshes can be directly wired into the circuit.

3. ELECTROLYTE SYNTHESIS AND CHARACTERIZATION

The electrolytes are designed to carry and transfer loads while maintaining satisfactory ion transport capabilities. These objectives are being engaged through progressive development of load bearing ion conductive resins and nanocomposites of those resins. Battery power and structural modulus are improved by using a processable electrolyte resin that performs well as a thin film. For a battery, minimizing the electrolyte thickness increases the current by increasing the rate of ion conduction between the electrodes. Additionally, the ability to process a composite with only a small quantity of polymer electrolyte binder allows for a greater volume fraction of structural electrode materials, permitting the development of higher capacity, higher strength structural composite batteries.

In this study, electrolyte development is centered on polymerized vinyl ester derivatives of poly(ethylene glycol) (PEG). Polyacrylates have been previously examined for electrolyte use owing to their dimensional stability, however they are typically plasticized (Kono et al., 2000). Here, a broad selection of monomers has been complexed with lithium triflate and thermally cured as solvent-free polymers. The PEG etheric oxygen groups are capable of dissociating and transporting the donor salt ions in absence of solvent (Berthier et al., 1983), while structural properties are provided by cross-linked vinyl ester networks. Varying the proportions, architecture, and functionalities of the vinyl ester and PEG constituents has permitted for a wide range of tailorable structural and electrolytic properties. The resins provide an added benefit of favorable processing through VARTM (vacuum assisted resin transfer molding) distribution of the monomer through the stacked electrode and separator layers preceding a thermal cure.

To characterize the electrolyte resins, 1-cm-diameter discs, ~ 0.5 mm thick, were cast, carefully dried, and coated on their faces using silver paint. Impedance measurements were completed using a Solartron 1260

Impedance / Gain-Phase Analyzer and Solartron 1287 Electrochemical Interface across a frequency range of 106 Hz to 10 Hz at room temperature (18 - 20 °C).

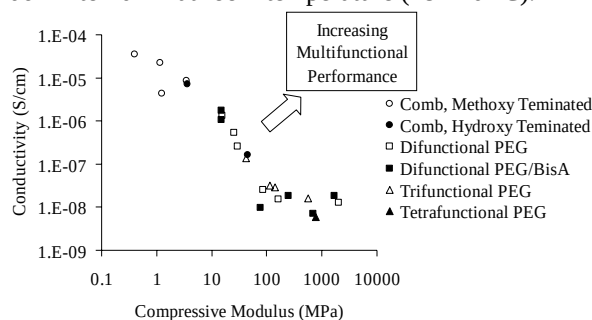


Figure 5. Room temperature ion conductivity vs. stiffness for vinyl ester homopolymer electrolytes of assorted architectures and functional groups.

Mechanical characterization was completed by compressing cast disks of similar geometry in an MTS load frame employing a 5 kN load cell and a cross-head speed of 1 mm/min. The reported compression stiffness values are calculated from the initial, relatively elastic portion of material loading curves.

Figure 5 shows the impact of a series of variables on multifunctional behavior for homopolymer resin electrolytes. A log-log plot is employed since the axes in Figure 5 cover several orders of magnitude. The homopolymers included a systematic investigation of different PEG lengths, degree of crosslinking, acrylated versus methacrylated reactive groups, endgroups terminating the sidechains, and additional chemical functionalities introduced into the monomers such as bisphenol-A. The results show that as the nature of the monomer is modified there is a consistent tradeoff between structural and transport properties, with no strongly multifunctional outliers demonstrating uncommonly high conductivity and stiffness. The number of vinyl ester (VE) groups on each monomer largely determines the position of the material along the performance curve. One VE group per monomer results in linear “comb” polymers with mobile PEG sidechains that assist ion transport and result in high conductivities but low stiffnesses. Multiple VE groups result in networking via PEG crosslinks and result in orders of magnitude improvement in mechanical behavior, but similar decline in conductivity when the PEG chains become immobilized.

In the second phase of this study, comb monomers with one VE group were blended with networking monomers with multiple VE groups and the solution was prepared, cured, and tested. The resulting copolymers contained controlled proportions of extremely mobile ion-conductive PEG sidechains and immobilized structural PEG crosslinks. Figure 6 illustrates one set of

results from this copolymer investigation. The comb monomer used for the materials described by Figure 6 is PEG 550 methyl ether acrylate, which was combined

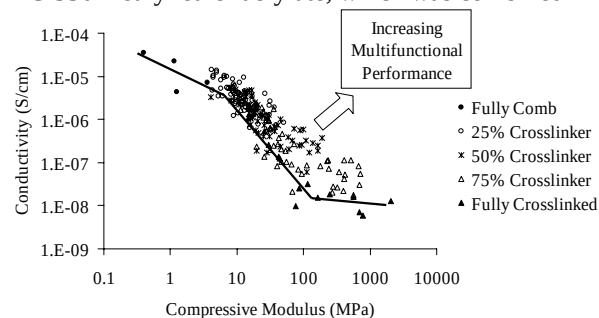


Figure 6. Room temperature ion conductivity vs. stiffness for vinyl ester copolymer electrolytes.

with fifteen of the networking monomers in volume fractions of 0% to 100% of the comb monomer. The solid line in Figure 6 represents the homopolymer trend described in Figure 5. Most of the copolymers outperformed the homopolymer trend, providing higher conductivity at a known mechanical stiffness. While monomer reformulation was not shown to be effective at improving multifunctionality, we have discovered that copolymers of these same monomers do yield simultaneous improvements in ion conductivity and compressive modulus. While the improvements are noteworthy, more substantial increases in performance are required for use in competitive multifunctional structural battery devices.

In a push to further increase multifunctional performance in structural electrolytes, nanocomposite copolymer electrolytes have been developed using the previously described resin electrolyte systems. Addition of nanofillers has been previously shown to improve the mechanical and even electrochemical properties of solvent-free polymer electrolytes (Scrosati et al., 2001). After preparing the monomer or comonomer solution with lithium salt, nanofiller additives were dispersed into the mixture and the samples were cured and tested. The fillers that have been looked at include colloidal silica and fumed silica and were varied in concentration, size, shape, and surface treatment. The polymers were made from comonomer solutions of PEG 550 methyl ether acrylate and PEG (660)₂ bisphenol-A diacrylate, which form combs and networks, respectively. These monomers were selected since they have very similar volume fractions of PEG and VE groups and the PEG oligomers are of comparable size. Since the chemical composition is similar, copolymers ranging from 0% comb to 100% comb will track changes in the matrix resulting from formation of crosslinks without complication from other variables.

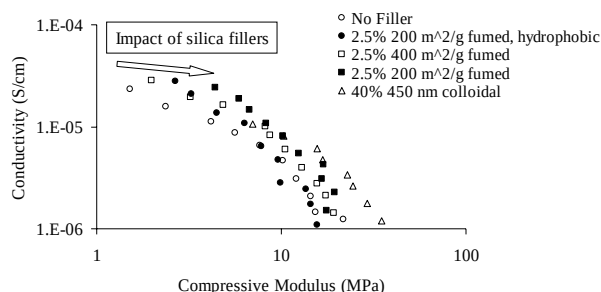


Figure 7. Room temperature ion conductivity vs. stiffness for vinyl ester copolymer electrolytes with indicated fillers.

Figure 7 compares many highlights from these nanocomposite studies. It was found that fillers can simultaneously improve conductivity and modulus but that this improvement depends strongly on the nature of the polymer matrix as well as the nature of the filler. 400 nm colloidal silica additives were examined in concentrations that range from 5 wt% to over 50 wt%. The relatively large colloidal particles do result in some multifunctional increases, chiefly by increasing modulus at a higher rate than reducing conductivity. It seems that addition of these particles results in rule of mixtures effect rather than the synergistic effects that are more useful in multifunctional materials. As Figure 7 shows, the impact on both properties at 40 wt% filler is substantial. Fumed silica has a much higher surface area with which to interact with the polymer. At 2.5 wt% filler, fumed silica had little impact on conductivity for any copolymer but resulted in markedly improved modulus of highly compliant polymer electrolytes. The improvement in modulus declined with increased crosslinking signifying that there is greater benefit to form fumed particle nanocomposites with highly conductive compliant polymers. The diminishing effect as the copolymer is crosslinked may point to that the silica is providing networking capability that is less noticeable as the polymer itself becomes networked. Hydrophobic surface treatment of the fumed particles would be expected to inhibit polymer-particle interaction, and the treated particles underperform their untreated counterparts. Additional studies are being performed using copolymers with a higher modulus structural component. On the whole, it was found that it is possible to engineer polymer electrolytes with both ion conductivity and structural capacity through targeted formulation of the polymer in conjunction with addition of nanoparticle fillers.

4. BATTERY COMPOSITE FABRICATION AND CHARACTERIZATION

4.1 Processing

Vacuum assisted resin transfer molding (VARTM) was used as a processing route for our composite structural batteries. Using a VARTM approach minimizes void content, enables higher fiber volume fractions than simple hand-layup techniques, and is a highly scalable manufacturing route. The liquid resin monomer electrolytes as described in section 3.3 have been engineered to have sufficiently low viscosity such that they are amenable to VARTM processing. Our anode, cathode, and separator materials are also permeable and wettable, and are therefore compatible with traditional composite processes.

Figure 8 illustrates the fabrication of a typical composite battery. Between the carbon fabric-based anodes and the thin film-coated, metal mesh cathode are 0.18-mm-thick glass veil separators (Grade 8000100, Hollingsworth and Vose). Using this separator allows compaction of the preform and high fiber volume fraction, while ensuring complete electrical insulation between the anode and cathode. A release ply and distribution media layer are then placed on top of the composite stack, and the preform is vacuum-bagged and ported for resin inflow and outflow. The resin is pulled from a reservoir through the inflow port, wetting out the composite part, through suction provided at the outlet port. The part is then cured at 80°C in an oven overnight.

The preform example in Figure 8 is a symmetric, double-cell design. Note that, this same approach can be easily scaled to many more cells and increasing cell areas, simply by changing the size and number of material layers. Integrated electrical bussing (not shown in this example) can also provide a means of creating series or parallel cell voltage arrangements, allowing for tailoring of the voltage and current capabilities of the cell. In addition, this VARTM technique is adaptable to complex part shapes and geometries through the use of contoured release plates, custom-geometry preforms, and carefully designed multi-port resin injection and venting schemes.

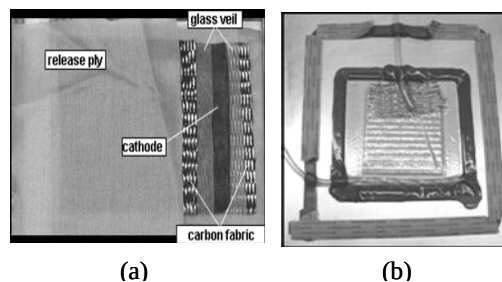
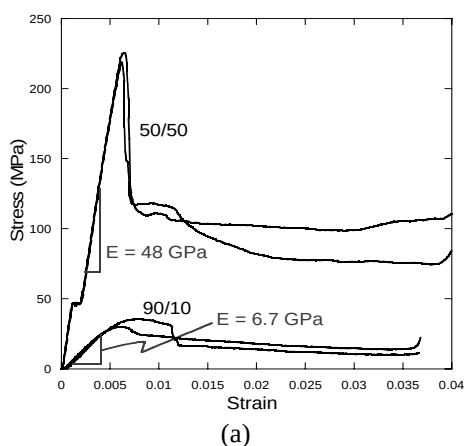


Figure 8. (a) Structural battery layers and (b) undergoing VARTM processing.

4.2 Mechanical Properties

The basic mechanical properties of the battery composites were characterized by performing a basic three point bend test. A span of 5.08 cm and a loading rate of 5 mm/min were used for the mechanical characterization. Figure 9 illustrates the results for two composite battery materials. Both composites use identical processing and reinforcement, as described in Section 4.1, but employ different polymer electrolytes. The "50/50" curve was generated for a composite whose polymer electrolyte is composed of 50 vol% PEG methyl ether acrylate and 50% PEG(660)₂ bisphenol-A dimethacrylate, while the "90/10" curve was measured for a composite with a polymer electrolyte composed of these two species at 90% and 10%, relatively. Both composites showed reasonable stiffnesses, between 5-50 GPa. The more compliant 90/10 composite demonstrates a lower stiffness, and a more graceful failure. Figure 9b illustrates that under this bending loading condition, failure was dominated by interply failure and fiber buckling. Both failure modes are expected for composites with compliant matrices. The interply failure mode also indicates the importance of matrix-reinforcement adhesion. Systematic characterization and enhancement of the interfacial adhesion for cathode-electrolyte and anode-electrolyte pairs is in progress.



(b)

Figure 9. (a) Three-point bend results for two different battery composites. (b) Modes of failure for 50/50 battery composites.

4.3 Electrochemical Performance

Composite batteries such as the ones shown in Figure 8 have shown basic electrochemical charging and discharging cycles. Full quantitative electrochemical performance characterization is in progress, and will be reported in a future publication.

5. CONCLUSIONS

In summary, we have successfully fabricated and tested multifunctional composite batteries employing structural polymer electrolytes binding together layers of electrochemically active material. Each of the components in the composite device is itself a multifunctional material. This design concept potentially allows for greater overall mass and/or volume efficiency in any Army platform that utilizes both structural components and energy storage devices.

Towards development and optimization of these high performance structural batteries, our research program is investigating structural resin electrolytes, structural carbon anodes, structural cathode-layered metal meshes; and integration of these components using scalable composite processing methods. The resin electrolytes allow for a wide range of tailorable properties that may be further optimized through the use of inorganic nanofillers. Novel fillers and the impact of liquid plasticizers are currently being explored and will be reported in a future publication. The carbon anodes demonstrate electrochemical capacities competitive to that of the polymer-bound graphite. The nonwoven carbon fiber mats are particularly attractive for their compatibility with VARTM processing and the wide range of readily available mat thicknesses allowing for facile changes in specific loading. New materials are being explored as well as full battery tests using the materials described here. The cathodes demonstrate excellent electrochemical capacities and new substrates and film compositions are under investigation. The anodes and cathodes described here are particularly attractive for stacked systems owing to the symmetrical electrochemical activity on both faces. Overall, our results indicate that multifunctional structural materials can be realized through the focused development of new materials, material architectures, and low cost scalable fabrication routes. Further quantification of mechanical and electrochemical behavior of the battery composite is required to fully demonstrate the potential of this technology.

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