

Multifunctional Structural Power and Energy Composites for U.S. Army Applications

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ABSTRACT

The performance of many U.S. Army systems depends on the efficient use of material mass and volume. In particular, many components on these systems are often dedicated to power generation and energy storage. Examples include next-generation ground vehicles, which utilize hybrid powertrains requiring large banks of batteries; unmanned aerial vehicles, whose range and speed are currently limited by battery life; and individual soldiers, whose sensing and communication equipment requires both continuous and burst power. Many of these systems also include a significant amount of structural and/or armor materials. Therefore, important system-level reductions in mass and volume are possible by creating multifunctional materials that simultaneously offer both power generation or energy storage capabilities with structural or armor properties.

Three candidate multifunctional materials are under investigation. First, structural fuel cells have been fabricated by creating skin-core composite structures. In these fuel cells, the skins are composed of thin, glass fiber or carbon fiber-reinforced composite laminates. The core consists of layers of open-cell metal foam with a Nafion[®]-based membrane electrode assembly interlayer. This core generates power when hydrogen and oxygen sources are circulated through the porous foam layers. Simultaneously, the high shear and compressive stiffness of the core transfers loads efficiently to the skins, resulting in a structure with high specific stiffness and strength. Secondly, structural lithium-ion batteries are being designed by formulating ion-conductive polymer electrolytes with continuous fiber reinforcement. The electrolytes are designed to balance structural and ion-conduction properties, through the use of functionalized structural polymers, block copolymers, or microscale mixtures of conductive and structural materials. Finally, electroded surfaces have been integrated into continuous fiber-reinforced polymeric composites, to create structural capacitors.

1.0 INTRODUCTION

Energy and power management is a critical aspect of military vehicle design. Fundamentally, the duration and intensity of a mission are limited by the energy and power density, respectively, available to the vehicle. Therefore, engineers are challenged to increase energy storage and power generation output, while simultaneously minimizing overall system mass. For example, next generation military ground vehicles are expected to utilize hybrid hydrocarbon-electric drivetrains and lightweight metal alloys and polymer

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composite materials. Both of these technological advances will enable higher fuel efficiency, increasing range and decreasing logistical support requirements, as well as higher vehicle speeds, for faster tactical positioning and improved survivability through evasion and avoidance.

The conventional approach for improving power and energy density of these military systems is to optimize the performance of individual subcomponents. One set of engineers works to improve the powerplant to require less fuel or produce a higher power density. In parallel, and independently, materials and structural engineers labor to utilize novel lightweight materials in frame and armor components that provide high mechanical efficiency at low weight. The overall system is created by fastening the powertrain to the vehicle structure.

A different approach for creating complex systems with high power and energy density is to utilize multifunctional design [1-4]. This concept requires power and energy components to also act as structural elements. By having components acting both to carry loads and participate in power generation or energy storage, overall system weight and efficiency can be improved.

In this paper, we explore three concepts for multifunctional, structural power and energy elements: structural fuel cells, structural batteries, and structural capacitors. Each of these designs utilize fiber-reinforced polymer matrix composite materials, for a number of reasons. First, composites are inherently multi-material systems. Similarly, our power and energy components require combinations of dielectrics, electrical conductors, and catalytic or reactive surfaces, making composite architectures well-suited to these complex systems. Secondly, composites processing provides a great degree of fabrication flexibility. Composites processing requires relatively low temperatures, preventing damage to embedded components, can accommodate complex geometries and subcomponents, and is scalable to manufacturing settings. In particular, the laminated structure of many composites is very similar to laminated configurations in conventional batteries and capacitors. Finally, the high specific strength and stiffness of composite materials is critical for achieving mass efficiency. The tailorability of these mechanical properties, through selection of fibers, matrix, and architecture, is also advantageous.

In order to improve mass efficiency through multifunctional design, it is essential that material elements (i.e. atoms, molecules) simultaneously participate in both load-bearing and power/energy functions. In contrast, systems that simply combine structural materials with power/energy materials such that each set of materials are acting independently will provide no advantages in system efficiency. For example, bonding conventional battery components to a traditional structural composite, so that the battery components are bearing no load, will not result in significant benefits. Instead, the objective is to create battery composites that are inherently structural, so that the electrodes and electrolyte of the battery are primarily load-carrying elements.

The following sections summarize the activities of the U.S. Army Research Laboratory in creating these structural power and energy components.

2.0 STRUCTURAL FUEL CELLS

2.1 Design and Fabrication

Fuels cells consist of hydrogen and oxygen sources, separated by a proton exchange membrane (PEM) with integrated electrodes, together called the membrane electrode assembly (MEA). An important challenge in designing a fuel cell is engineering a means for continuous circulation of hydrogen and oxygen sources past

the MEA, as well as removal of reaction products. Multifunctional structural fuel cells present an even greater challenge, requiring load-bearing capacity in a material that is permeable to reactant flow.

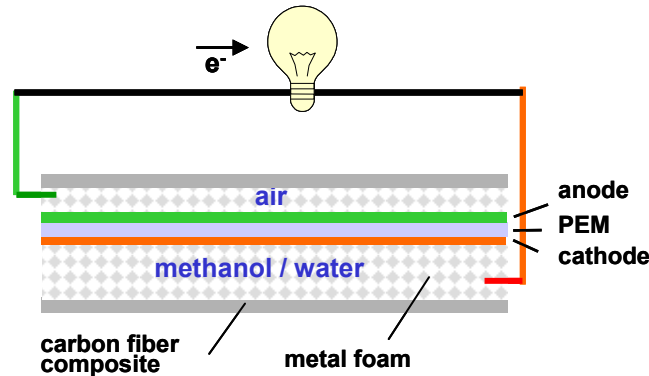


Figure 1: Structural fuel cell concept.

Figure 1 presents a schematic of our structural fuel cell concept. The MEA is sandwiched between layers of open cell metal foam. The metal foam provides a pathway for flow of hydrogen and oxygen sources, but is also structural with high specific stiffness. Since the metal foam is electrically conductive, it can also simplify connectorization by acting as an electron bus between the MEA electrodes and external power wiring. The MEA-foam core is contained between thin skins of carbon fiber composite. The overall skin-core sandwich structure is a common design approach for creating light structures with high bending stiffness. An excellent example application of such a structural fuel cell would be the wing of an unmanned aerial vehicle (UAV), where a stiff, lightweight structure that can also generate power could prove advantageous.

The structural fuel cells demonstrated in this report utilize unidirectional epoxy-carbon fiber prepreg (Bryte Tech AS4) materials, aluminum foams of 6-20% relative density and 10-40 ppi (ERG Aerospace), Nafion-based MEAs with Pt/Ru catalyst, and epoxy film adhesive. The various layers are cut and stacked as shown in Fig. 2, and then processed under vacuum at 120°C for 1 hour. Other structural fuel cells (not presented here) have been fabricated with glass-fiber composite skins.

2.2 Testing and Performance

To demonstrate the mechanical performance of the multifunctional fuel cell concept, specimens were sectioned into 1.78-cm-wide samples and subject to 3-point bending based on ASTM C393. Figure 3 shows a typical loading history. The initial, linear loading portion of the curve is followed by a loss in stiffness and a gradual damage zone under load, eventually leading to sudden failure and a sharp load drop. During the elastic portion of the loading curve, bending stiffnesses (as defined by Fig. 3) of 1-10 GPa have been observed. Damage typically originates as a shear failure at the MEA-foam interface, followed by compressive or shear failure in the foam core, buckling of the composite skins, and eventually composite delamination at the ends of the beam. Typical bending stresses at initial failure are 10-50 MPa.

These observed stiffnesses are comparable to typical sandwich-construction composites. Ultimate stresses are primarily limited by the relatively low shear strength of the foam-MEA-foam interface. The photograph in Fig. 3 shows this shear failure, as markings placed on the core during a no-load condition lose registry at high loads. Research is underway to improve the mechanical integrity of these interfaces, including engineering of non-planar interfaces, selectively bonded interfaces, and structurally reinforced MEAs.

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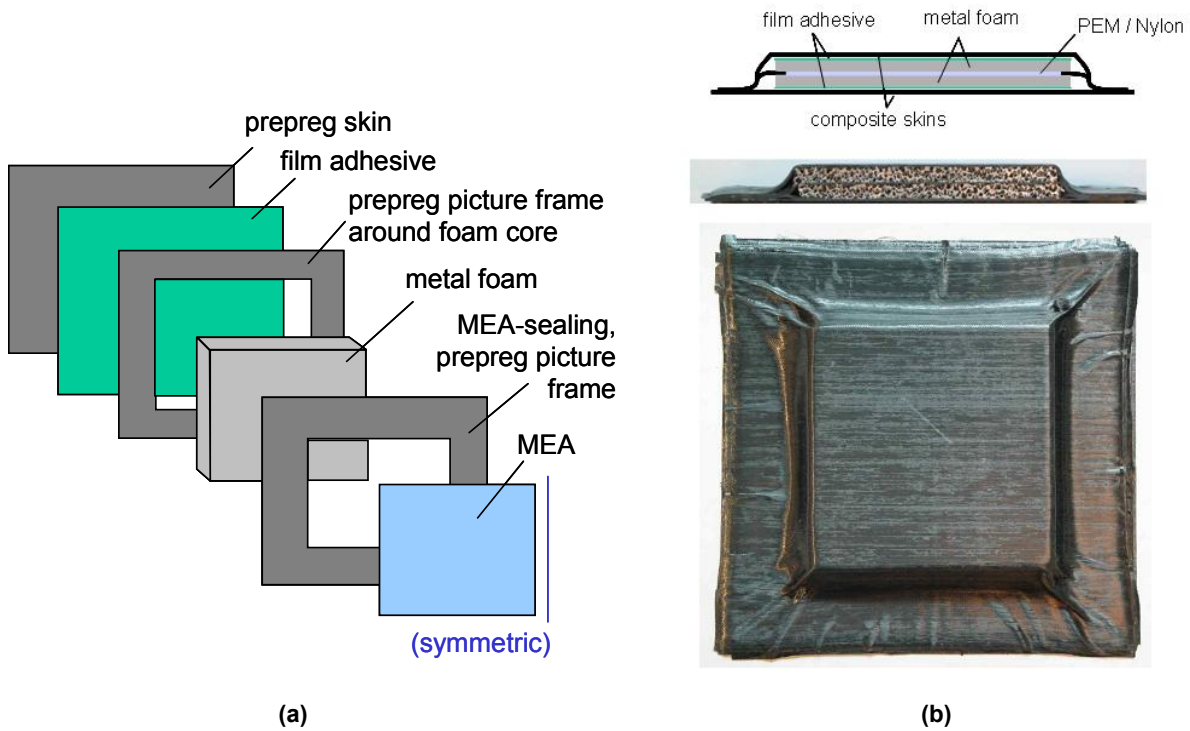


Figure 2: Structural fuel cell (a) fabrication layup and (b) after fabrication.

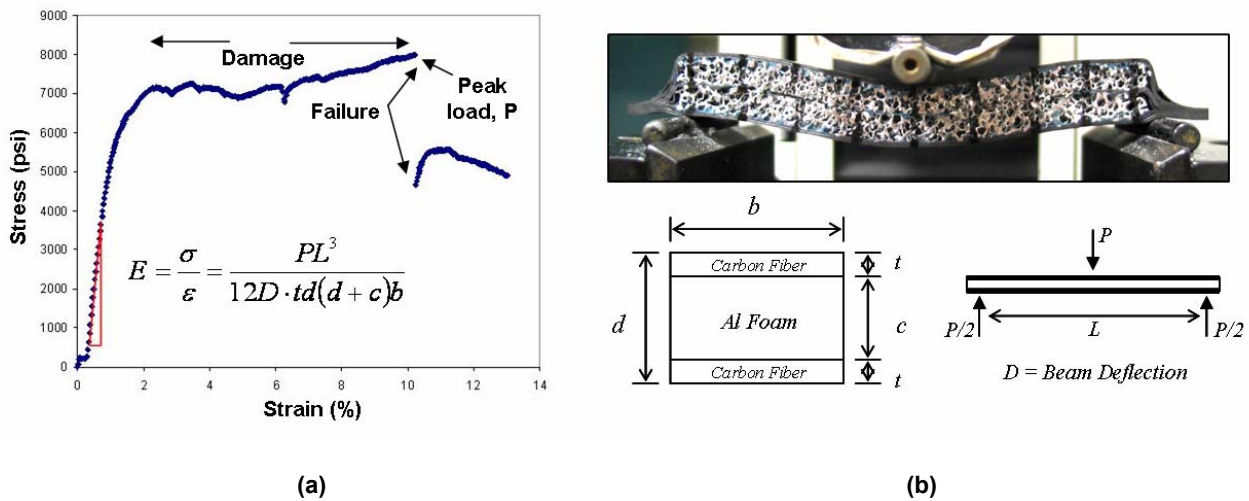


Figure 3: Mechanical performance of structural fuel cells. (a) Loading curve during three-point bend, and (b) test specimen during loading and geometric parameters.

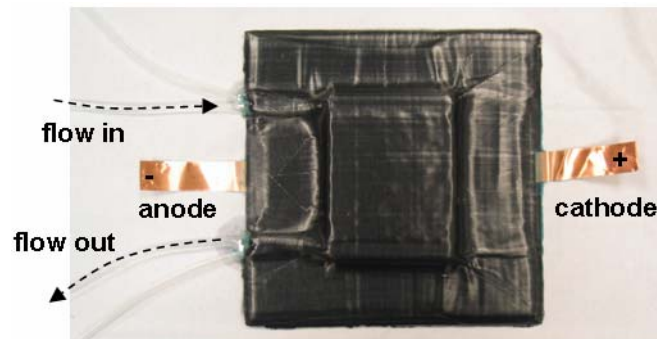


Figure 4: Structural fuel cell with integrated flow and electrical lines.

Figure 4 shows a typical connectorized structural fuel cell. Polymer tubing is integrated into the layup of prepreg and core materials prior to fabrication, and interfaced with an internal flow manifold to improve flow uniformity. Copper tape is soldered to the metal foam core and traced out of the composite. Processing to cure and consolidate the composite also serve to bond and seal the electrical and flow lines. Testing of this configuration using aqueous methanol solution flow past the anode and air flow past the cathode have demonstrated open cell voltages of ~ 0.5 V, a typical value for single cell fuel cells. Our current densities, however, are still relatively low due to the relatively low MEA surface area per unit volume. Continuing studies are underway to increase the amount of available exchange area. Other studies are underway to improve flow uniformity in the structure, and address sealing and scaling issues for the fluid flow lines.

3.0 STRUCTURAL BATTERIES

3.1 Design

Batteries store and release energy through electrochemical reactions at anode and cathode, made possible by the transport of ions through an electrolyte bridging the electrodes. High power density is achieved by using thin electrodes, and minimizing distances between electrodes. These power density considerations must be balanced with the need to maintain sufficient anode and cathode volume for overall energy density, and adequate electrode conductivity for effective current bussing. The electrolyte must allow for efficient ion transport, while providing electrical isolation between the electrodes.

Figure 5 shows a schematic of our structural battery concept. The thin, planar architecture of batteries provides an elegant analogue to laminated, fiber-reinforced composite materials. The structural battery concept uses structural anodes, cathodes, and separator layers to provide mechanical reinforcement to a polymeric, electrolyte matrix. Conductive materials like carbon fabrics, woven metal fabrics, or perforated metal foils are excellent structural electrode candidates. Conductive electrode coatings onto the current collecting substrates provides the anodic and cathodic surfaces for electrochemistry. The electrolyte permits ion transport, while providing load transfer between the reinforcing elements. We prefer to use a lithium-ion chemistry, for high energy density and cyclability [5].

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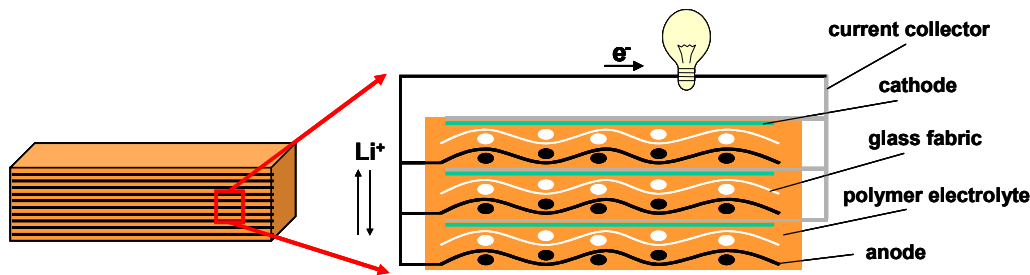


Figure 5: Schematic of structural battery concept.

3.2 Electrolyte Synthesis and Properties

A critical challenge to structural battery development is the synthesis of electrolytes that are both ion-conductive as well as mechanically robust. Typically, ion transport is enabled by engineering high molecular mobility into a polymer electrolyte. Structural polymers, in contrast, provide stiffness, strength, and environmental durability through high crosslink density and low chain mobility. To provide simultaneous stiffness and ion transport, we are exploring various hybridization schemes to combine highly conductive and highly structural polymer components. These strategies include synthesis of block copolymers, physical blending of polymers, and formation of partially crosslinked polymer networks.

Figure 6 shows multifunctional properties for one series of partially crosslinked structural electrolytes. The polymers are composed of methacrylated polyethylene glycol-based comb polymers incorporated into a cross-linked vinyl ester network, with various molecular weights, functional groups, and comb-to-crosslinked polymer ratios. Ion conductivity is enabled by complexing with lithium triflate, and the system remains solvent-free. Ion conductivity is measured using impedance measurements on 1-cm-diameter discs, with the same geometry used for characterization of compressive stiffness in a conventional load frame.

The data shows that, by varying the architecture of the polymer electrolyte, a range of compromised conductive and structural materials can be created. To create a highly efficient structural battery, the structural electrolyte needs to possess both high stiffness and conductivity, trending towards the upper right-hand corner of the plot in Fig. 6. The data shows that particular combinations of polymeric elements enable unusually high multifunctional performance. We are continuing to explore various polymer architectures to better understand the physics behind these trends, and to enable the synthesis of polymer electrolytes with even higher multifunctional performance. Additional studies are underway to assess the effect of hard nano-fillers on electrolyte performance.

3.3 Electrode Fabrication and Properties

We have focused on carbon-based anode materials to enable high electrochemical activity and high specific strength. Woven carbon fabrics, non-woven carbon fabrics, and carbon nanofoam papers have all been considered as anode supports. As received, these carbon-based anodes have demonstrated efficient anodic activity that should be sufficient for typical electrochemical cell chemistries.

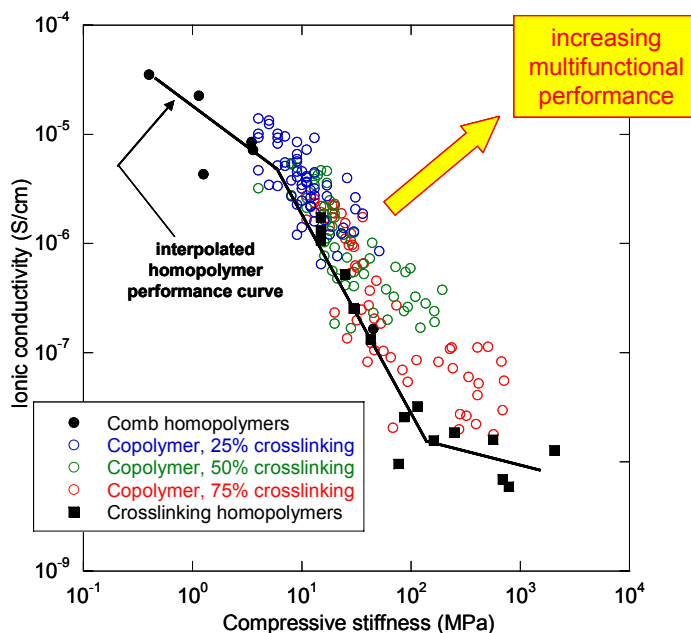


Figure 6: Multifunctional performance of various structural polymer electrolytes.

Metal supports, including metal foils, woven metal meshes, perforated metal foils, and expanded metal foils, have been considered as cathodic supports. Metals with high electrical conductivity, like Al, Cu, and Ti, are attractive material candidates provided that they are stable under the desired electrochemical conditions. Coatings consisting of acetylene black (for electrical conductivity within the film) combined with LiCoO_2 or LiFePO_4 cathode materials have been deposited onto the metal substrates using conventional solution-based deposition with a polymeric binder, as well as novel thin-film sol gel coating techniques. Figure 7 shows an example of a thin-film cathodic coating on a titanium woven metal mesh. The binder-based coatings have demonstrated higher cathodic activity, comparable to conventional cathodes, but the thin-film coatings could provide higher mechanical robustness. Evaluation and modification of the various coating approaches is continuing, in order to provide the optimal balance of mechanical integrity and cathodic activity.

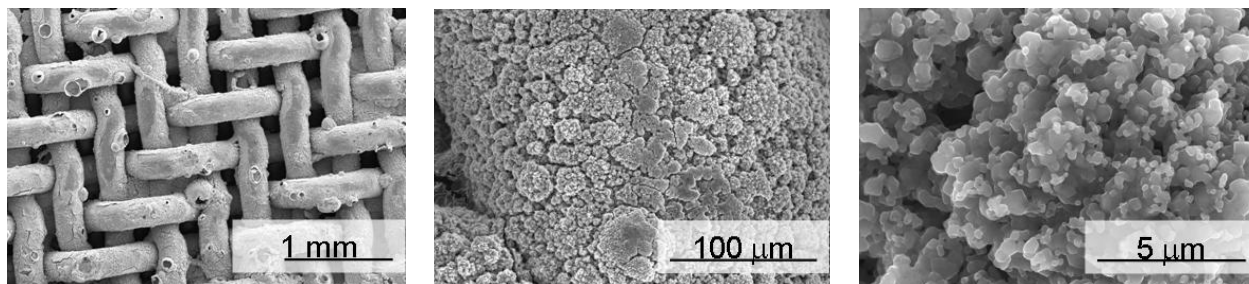


Figure 7: Thin film $\text{Li}_{1.1}\text{Mn}_2\text{O}_4$ cathodic coatings on titanium woven metal mesh.

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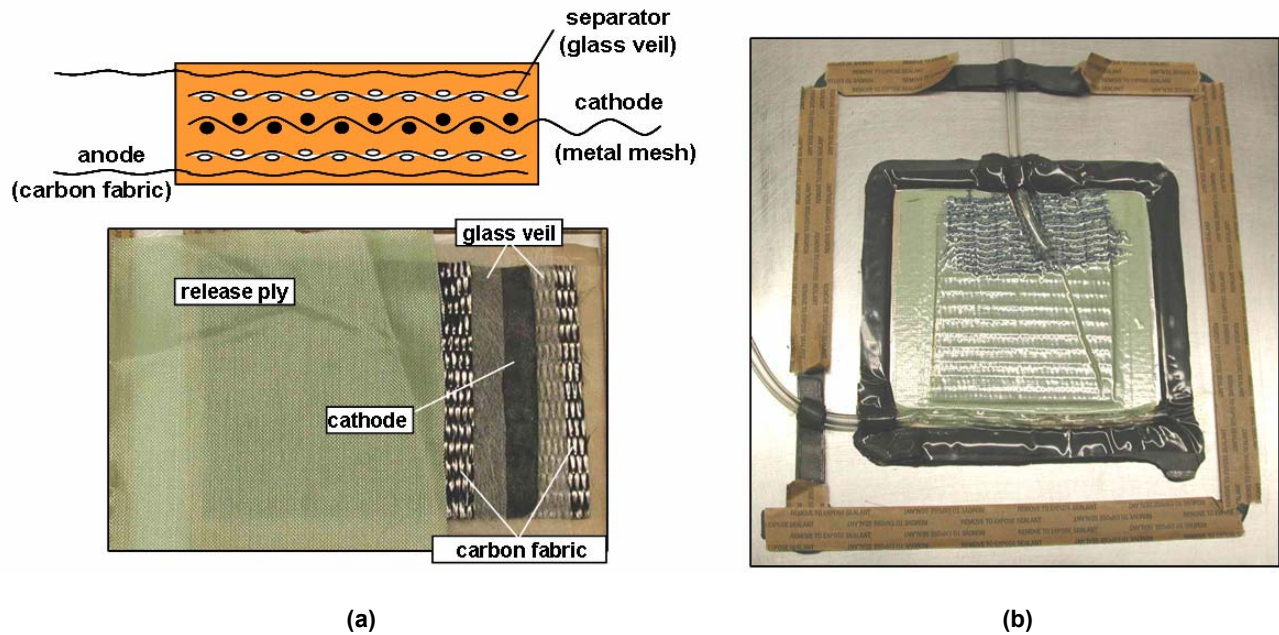


Figure 8: Fabrication of composite battery. (a) Schematic and preform arrangement, and (b) preform undergoing vacuum infusion of electrolyte resin.

3.4 Composite Battery Fabrication and Performance

In order to enable scalable manufacturing of our battery composites, all components have been engineered to be compatible with vacuum-assisted resin transfer molding (VARTM)-type processes. The electrolyte viscosities are low enough for vacuum-driven flow, and the anode, cathode, and separator materials are permeable to allow for wet-out and through-thickness flow. Figure 8 shows steps in a typical two-cell battery composite fabrication process. The preform includes two unidirectional carbon fabric anodes, a thin-film coated metal screen cathode, and glass veil cloth separators. These preform layers are sandwiched between release film, then vacuum-bagged and infiltrated with electrolyte resin. The composite is then typically cured at 80°C for 6 hours, followed by a 1 hour post-cure at 100°C.

Figure 9 shows three-point bend results for fiber-direction specimens sectioned from two composite batteries. Both composites use identical processing and reinforcement, but utilize different polymer electrolytes. The "50/50" curve was generated for a composite whose polymer electrolyte is composed of 50 vol% comb (ion conductive) polymer and 50 vol% networking (structural) polymer, while the "90/10" curve was measured for a composite with a polymer electrolyte composed of these two species at 90% and 10%, respectively. Both composites demonstrate reasonable stiffnesses, between 5-50 GPa. The more compliant 90/10 composite shows a lower stiffness, and a more graceful failure. The photos in Fig. 9 show that, under this bending loading condition, failure is dominated by interply failure and fiber buckling. Both failure modes are expected for composites with compliant matrices. The interply failure mode also reflects the importance of matrix-reinforcement adhesion. Systematic characterization and enhancement of the interfacial adhesion for cathode-electrolyte and anode-electrolyte pairs is underway.

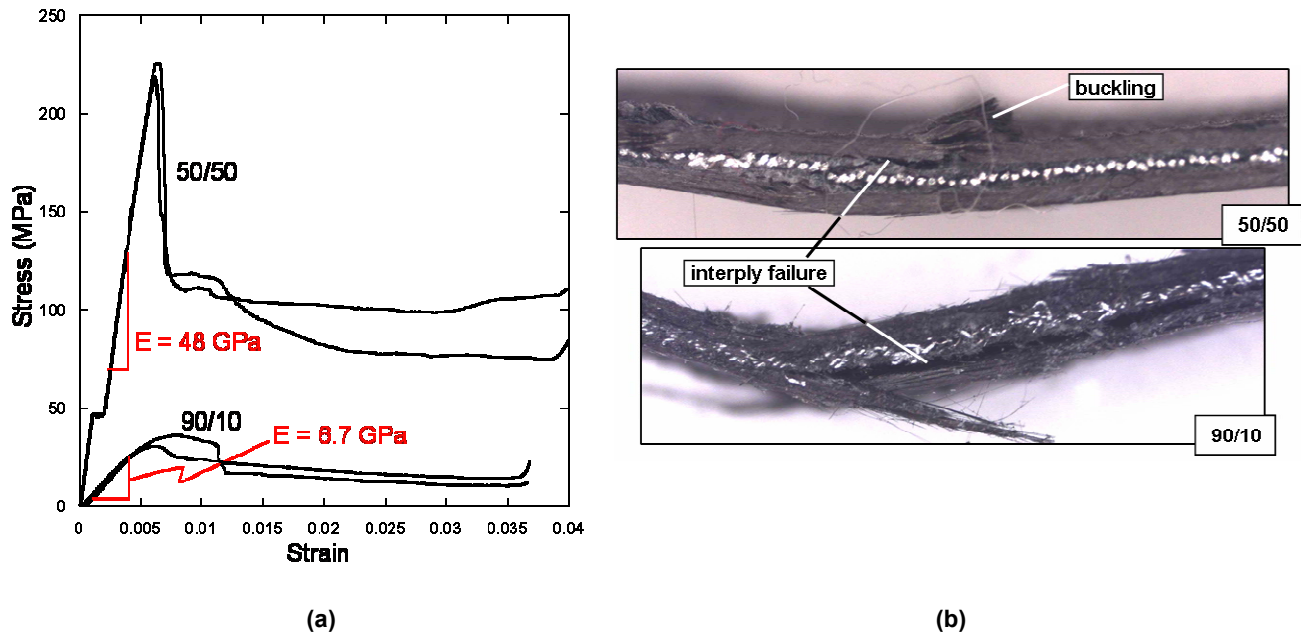


Figure 9: Mechanical performance of structural batteries.
 (a) Loading curve during three-point bend, and (b) test specimens after failure.

4.0 STRUCTURAL CAPACITORS

4.1 Design and Fabrication

Figure 10 shows the structural capacitor concept. Structural dielectrics consisting of glass fiber- or polymer fiber-reinforced polymer are laminated between thin, electrically conductive electrode layers. The dielectric and electrode layers can both be engineered to provide high mechanical strength and stiffness. The capacitor's energy density can be maximized by utilizing dielectrics with high dielectric strength, and high dielectric constant. The capacitance of the capacitor can be engineered through selection of layer thickness and electrode area. The layer thickness is largely designed based on the required operating voltage, with capacitors usually designed so that their maximum operating voltage approaches, but does not exceed, the rated dielectric strength of the dielectric layers.

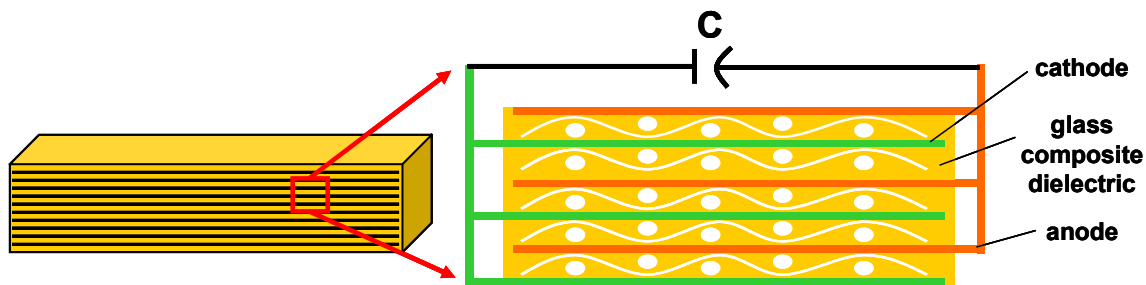


Figure 10: Schematic of structural capacitor concept.

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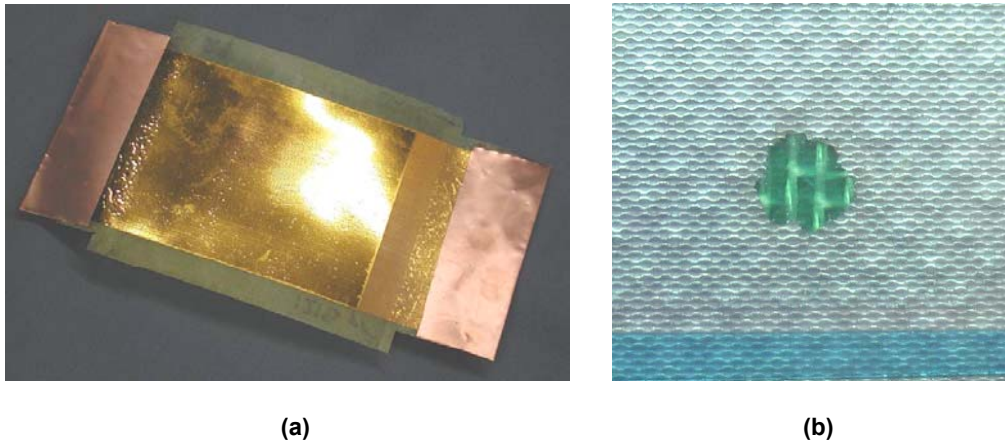


Figure 11: (a) Structural capacitor and (b) self-cleared electrode.

Figure 11a shows a typical structural composite capacitor. We have fabricated structural capacitors utilizing a range of composite dielectrics and processing routes, including thermosetting and thermoplastic matrices; glass and polymeric fibers; and woven and unidirectional fabrics. Metallized polyimide (aluminum-coated Kapton) film are typically used for electrodes, although some specimens have utilized thin aluminum layers directly metallized onto composite dielectrics. In both cases, very thin electrode thicknesses (< 50 nm) are preferred in order to allow for self-clearing of local dielectric breakdown events. Figure 11b shows such a self-clearing event. A local flaw has caused electrode shorting, which evaporated the thin aluminum electrode coating and effectively insulated the flaw from the rest of the capacitive element. With self-clearing electrodes, capacitors can sustain multiple isolated dielectric breakdown events without global, catastrophic dielectric failure.

For capacitors utilizing metallized film electrodes, the composites are fabricated under heat and pressure using traditional processing routes (such as wet lay-up, prepreg, or melt infusion) with interlayers of metallized film. The cure and consolidation process both completes the composite and bonds the electrode layers to the other material layers. For capacitors using direct metallization for electrodes, thin composite dielectrics are fabricated using conventional processing routes, and then the electrodes are deposited onto the cured composite surface.

4.2 Testing and Performance

Figure 12 shows the setup used for dielectric characterization of the composite dielectrics. The composites are immersed in mineral oil, and then subject to increasing applied voltage. Figure 12b shows a typical voltage loading curve. The first clearing event represents the first instance of localized dielectric breakdown. This first clearing event is followed by other isolated clearing events as the voltage increases. At the subjective failure voltage, clearing begins to occur regularly and repeatedly across the dielectric. As voltage is increased further, eventually the capacitor catastrophically fails at its maximum voltage.

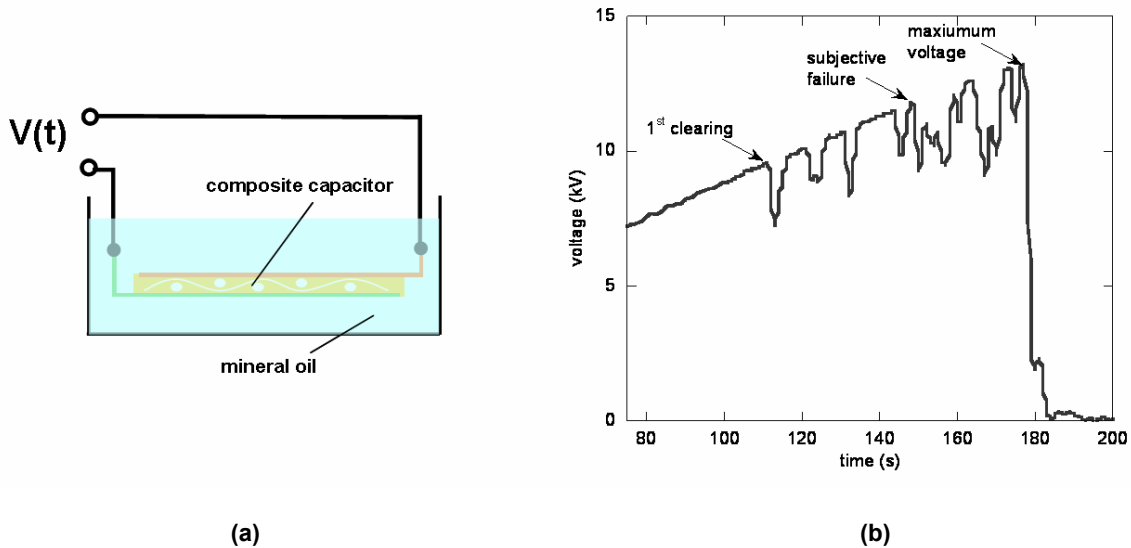


Figure 12: (a) Schematic of voltage characterization setup and (b) definition of failure points.

Figure 13a shows dielectric strength as a function of thickness for various polymer and polymer-composite dielectrics, including both our own measurements and previously reported values from the literature [6-9]. In general, dielectric strength increases as the dielectric thickness decreases. Therefore, capacitor energy density (which is proportional to the square of the dielectric strength) can be improved by using very thin composite dielectric layers. The composites with the best dielectric strength in Fig. 13a are printed circuit board prepregs (N4205-6FC, Nelcote, Inc., Waterbury, CT), which we refer to as glass-FR4. These prepregs consist of woven glass fabric in a brominated, fire-resistant epoxy matrix, and are much thinner ($\sim 40 \mu\text{m}$) than conventional structural prepregs ($\sim 200 \mu\text{m}$).

Figure 13b shows the resulting structural capacitor energy density as a function of capacitor stiffness. The capacitor stiffness values are either measured or calculated based on simple rule-of-mixture relations. The glass-FR4 composites possess a unique combination of energy density and structural stiffness that make them viable candidates for structural capacitors. The dashed lines in Figure 13b represent design curves for achieving beneficial weight savings within particular design constraints. The glass-FR4 materials approach or exceed these design curves, indicating that they may provide useful multifunctional performance.

5.0 CONCLUSIONS

The multifunctional structural fuel cell, battery, and capacitors discussed in this report represent new concepts in material and system design. These novel composites could enable highly efficient military vehicles, increasing the range, speed, or payload of systems such as ground vehicles or unmanned aerial vehicles. While the structural and power/energy density of the existing systems represent state-of-the-art performance, these performance levels are still inadequate for most practical applications. Further work is required to increase both mechanical and power/energy performance of these systems, through novel materials development and design. These new materials, however, must be engineered to accept scalable and cost-effective manufacturing routes. Further challenges include integration with other subsystems on military vehicles, as well as maintenance, repair, and sustainability.

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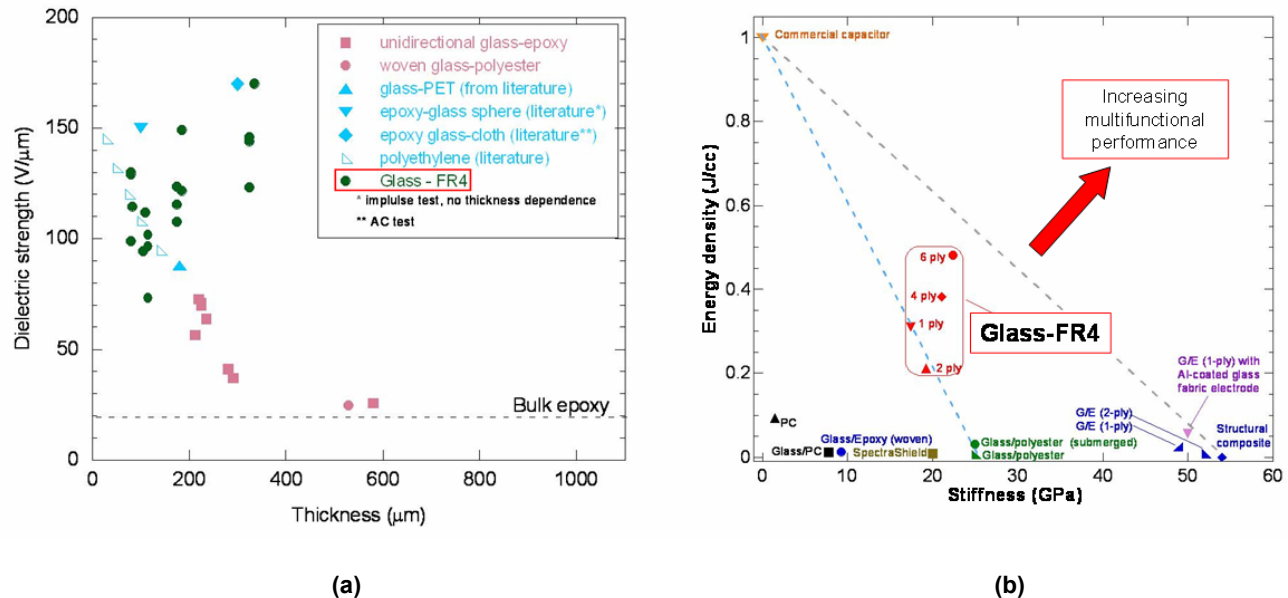


Figure 13: (a) Dielectric strength versus thickness for various dielectrics (literature data from [6-9]), and (b) multifunctional performance comparisons for various composite dielectrics.

ACKNOWLEDGEMENTS

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SYMPOSIA DISCUSSION – PAPER NO: 2

Author's Name: E.D. Wetzel

Question (P. Knott):

You have described the use of FR4 PCB material for structural capacitors. How can you get the material into a particular/curved shape?

Author's Response:

So far, we have only used this material for planar multi layer structures.