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September 2007

*A reprint from the Proceedings of Society for the Advancement of Material
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MULTIFUNCTIONAL STRUCTURAL COMPOSITE BATTERIES

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ABSTRACT

We are developing structural polymeric composites that both carry structural loads and store electrochemical energy. These multifunctional batteries could replace inert structural components while providing supplementary power for light load applications. If designed with sufficient structural and energy efficiency, these materials could also enable significant system-level weight reductions. To enable this concept, load-bearing properties must be engineered into the battery packaging, electrolyte, and / or electrodes. Previous examples of structural batteries have primarily utilized structural packaging. However, in this study, structural properties are designed directly into the electrolyte and electrode materials such that each component is itself multifunctional. Novel electrode and electrolyte materials are being synthesized to optimize both electrochemical and load-bearing capacity. One focus of our research is the development of solvent-free structural polymer electrolytes based on vinyl ester resins that exhibit a desirable combination of mechanical strength and ion conductivity. Using these resin electrolytes the components are being integrated using moldable, scalable, cost-effective composite processing techniques.

KEY WORDS: Applications – Energy, Battery Systems, Graphite Fiber Composites

1. INTRODUCTION

The weight and volume of conventional battery 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 energy density. However, a different approach is to design batteries that are also load-bearing [1]. These structural batteries could be used to replace conventional structural components, such as vehicle frame elements or a UAV wing structure, with power-generating components. If designed with sufficient structural and energy efficiency, these structural batteries could enable significant system-level weight reductions [2].

The multifunctional composite battery concept described in this study utilizes a fiber-matrix composite platform in which each structural component is designed to function as an electrochemical battery component. The current design (Fig 1) consists of a metal mesh coated with a cathode material, a carbon fiber fabric acting as an anode, a fiberglass separator layer, and a structural solid polymer electrolyte binding the components. The cathode coated mesh and carbon fiber electrodes both carry load and are electrically conductive current collectors. The fiberglass separator layer provides additional structural support and ensures electrical isolation of

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the electrode layers. The polymer electrolyte transfers load to the other components while simultaneously conducting ions between electrodes. Since each component is fulfilling multiple roles in the composite device, a synergistic weight or volume reduction may be accomplished compared to the individual state-of-the-art (SOA) battery and structure even if performance of the individual roles fall short of SOA property values. However, each component in the composite device must fulfill their multiple roles simultaneously and cooperatively.

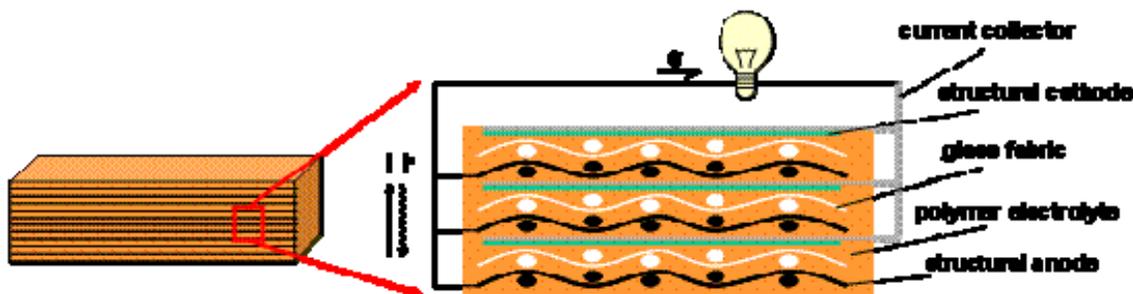


Figure 1. Concept for a structural battery

In this paper, we discuss the development and optimization of the anode, cathode, and electrolyte materials for a structural lithium-ion battery. Each component is designed to provide multifunctionality through consideration of both structural and electrochemical properties. A lithium-based chemistry has been selected due to its high energy density and compatibility with polymer-based electrolytes [3]. We then describe the fabrication approach used to combine these components into an integrated structural battery composite, with special emphasis placed on selecting scalable composites manufacturing routes. Finally, the overall electrochemical and mechanical properties of the composite battery are characterized.

2. ELECTRODE DESIGN AND CHARACTERIZATION

2.1 Anode The current device design uses conventional carbon fiber fabrics as an anode material [4]. A carbon fiber-based anode material is used because of its inherent multifunctionality for this application. The high stiffness and strength of carbon fibers provide mechanical reinforcement for the composite battery, while its electrical conductivity allows for transport of electrons into and out of the cell. Furthermore, for our lithium-ion battery chemistry, the carbon can serve as an intercalation media for the lithium ions.

2.1.1 Anode materials and sample preparation Three forms of structural carbon have been considered for these initial stages of anode research, including woven carbon fabrics, nonwoven carbon fabrics, and carbon nanofoam papers. The woven fabrics are grade SP-381 prepreg unidirectional mats received from Cytec. The nonwoven mats were received from Hollingsworth and Vose in grades 800015, 800020, 800028, 800036, 800039, and 800047, which pertain to thicknesses from 0.05mm to 0.84mm. The carbon papers were received from Marketech as both Grade I and Grade II. Elemental graphite has been selected as a benchmark anode since it is considered to be a highly efficient form of carbon for intercalation of lithium ions in an electrochemical cell, and is commonly used in commercial lithium cells. Accordingly, structural forms of carbon employing mostly graphitic composition, such as PAN-based fibers, are most likely to provide efficient anodic properties.

Anode materials were characterized as half cells paired with lithium foil, immersed in a liquid electrolyte composed of 1.0 m LiPF₆ in EC/DMC at 30:70 by weight. A polypropylene separator was situated between the lithium foil and anode, 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 fabricated by directly stamping 10 mm discs out of the materials. The unidirectional carbon weave did not retain its form when cut into small samples, but cycle tests were still performed on the bed of loose fibers. Elemental graphite anodes were fabricated using a poly(ethylene oxide) (PEO) binder, solvent cast from acetonitrile onto a nonporous stainless steel disk. A loading of approximately 25 wt% PEO binder was found to provide an optimum of mechanical binding and electrochemical activity.

2.1.2 Anode Testing and Properties The half-cell battery cycling protocol 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 [5], after which the current was increased to 4.0×10^{-4} A for the remainder of the test. Tests were run for two weeks, yielding about 50 cycles depending on the quantity of material in the film. Each sample was run in duplicate and the results averaged.

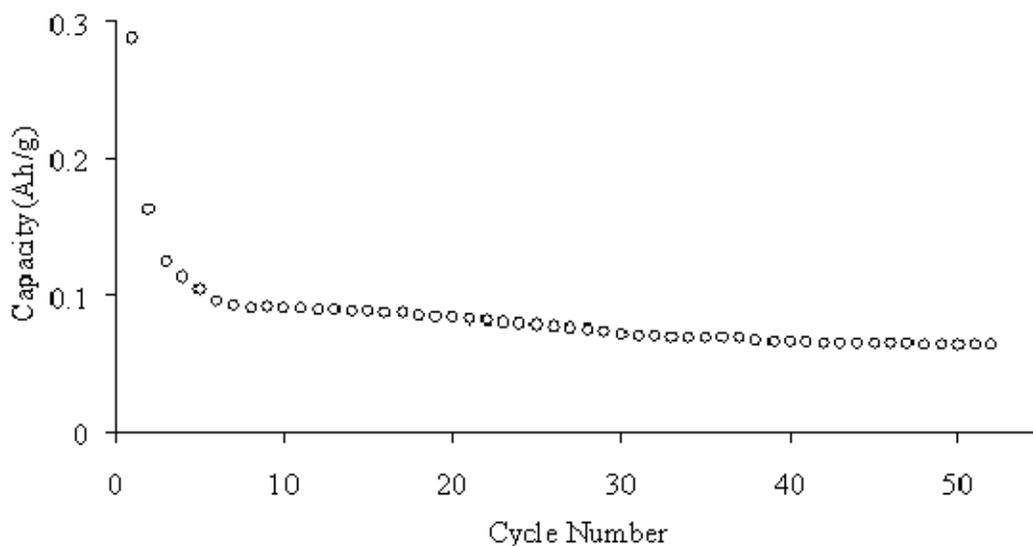


Figure 2. Capacity fade for a nonwoven carbon fiber mat in a half cell vs. lithium foil

Figure 2 shows the loss in capacity with cycling for a nonwoven mat 0.25mm thick. Specific capacity was found to decrease significantly over the first few cycles and then to plateau to less than 1% loss between cycles. Figure 3 is a plot of specific capacity at the third cycle versus anode type. Our measured graphite capacity is lower than the ideal value likely due to our use of a binder, which may reduce the available anodic active area. The carbon papers and non-woven carbon mats showed very good capacity. For the carbon papers, little variation in capacity was found for different grades, so the data point in Figure 3 is an average over both grades. For the non-woven mats, the data point in Figure 3 is an average over the four grades pertaining to mat thicknesses greater than 0.25 mm. Note that, for the non-woven mats, the specific capacity was found to drop by about 75% when the mat thickness was less than 0.2 mm. This result could be due to partial electrical isolation of fibers in the low thread count mats. The unidirectional

carbon weave showed virtually no capacity. This low performance could be due to interference with electrical or ionic conduction pathways by the polymeric sizings that are put on the surface of the fibers for improved compatibility with structural polymer matrices. Further testing is underway to understand the impact of fiber density and sizings on capacity. Based on this existing data, carbon papers and nonwoven mats are the strongest candidates for multifunctional anodes.

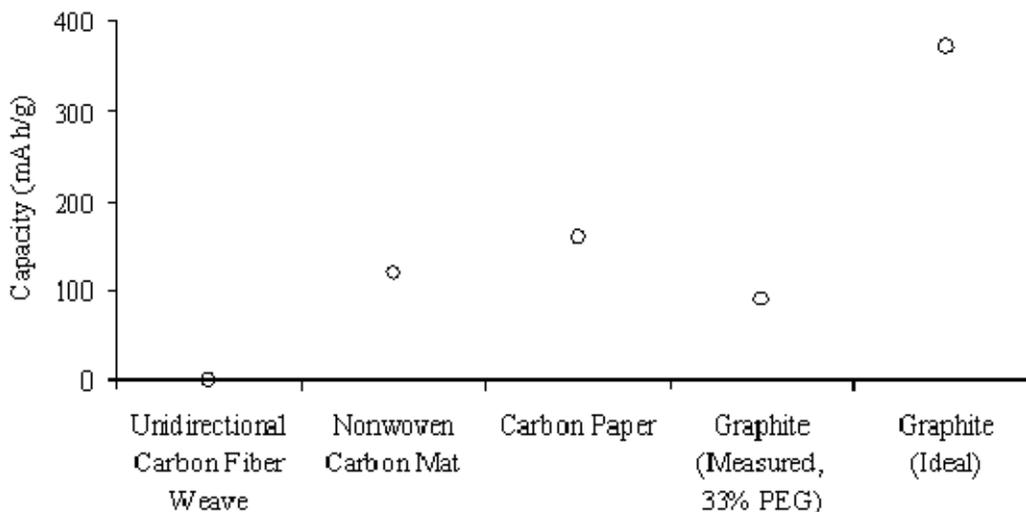


Figure 3. Measured capacity at third cycle for carbon anode half cells vs. lithium foil

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

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

Acetylene black is a high conductivity form of carbon powder that is used to optimize electronic conductivity of the cathode film. The carbon powder and cathode powder are milled together for several days to minimize particle size and to ensure sufficient integration of the two materials. The carbon is essential for facilitating electron transport between the cathode particles and the metal current collector. It was found that using less than 8% carbon powder in the films yielded too high of an electrical resistance to be useful, and the corresponding measured capacities were orders of magnitude lower than the theoretical values. Increasing the volume

fraction of carbon powder increases the electrical connectivity of the film but 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 produce the best overall cathodic activity.

A high molecular weight (2×10^5 Da) PEO binder was used to adhere 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 optimal mechanical integrity and cathodic activity. Note that traditional lithium-ion batteries use a polymer binder with the electrode materials, a polypropylene separator between the electrodes, and a liquid electrolyte saturating the assembly. The binder does not directly transport ions, but absorbs the liquid electrolyte which then transports ions between cathodic particles. In contrast, our PEO binder acts as a solid state ion conductor that 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 while acting as a current collector that efficiently transports electrons between the circuit and the cathode film. Aluminum was used in this study with lithium cobalt oxide due to its high specific strength and stiffness, high electrical conductivity, and favorable inertness to the cathode materials under the conditions studied. Both woven wire cloth and expanded foil substrates are being tested. These material forms are structurally robust and porous, allowing the polymer matrix to wet out the cathode and mechanically bridge the various material layers together. As a comparison, a control set of additional 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. Note that many conventional batteries use nonporous metal cathodes (e.g. foils) to maximize surface area, which would likely present sources of delamination if used in a structural battery design.

To create 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 achieve homogenization. This mixture was then stirred into a solution of PEO in acetonitrile, and dip coated or brushed onto the metal substrate. The film was allowed to air dry, followed by heating under vacuum to ensure complete drying. These cathodes were characterized as half cells paired with lithium foil using a coin cell configuration similar to the one described in Section 2.1.1.

3.2.2 Cathode Testing and Properties The cathode half cells were run at a constant current of 9×10^{-5} A for the first two cycles while the SEI layer forms, and 3×10^{-4} A for the remainder of the test. Capacity fade between the first and third cycles was found to be significantly less than that of the anodes, about 20% for most cathode configurations. After the third cycle the capacity was usually found to plateau until the test was terminated. Tests were run for two weeks, yielding 15-25 cycles depending on the quantity of material in the film.

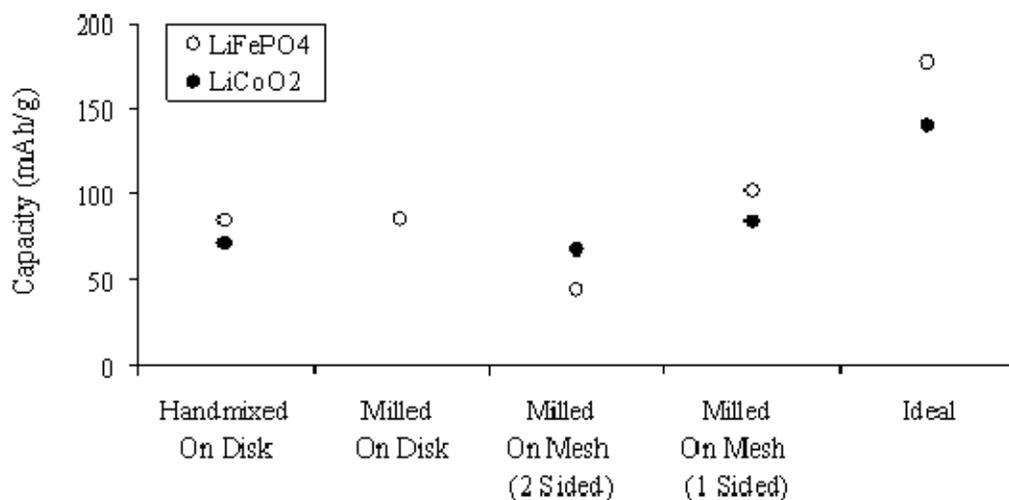


Figure 4. Measured capacity at third cycle for LiFePO₄ and LiCoO₂ half cells vs. lithium foil. The cathode films employ 8 wt% acetylene black and 20 wt% PEO binder.

Figure 4 indicates the average specific capacity measured for several processes at the third cycle. The film composition for each sample included 8 wt% acetylene black and 20 wt% PEO binder. Results from one to three cells are averaged to yield each data point. The ideal cathodic capacity value is also plotted for each of LiCoO₂ and LiFePO₄. For the nonporous current collectors, handmixed and milled cathodic materials produced similar results. This trend indicates that our current milling procedure is not providing enhanced mixing of the constituents. Other milling and mixing techniques are under consideration for improving this process. The metal mesh current collectors show performance comparable to the nonporous substrates. It is interesting that the one-sided coating (brushed coating) exhibits higher specific performance than the two-sided coating (dip coating). This possibly indicates prohibitively slower rates of ion transport to the back side of the mesh or increased electrical resistivity between the mesh and current collector. These complications 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 acceptable ion transport capabilities. These goals are being engaged through progressive development of load bearing ion conductive resins and nanocomposites of those resins. Battery power and structural modulus are enhanced by using a processable electrolyte resin that performs well as a thin film. For a battery, reducing the electrolyte thickness increases the current by increasing the rate of ion conduction between the electrodes. In addition, 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, enabling the development of higher capacity, higher strength structural composite batteries.

In this study, electrolyte development is focused on polymerized vinyl ester derivatives of poly(ethylene glycol) (PEG). Polyacrylates have been previously studied for electrolyte use owing to their dimensional stability, however they are typically plasticized [6]. Here, a broad selection of monomers have 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 [7], 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 allowed for a wide range of tailorable structural and electrolytic properties. The resins provide an additional benefit of favorable processing through VARTM (vacuum assisted resin transfer molding) distribution of the monomer through the stacked electrode and separator layers prior to thermal cure.

To characterize our electrolyte resins, 1-cm-diameter discs, ~ 0.5 mm thick, were cast and carefully dried and coated on their faces using silver paint. Impedance measurements were performed 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). Mechanical characterization was performed by compressing cast discs of similar geometry in an MTS load frame using 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.

3.1 Neat Homopolymer Resins Figure 5 reflects the impact of a series of variables on multifunctional behavior for homopolymer resin electrolytes. A log-log plot is used since the axes in Figure 5 cover several orders of magnitude. The homopolymers included a systematic exploration 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 (“BisA”). The results show that as the nature of the monomer is altered there is a systematic tradeoff between structural and transport properties, with no strongly multifunctional outliers with unusually high conductivity and stiffness.

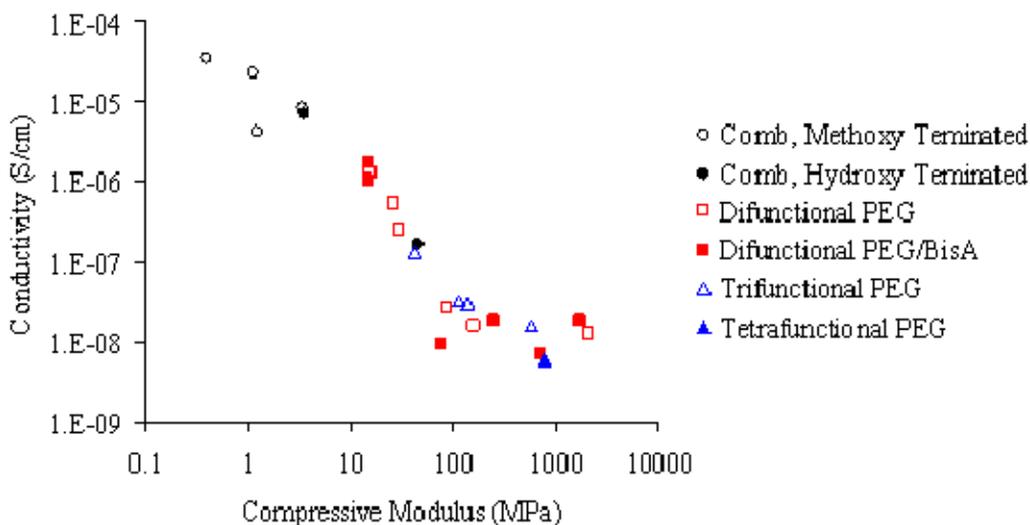


Figure 5. Room temperature ion conductivity vs. stiffness for vinyl ester homopolymer electrolytes of various architectures and functional groups.

The methacrylated and acrylated vinyl ester (VE) reactive groups demonstrate comparable behaviors in Fig. 5, but the number of VE groups on each monomer largely determined the position of the material along the performance curve. One VE group per monomer results in linear “comb” polymers with mobile PEG sidechains that facilitate 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 as the PEG chains become immobilized. For a given number of VE groups per monomer, increasing the relative concentration of the ion-conducting PEG versus the polymer-forming VE groups yields materials that tend towards the upper left quadrant of Figure 5. Incorporating additional chemical functionality such as bisphenol-A into the monomer resulted in additional improvements in modulus.

3.2 Neat Copolymer Resins In the second phase of this investigation, comb monomers with one VE group were blended with networking monomers with multiple VE groups and the solution was prepared, cured, and tested according to the protocols following in section 3.1. The resulting copolymers contained controlled proportions of highly mobile ion-conductive PEG sidechains and immobilized structural PEG crosslinks. Figure 6 illustrates one set of results from this copolymer study. The comb monomer used for the materials described by Figure 6 is PEG 550 methyl ether acrylate, which was mixed with fifteen of the networking monomers in volume fractions of 0.0, 0.25, 0.5, 0.75, and 1.0 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 given mechanical stiffness. While the results from section 3.1 suggested that monomer reformulation may not be effective at improving multifunctionality in structural homopolymer electrolytes, we have found that copolymers of these same monomers do yield simultaneous improvements in ion conductivity and compressive modulus. However, while the improvements are significant, more substantial increases in performance are required for use in competitive multifunctional structural battery devices.

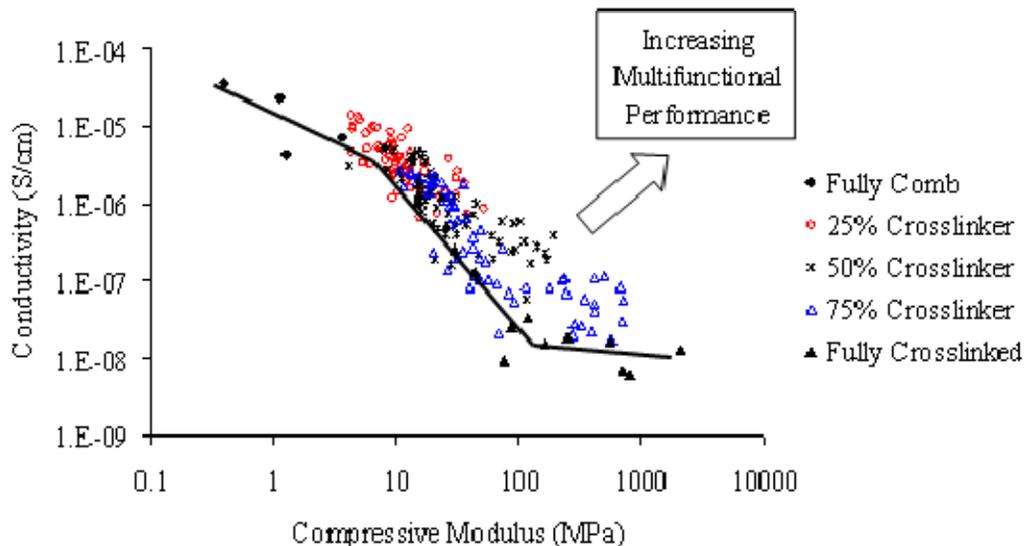


Figure 6. Room temperature ion conductivity vs. stiffness for vinyl ester copolymer electrolytes.

3.3 Silica-Resin Nanocomposites In an effort to further increase multifunctional performance in structural electrolytes, nanocomposite copolymer electrolytes have been developed using the resin systems described in sections 3.1 and 3.2. Addition of nanofillers has been previously shown to enhance the mechanical and even electrochemical properties of solvent-free polymer electrolytes [8]. After preparing the monomer or comonomer solution with lithium salt, nanofiller additives were dispersed into the mixture and the samples were cured and tested according to the methods described previously. The fillers that have been considered include colloidal silica and fumed silica and were varied in concentration, size, shape, and surface treatment. The polymers were formed 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 chosen since they have very similar volume fractions of PEG and VE groups and the PEG oligomers are of similar size. Since the chemical composition is comparable, 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 compares several highlights from these studies. It was found that these fillers can simultaneously improve conductivity and modulus but that the improvement depends strongly on the nature of the polymer matrix as well as the nature of the filler. 400 nm colloidal silica additives were tested in concentrations that range from 5 wt% to over 50 wt%. The relatively large colloidal particles do result in some multifunctional increases, predominantly by increasing modulus at a higher rate than reducing conductivity. It appears 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 illustrates, at 40 wt% filler the impact on both properties is considerable. 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 noticeably improved modulus of highly compliant polymer electrolytes. The improvement in modulus declined with increased crosslinking suggesting that there is greater benefit to form fumed particle nanocomposites with highly conductive compliant polymers. The diminishing effect as the copolymer is crosslinked may indicate 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 indeed the treated particles underperform their untreated counterparts. Further studies are being performed using copolymers with a higher modulus structural component. Overall, 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.

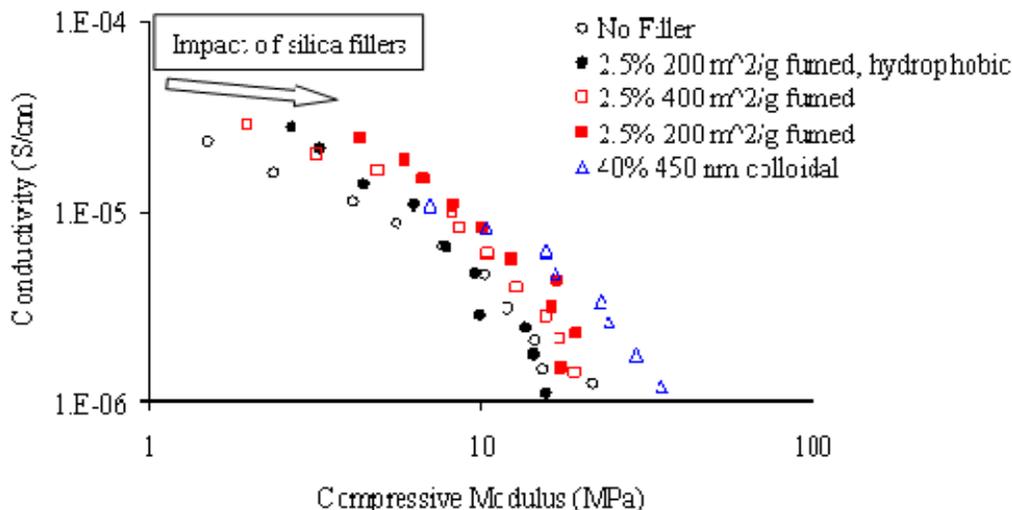


Figure 7. Room temperature ion conductivity vs. stiffness for vinyl ester copolymer electrolytes with the indicated fillers.

4. BATTERY COMPOSITE FABRICATION AND CHARACTERIZATION

4.1 Processing Vacuum assisted resin transfer molding (VARTM) was used as a processing route for our composite batteries. This 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 described in section 3.3 have been engineered with 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 also highly compatible with traditional composite processes.

Figure 8 shows the fabrication of a typical composite battery. 0.18-mm-thick glass veil separator (Grade 8000100, Hollingsworth and Vose) layers are placed between carbon fabric-based anodes and a thin film-coated, metal mesh cathode. This separator allows for preform compaction 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 material 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 the composite part, through suction provided at the outlet part. 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, however, this same approach could be 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) also provide a means of creating series or parallel cell voltage arrangements, allowing for tailoring of the voltage and current capabilities of the cell. Also note that 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.

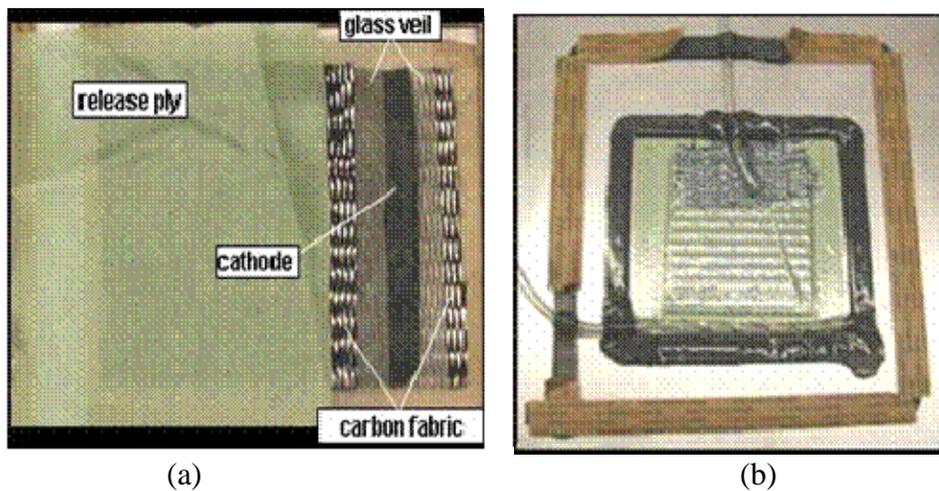
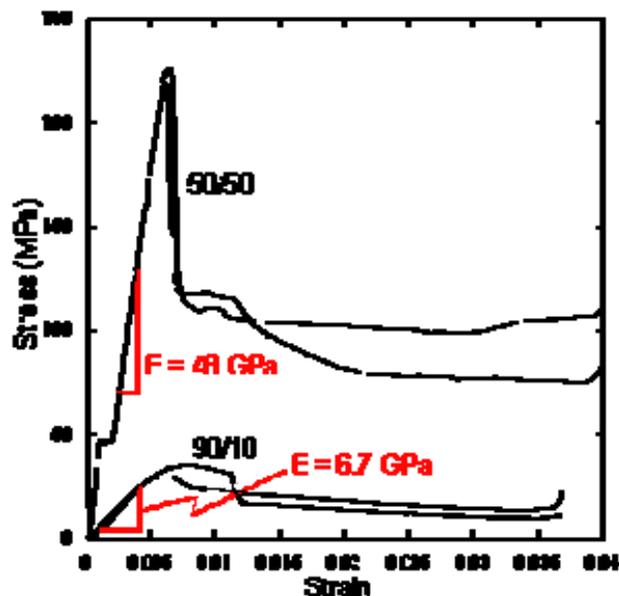


Figure 8. (a) Structural battery layers and (b) undergoing VARTM processing.

4.2 Mechanical Properties Three point bend testing was performed to characterize the basic mechanical properties of the battery composites. A span of 5.08 cm and a loading rate of 5 mm/min were used for the experiments. Figure 9 shows the results for two composite battery materials. Both composites use identical processing and reinforcement, as described in Section 4.1, but utilize 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 demonstrate reasonable stiffnesses, between 5-50 GPa. The more compliant 90/10 composite shows a lower stiffness, and a more graceful failure. Figure 9b shows 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 reflects the importance of matrix-reinforcement adhesion. Systematic characterization and enhancement of the interfacial adhesion for cathode-electrolyte and anode-electrolyte pairs is underway.



(a)



(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 demonstrated basic electrochemical charging and discharging cycles. Full quantitative electrochemical performance characterization is underway, 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. Our research program is exploring development of structural resin electrolytes, structural carbon anodes, and 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. The carbon anodes demonstrate electrochemical capacities competitive to that of the graphite, which is the industry standard. 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 also demonstrated 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 identical electrochemical activity accessible to 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.

5. ACKNOWLEDGMENTS

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