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Title: *Multifunctional Energy Storage Composites for SHM Distributed Sensor Networks*

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ABSTRACT

SHM-based structures with embedded sensors and hardware have posed a great demand in distributed, in-situ power sources. This paper introduces the novel Multifunctional-Energy-Storage Composites (MES Composites) which highlights a unique integration technique for embedding lithium-ion battery materials in structural carbon-fiber-reinforced-polymers (CFRP). Unlike standard lithium-ion pouch cells, the MES Composites maximizes material utilization by using CFRP facesheets to house the electrochemistry. Through-thickness polymer reinforcements are implemented to allow load transfer between the two facesheets, analogous to the sandwich structure construction. A feasibility study and preliminary characterization have been completed and have shown that the same electrochemical performance as a standard Li-ion cell could be maintained, while achieving high bending rigidity.

INTRODUCTION

Structural Health Monitoring (SHM) has become a new paradigm in the structural design philosophy. Through integration of sensor networks, controllers and signal processors, the health of a structure can be constantly interrogated in an automated manner, resulting in the lighter, more efficient, so-called ‘smart’ or ‘multifunctional’ structure. In recent years, breakthroughs in sensor network and hardware technologies have made it feasible to disseminate and embed the sensors in hotspots of a structure where access is limited [1-3]. However, the hardware still requires a great amount of wiring to access traditional, centralized power sources required for

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signal conditioning and processing, preventing the full potential of weight saving to be realized.

Research on creating energy-storage structures has been ongoing, of which one discipline focuses on formulating the structure's constituent materials to have an energy storage capability. For instance, Greenhalgh [4] and Snyder [5] fabricated CFRP supercapacitors, by combining the intrinsic electrochemical nature of carbon fibers and polymer-based electrolyte matrix. However, suffering from the poor electrochemical performance of the constituents, the energy capacity of the structural capacitors is considerably low. Efforts have also been made to instead create a secondary structural battery for improved energy density; for example, Liu [6] used electrolyte-filled polymer matrix as a binder to laminate conventional lithium-ion (Li-ion) battery electrode layers. Yet, a great amount of energy density had to be sacrificed to achieve useful mechanical strength.

Another strategy aims at modifying and optimizing the existing structural components to serve as a secondary, mechanical enclosure for already existing, pre-packaged cells. Parts of the core material in sandwich panels were displaced and substituted with commercial off-the-shelf Li-ion pouch cells [7-8]. However, these systems still lacked the synergy between the disparate, unifunctional subcomponents. Disbonds and limited load transfer between the cells and the structural enclosure prevented the inherent structural properties of the battery to be harnessed.

This paper presents the development of the Multifunctional-Energy-Storage Composites (MES Composites). The MES Composite features a unique integration method - an intermediate strategy - that allows the functional secondary-battery materials, including but not limited to Li-ion battery materials, to be directly embedded in structural CFRP. The concept leverages the feasibility of using CFRP as the electrochemistry housing and the inherent mechanical properties of the battery materials to multifunctionality by permitting the two parts to be mutually beneficial.

PROBLEM STATEMENT

The driving force behind the design of SHM-enabled smart structures has primarily been weight saving by introducing multifunctionality to the structures. However, the design still is suboptimal given there still is the penalty of added weight for the embedded sensors and hardware to access power. It thus becomes imperative to develop an energy-storing structure that allows power sources to be distributed ad-hoc and in-situ of the SHM hardware.

A novel integration technique will be proposed to embed the Li-ion battery materials in the structural CFRP. Optimal material utilization needs to be achieved by: 1) exploiting the intrinsic load-carrying capacity of the battery materials, and 2) using the structural CFRP to house the electrochemistry and eliminating added weight from non-load-bearing standard pouch cell packaging and additional metallic enclosure components.

APPROACH

Architecture of MES Composite

Standard Li-ion pouch cells are constructed from a stack of alternating anode and cathode layers, with each adjacent electrode separated by a thin polymer separator layer. The stack is then vacuum-packed in a polymer laminate film package, infused with ionic electrolyte liquid. The layers are loose - no discernable bonding between each other. Thus load transfer through the cells is minimal if any. Excessive relative sliding between the layers or delamination can occur under mechanical loads and most likely cause the cells to short-circuit.

The MES Composite implements through-thickness polymer reinforcement, similar to the Lithylene technology [9]. Polymer pillars extend through perforations in the electrode stack and mechanically connect to and link the two structural CFRP 'facesheets' on either side together. The construction is akin to a sandwich structure – the stiff CFRP facesheets are placed further apart, thus increasing the moment of inertia and resulting in a higher bending rigidity [10]. However, without the shear load transfer resistance in the core, this structural concept would fall apart as the thin layers bend individually about their own neutral axes. The through-thickness reinforcements prevent the relative sliding between the electrode layers, enabling load transfer between the two facesheets and allowing the structure to flex about a common neutral axis (Figure 1).

Fabrication

The MES Composite cell consists of three fundamental components, namely the battery electrode stack, the CFRP facesheets, and the polymer reinforcements. The battery stack consists of Li-ion battery active layers – i.e., cathode, separator, and anode – stacked in an alternating fashion. Prior to lamination, the electrodes are perforated as per the desired placement of the through-thickness reinforcements. Conventional production active materials are used for the cathode and the anode, which are lithium-NCM and graphite respectively, separated by layers of polyolefin separator.

3K plain-weave T300 carbon fiber fabric (Toray) was used in a vacuum-assisted resin infusion process to fabricate the CFRP facesheets. The carbon fiber layers were infused with the unmodified liquid epoxy system (DGEBA + TETA, Sigma Aldrich). The laminate was then cured at room temperature for 24 hours, followed by a post-cure at 90°C for 30 minutes.

The perforations in the electrode stack were then filled with thermoplastic polymer plugs and sandwiched between two facesheets. The assembly was hot-pressed to melt and fuse the polymer reinforcements to the facesheets. It should be noted that even without the standard Li-ion battery pouch, the cell could subsequently undergo a standard cell fabrication process, as the facesheets and the reinforcement polymer serve as the cell enclosure. The cell was filled with electrolyte ($LiPF_6$ in organic solvent), thermally-sealed, formed, degassed, and re-sealed.

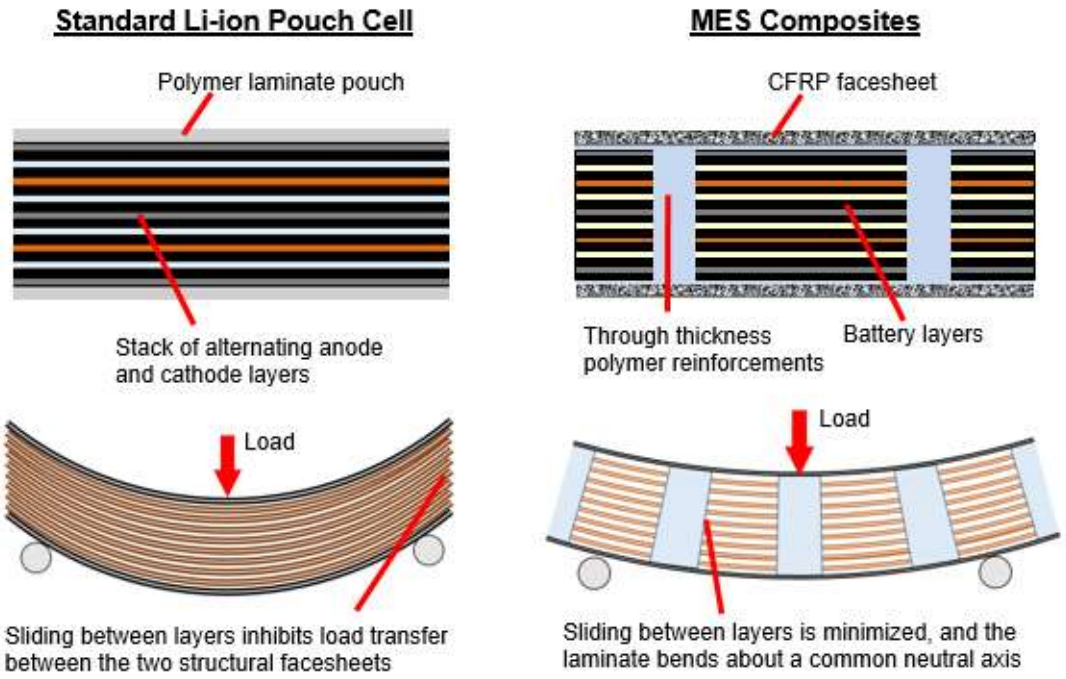


Figure 1. Comparison between standard Li-ion pouch cells (left) and MES Composites (right) – MES Composites employ through-thickness reinforcements which transfer mechanical loads between two structural facesheets and improve shear resistance of the battery core

EXPERIMENTAL CHARACTERIZATION

Electrochemical Performance Feasibility Study

The MES Composites require a thorough electrochemical feasibility study, namely the apparent cell capacity and the cycling performance, as its construction significantly differs from that of a conventional Li-ion cell. MES Composite samples with 11 anode and 10 cathode layers were built – the electrode geometry measured 1.71”x1.22” with four 0.4”-diameter perforations, as shown in Figure 2. Separate designs for the cathode and anode were made with anode coverage larger than the cathode to ensure that excess anode is present and reduce the possibility of shorting. The quantity of active material included in each cell theoretically amounted to a capacity of 0.46 Ah.

After a solid electrolyte interphase (SEI) formation and an activation step, the cells were subject to charge-discharge cycles, where the testing protocol first was calibrated to ensure a C/3 (3-hour) charge and discharge, followed by cycling the cell at a voltage of 4.3V-2.5V. The capacity retention at C/3 cycling with increasing cycle number was compared with a baseline standard 1-Ah automotive pouch cell.

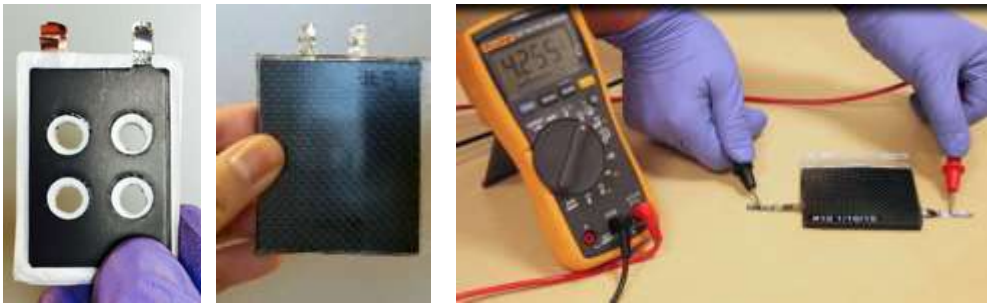


Figure 2. (left) Li-ion battery electrode stack with perforations for placement of through-thickness reinforcements; (center) finished MES Composite single cell; (right) 0.46-Ah MES Composite single cell showing 4.25V.

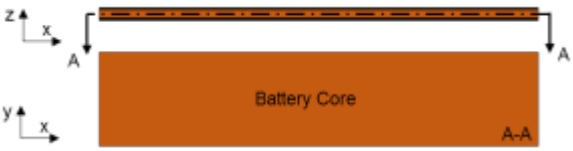
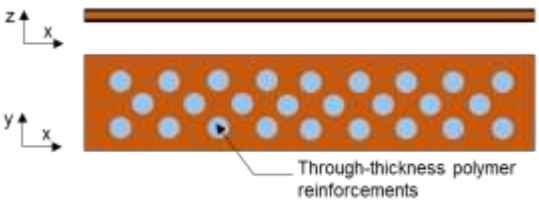
Mechanical Characterization

A flexural (three-point bending) test was used to evaluate the feasibility of the MES Composite through the bending rigidity values. Testing was performed on a three-point bending fixture with 3.15-inch span, on an MTS test system. The samples measured 5.75" long, 1.18" wide, and 0.15" in depth. The support span was approximately 20 times the depth, which was sufficient to avoid significant influence from transverse shear. The displacement at the mid-span was constantly measured while the crosshead was displaced at the rate of 0.01 in./in./min. The bending rigidity can be determined from the slope of the load-displacement curve using Equation 1.

$$EI = \frac{L^3}{48}\frac{dP}{d\delta_p} \tag{1}$$

where EI is effective bending rigidity, L is the support span, $dP/d\delta_P$ is the slope of the load-displacement curve. Two configurations of coupons were manufactured and compared to evaluate the benefit of the polymer reinforcements for bending rigidity. The specifications are summarized in TABLE I.

TABLE 1. SAMPLE CONFIGURATION FOR 3-POINT BENDING TESTING

Sample Configuration	Description
	A) No through-thickness reinforcement • Facesheets – 3 plies, 3K PW T300 (0° along span) • 11 anode and 10 cathode layers
	B) 26 off-grid through-thickness reinforcements • 0.25"-diameter perforations • Facesheets – 3 plies, 3K PW T300 (0° along span) • 11 anode and 10 cathode layers

Proof-of-Concept Integration of a Multi-Cell System

To demonstrate the concept of integrating MES Composites into actual structural components, a 10”-long, 2”-tall multifunctional multi-cell structural I-beam was constructed. The I-beam comprised the MES Composite with three 0.46-Ah Li-ion cells (same geometry as electrochemical testing cells), connected in series (3S1P configuration), in a configuration shown in Figure 3. The complete beam had a nominal voltage of 11.1 V, and a total theoretical energy of 5.1 Wh.

To connect the three separate cells in the module, the current collector foils of one cell’s cathode were ultrasonically welded to the anode current collector of the adjacent cell, through a nickel tab. The positive and negative terminals extended out from either end of the I-beam. The electrical conductivity of the MES Composite module could be measured prior to addition of electrolyte (while the cell is dry) in order to ensure proper connection between the modules of the I-beam.

Two CFRP C-beams (each making half of the I-beam) were made with the aforementioned wet-layup process. The three-cell string was then sandwiched between the two C-beams, with polymer plugs inserted in the perforations. The assembly was then hot-pressed to melt the thermoplastic, join the two halves of the I-beam, and encapsulate the cells. The three cells were then filled with electrolyte, went through an SEI formation process, degassed and re-sealed.

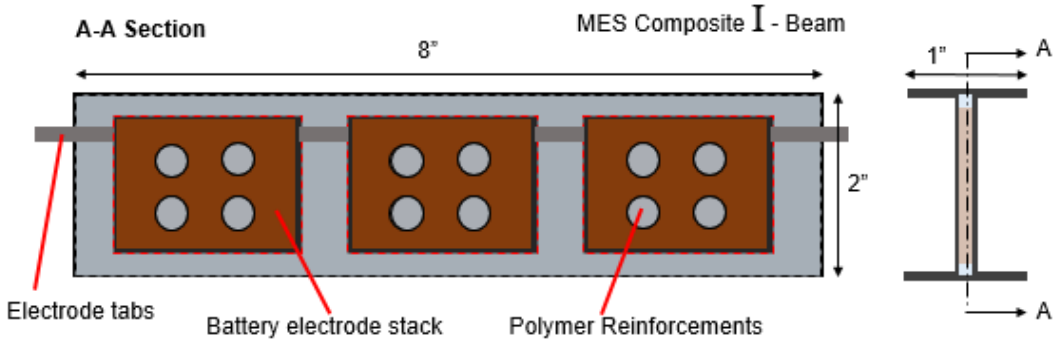


Figure 3. Configuration of the 3S MES Composite I-Beam module

RESULTS AND DISCUSSION

Electrochemical Performance

The apparent first-discharge capacity of the MES Composite cells was reproducibly measured to be 0.444 Ah, or 97.3 ± 1 % of the theoretical capacity calculated from the added amount of materials. Figure 4 shows the C/3 cycling performance of the 0.46-Ah MES Composite single cells described earlier. The capacity retention with increasing number of cycles, in percentage with respect to the first discharge capacity, of the MES Composite is shown in comparison with the data obtained from the standard automotive 1-Ah cells.

As can be seen from the curve, the capacity retention after 50 cycles of the MES Composite remained at approximately 97% of the first-discharge capacity, similar to the cycle-life performance of the baseline cells. This shows that in spite of substantial deviation from a conventional Li-ion pouch cell assembly, the MES Composite cells maintains the electrochemical performance tantamount to the standard Li-ion cells.

Small discrepancies exist between the electrochemical performance of the MES Composite and the 1-Ah baseline automotive cell. The electrodes in the MES Composite contain significantly more free edges than those in the baseline non-perforated cells. Imperfections that arise during the electrode cutting process, such as burrs and active material flaking, can be more prevalent in the MES Composite. With more free edges, misalignment between adjacent anode-cathode pair becomes immensely critical and will result in a greater hit in the apparent capacity than in a regular cell, and most importantly, possibility of soft-shorting. There might also be a negative impact on the capacity and cycle-life performance coming from the presence of the facesheet and the polymer reinforcements, as well as from the high-temperature, high pressure processing conditions.

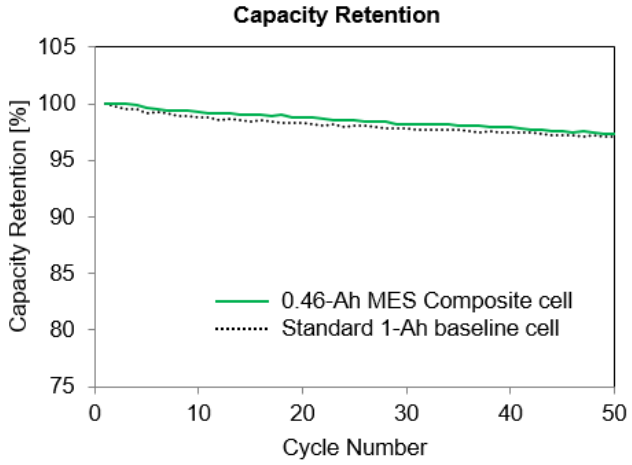


Figure 4. Capacity retention (retained capacity –vs- number of cycles) of the 0.46-Ah MES Composite single cell, in comparison with a 1-Ah standard baseline cell

Mechanical Performance – Bending Rigidity

Figure X. shows the load and displacement curves for the three-point bending results. For samples from Group A (See TABLE I.), the battery stack core was sandwiched between two CFRP facesheets, without through-thickness polymer reinforcements. In this case, the three layers of structures were bent individually and no shear load was transferred through the core. The slope ($dP/d\delta_P$) of the initial linear part is approximately 169 lb./in. (dotted curve in Figure 5).

The slope in the case of Group B samples is around 1514 lb./in. (solid curve in Figure X.), which is more than 9 times higher than the without-reinforcement counterpart. These results show a clear enhancement of the bending rigidity by introducing through-thickness reinforcements. The polymer reinforcements in Group B samples served to transfer mechanical stress from one facesheet to the other. The

reinforcements also inhibited relative sliding between the electrode layers, allowing shear to be transferred through the core.

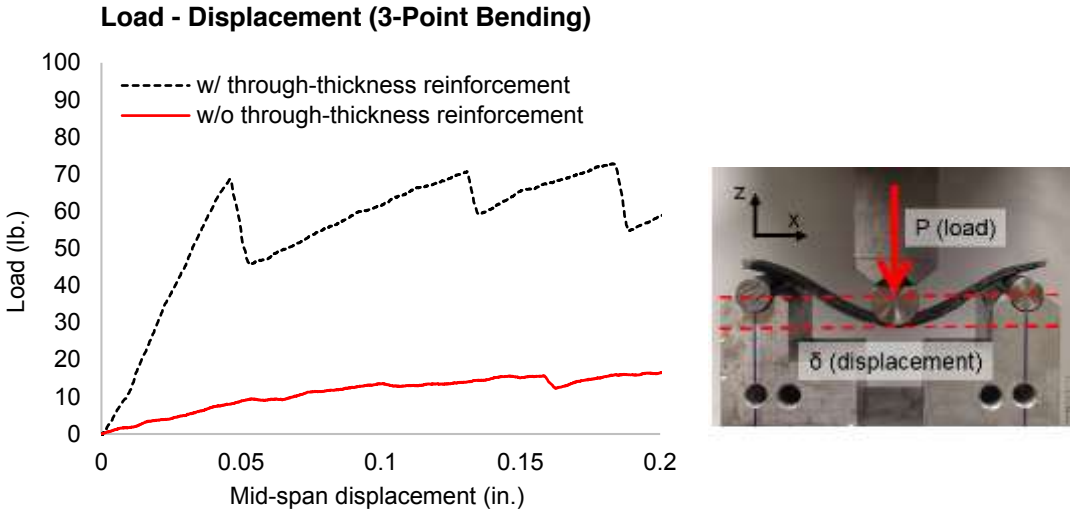


Figure 5. Load-displacement curve for the 3-point bending test comparing (dotted black line) samples with through-thickness reinforcements and (solid red line) samples without through-thickness reinforcements

Functionality of Multi-Cell MES Composites

The three-cell MES Composite prototype module is shown in Figure 6, demonstrating a small-scale proof-of-concept. The MES Composite I-beam is charged up the specified voltage and placed on a support span of 8" separation with a 2-lb weight applied at the midpoint (Figure 6). The I-beam is capable of concurrently supplying electrical power to operate a 12V DC fan, drawing 150 mA constant current or 1.8 W power (~C/3).

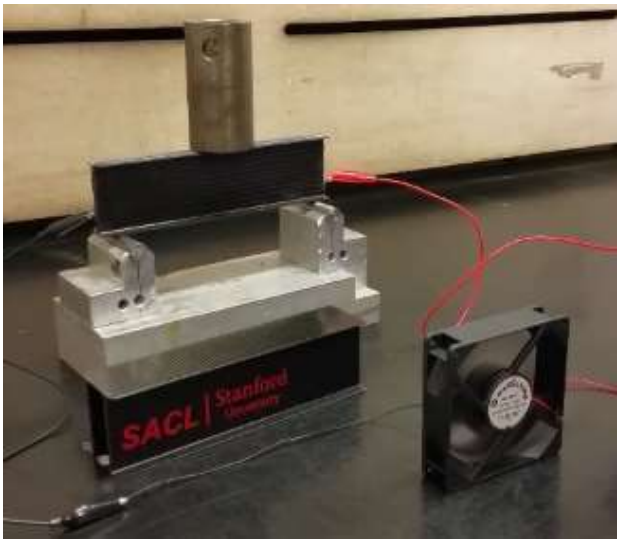


Figure 6. 3S MES Composite I-Beam module with nominal voltage of 11.1V, and 5.1Wh theoretical energy. The I-Beam can concurrently power a 12VDC fan while supporting a bending load.

This preliminary result shows that the MES Composites could be scaled up to a multi-cell structural system and still maintain the rate capability of the baseline single cells while carrying mechanical loads. As a safety measure, the testing for initial I-beam prototype presented here had to be conducted in an adequately-ventilated, hazard-proof containment. Therefore this did not allow neither a battery cycler nor a mechanical testing system to be properly operated on the beam. Nevertheless, this test has proved that multi-cell MES Composite modules can safely undergo concurrent mechanical/electrochemical experiments. More thorough experiments are underway to characterize the MES Composites in details.

CONCLUSION

The design rationale, fabrication, and preliminary characterization of the MES Composites have been presented in this paper. The MES Composites implement through-thickness polymer reinforcements through perforations in Li-ion battery electrode stacks, mechanically joining two structural CFRP facesheets that also serve as the electrochemistry housing. It has been shown that:

- Despite a large deviation from a standard pouch cell construction, the electrochemical performance, specifically the cycle-life and apparent capacity, of the MES Composites could be maintained at the same level as a Li-ion battery.
- The mechanical architecture of the MES Composites significantly increases the bending rigidity by preventing relative shearing of the layers, allowing the structural facesheets to be efficiently utilized.
- Small-scale multi-cell prototype modules have shown that the MES Composites are viable for concurrently providing electrical power and bearing mechanical loads, and potentially result in a light-weight multifunctional system.

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