Abstract

This paper reports on the recent progress towards the development of power composite structures capable of energy harvesting and storage in addition to load bearing. The process of physically embedding all-solid-state thin-film lithium-ion energy cells into a carbon fiber reinforced plastic (CFRP) and the performance of the resulting power composites are reported. The embedded thin-film lithium energy cells did not significantly alter the mechanical properties of the composite (modulus and strength) under quasi-static uniaxial loading conditions. The embedded energy cells performed at baseline charge/discharge levels up to a loading of about 50% of the CFRP tensile strength.

Keywords: A. Smart materials; A. Carbon fibres; B. Mechanical properties; B. Electrical properties

1. Introduction

Films, wires and particles up to a few hundred nanometers in their smallest dimension offer physical properties radically different from those found in their bulk counterparts [1]. A new frontier in materials science and engineering is now open to the development of new devices with configurations heretofore unthinkable. Hybrid composites can now be made by embedding micro-thin-film energy-storage [2], piezoelectric [3], photovoltaic [4,5], and thermoelectric [6] devices into composite laminates having multifunctional capabilities, thereby saving weight and volume. The properties of each component can be fine tuned to meet specific requirements.

Embedded technology is significant in applications where scattered ambient energy can be harvested from a variety of sources by utilizing piezoelectric, thermoelectric and photovoltaic generators to provide localized and autonomous power in remote locations where sensors and other devices may require, e.g., isolation from EMF or thermal radiation, thereby eliminating heavy power transmission cables to and from centralized power sources to save space and weight. The piezoelectric and thermoelectric generators can further benefit from optimization by being embedded in structural composites to take advantage of their superior strength to weight ratio, while photovoltaic generators, i.e., solar cells can be integrated directly into the CFRP surface by either direct printing of dyes to produce solar power [5] or by structural integration of photovoltaic thin-films, and thus realize additional space and weight savings. The harvested energy can be stored in thin-film energy cells directly embedded into CFRPs and further eliminate the weight and volume associated with their packaging.

The examination of the current difficulties in the field of multifunctional composites requires a systems perspective stance. The selection and optimization of substrates and their interfacial bonding to epoxy polymers, component resistance to pressure and temperature, analysis of micro stresses transfer between physically dissimilar interfaces, e.g., from substrate to matrix to carbon fiber and vice-versa...
and interconnection minimalization are some cases in point. The resulting hybrid composites should behave within established parameters in the allowable elastic region without adversely affecting the performance of its various components. Overcoming these difficulties is of significance to the multifunctional composites field at large, and in particular to the understanding of the elasticity of hybrid composites.

Particular care and consideration are required in the manufacture of multifunctional composites due to the different characteristics of their components. To this endeavor, work was done previously to ascertain the mechanical properties of thin-film devices, and their ability to undergo flexure and pressure without suffering damage [7,8]. The effects of flexure were investigated by introducing incrementally larger deflections to all-solid-state lithium energy cells, starting at its un-deformed state. At each successive flexure increment, a complete charge/discharge cycle was performed. Up to a flex ratio of about 2%, no effects of mechanical flexure on electrical energy cell performance were observed, and the energy cells exhibited no apparent degradation in their energy storage performance. However, more thorough testing is required to establish long-term performance and reliability after exposure to uniaxial tensile loading. Structural failure occurred at deflections higher than 2½% flex ratio [7]. Similarly, the ability of all-solid-state thin-film lithium-ion energy cells to withstand the uniaxial uniformly distributed surface pressure of about 0.55 MPa required for embedding in laminate carbon fiber reinforced plastics (CFRPs) composites in an autoclave, as well as their maximum uniaxial surface pressure operational limit were investigated. Uniform uniaxial pressure was introduced in incremental amounts to the energy cells and, while the uniaxial pressure was held constant, a complete charge/discharge cycle was performed. Up to a pressure of about 2 MPa, no discernible effects resulting from the applied uniaxial pressure were observed. The energy cell specimens under investigation performed reliably and predictably with charge/discharge rates well within the range of its baseline profile. Abrupt failure occurred for uniaxial pressures over 2 MPa [8].

The multifunctionality should be added optimally by taking advantage of the space traditionally reserved for simple load bearing. The embedded devices will benefit from this integration as they also become shielded from hostile external environments by the structural part. The key to the success of a multifunctional structure lies in the synergistic interaction between its structural and non-structural parts in a way that causes little or no degradation of the unifunctional structure and non-structural functional performance, and with measurable improvement in overall system performance.

When compared to other battery technologies, the overall energy density of the all-solid-state thin-film energy cells is low at present due to the weight ratio between its active components and the mica substrates [7]. Non-conducting substrates cannot be completely removed and are required due to the high conductivity of ubiquitous carbon fibers present in CFRPs. It is mandatory to have an electrically isolating layer between the anode/cathode and the conductive carbon fibers, as well a layer that effectively seals and prevents moisture and ambient air from coming into contact with the lithium metal in the anode, the solid electrolyte and the cathode. Thus, the mica substrates are in itself a multifunctional material, as they provide a suitable base to build the energy cell that must be electrically non-conductive, chemically stable, resistant to high temperatures, flexible, highly impermeable to ambient air and moisture, and have good adhesion characteristics to the composite epoxy matrix. Future technological developments may greatly reduce the thickness of the energy cell substrates to an absolute minimum, thus raising the overall energy density near or above 200 W h/kg when coupled to other improvements. Other battery technologies cannot be made into thicknesses of 150 μm or less, as it is currently possible with all-solid-state energy cells, and they often contain liquid VOC electrolytes. These and other considerations favor all-solid-state energy cells as viable candidates for embedding in micro-thin CFRPs undergoing 120–180 °C high-temperature autoclave curing. Due to their ultra-thin thickness, flexibility and appropriate resistance to temperature and pressure, all-solid-state energy cells offer the capability of being incorporated directly into CFRP composites to provide autonomous power that can be combined with other devices and enable multifunctionality. Power bussing and interconnection of the energy cells in the composite do require careful planning and attention. Flat flexible cable provides a resilient, easy to work with and customizable solution that performs well with the manufacturing and autoclaving process. Other, more recent technologies such as direct printing (DP) may also offer other viable solution alternatives and are being investigated.

Applications are plentiful in areas where an autonomous power source is required, i.e., electrical power is needed without the extra weight and difficulty of power distribution wires such as in medical implants, micropumps, micro-actuators [9], drug delivery systems, autonomous remote sensing, personal digital assistants (PDAs), portable personal computers (PCs) and electronics, mobile equipment, micro-electromechanical systems (MEMS) for satellites, micro-satellites [9–11], bio-MEMS, lab-on-a-chip, smart structures, health monitoring systems (HMS), active radio-frequency identification (RFID), autonomous micro-mechanical sensors and actuators [12], micro aerial vehicles (MAVs) [13], and unmanned aerial vehicles (UAVs) [14].

The main objective of this work was to develop an energy storage structure by embedding solid-state thin-film lithium energy cells into carbon fiber reinforced plastic composites. A successful energy storage structure must satisfy the following two requirements as a minimum: (1) the embedded energy cell is still able to charge and discharge not only as before embedding but also under mechanical loading, and (2) the energy storage structure
has no degradation in mechanical performance. We demonstrate that such an energy storage structure is possible.

2. Experimental

Two different types of 12 K unidirectional carbon fiber prepregs were used: AS4/3502 Magnamite from Hexcel Corp. with a curing temperature of 177 °C, and T700SC/RS-30G from YLA, Inc. with a lower curing temperature of 120 °C. The layup consisted of two layers of carbon fiber prepregs at 90° to each other laid up symmetrically on each side of the energy cell and expressed by [0/90]s, adding up to a total of four layers (see Fig. 1). The energy cell was located squarely in the geometric center of the test coupon as shown in Fig. 2. The cross-section changed in thickness in the embedment region by an out-of-plane amount of about 150 μm on average, about equal to the thickness of the energy cells. Average thickness profiles of the thin-film energy cells were reported in an earlier work [7]. The structural performance of the CFRP did not suffer any significant impairment under quasi-static uniaxial loading conditions, as demonstrated by the uniaxial tests described hereafter. The sampling rate for the uniaxial tensile loading data acquisition was taken at 20 samples per second. This multifunctional configuration can best be utilized in applications where both high strength and autonomous power are required.

Front Edge Technologies (Baldwin Park, CA) provided the thin-film lithium-ion energy cells used in this study, currently in commercial production, with a nominal voltage of 3.6 VDC [2], a lifetime of 1000 charge/discharge cycles of up to 100% depth-of-discharge and a specific energy of about 200 W h/kg without including the packaging mass. They have nominal square dimensions of about 25 mm on the side and an average mass of (0.1803 ± 0.0061) g, measured from a sample pool of 10 cells. The energy cell packaging for the configuration used in this study consists of similar top and bottom mica substrates about 50 μm thick each. The mica used as the substrate is muscovite, a phyllosilicate mineral of aluminum and potassium with chemical formula KAl₂(AlSi₃O₁₀)(F,OH)₂ having a highly perfect basal cleavage that yields remarkably thin and flexible laminae. The top and bottom mica substrates are held together by an all-around 40 μm polymer layer of Surlyn, poly(ethylene-co-methacrylic acid) (EMAA, Dupont) sealant that is impervious to moisture and air. In this configuration, the energy cells have a charge capacity of about 2 mAh/g and an energy density of about 7.2 W h/kg when the packaging mass is included.

The utmost care was taken in the preparation of the wiring connections to the energy cell electrodes due to their physical fragility. The anode and cathode electrodes consist of a 100 nm thick copper layer and a platinum layer of the same thickness, respectively. Both are directly applied onto the bottom mica substrate. These electrodes were found to be extremely fragile and easily peeled off from the substrate with only minimal stress. A polyester-coated flat flexible non-porous peel-ply is used to protect the electrodes and prevent them from peeling off during handling.

Fig. 1. Layup schematic to embed a thin-film lithium energy cell in CFRP.

Fig. 2. Charge/discharge testing of an embedded energy cell: (a) CFRP specimen with embedded energy cell (dimensions in mm) and (b) specimen installed on an Instron 4483 for tensile testing and hooked up to a Keithley Source Meter for charge/discharge measurements.
cable (FFC) (Nicomatic Inc., Warminster, PA 18974) 230 µm thick and about 1.5 mm wide was connected to the electrodes, having a single copper conductor, rated at 100 °C for continuous operation and 150 °C for short periods. The connections between the FFC and the energy cell electrodes were done using high purity silver paint (SPI, Inc.) cured in a regular oven at 65 °C in air for about 2 h. Afterwards, the energy cells were pre-sealed along the edges and over the electrodes with vinyl ester resin and cured in a regular oven at 65 °C in air for 8 h. The vinyl ester was chosen due to the compatibility of its functional groups with the mica substrate and high mechanical properties.

The all-solid-state thin-film lithium-ion energy cells to be embedded were initially subjected to three consecutive charge/discharge cycles to establish a performance baseline. The charging was done at a constant voltage of 4.2 VDC and a limiting current source of 1 mA using a Keithley SourceMeter 2400 under a General Purpose Instrument Bus (GPIB) control program written in Microsoft Development System (MDS) C specifically for this purpose. The real time discrete current and voltage were measured at one-second intervals and logged to a text data file with cycle start/end times and time sequence for each data set. The energy cells are considered to be fully charged when the voltage drops to 3.0 VDC. For the baseline tests, the energy cell was charged and discharged without being subjected to any mechanical loading and at ambient conditions. The charge/discharge current of 1 mA used in this work corresponds to an average 2.5 C discharge ratio (1 mA/0.4 mAh), which is more severe than the commonly used nominal discharge ratio of 1 C found in the literature [15]. However, the former value is within the normal operating parameters for this type of energy cells, which can accept charge/discharge ratios higher than what are normally expected, without suffering damage.

The discharge is used to define the energy cell capacity, C, in units of mAh. The discrete data acquired was taken to Matlab and integrated using the trapezoidal rule to calculate the energy cell capacity, with the total charge/discharge adjusted for time accuracy. The energy cell capacity is defined as

\[ C = \int_{0}^{\tau} i dt \] (1)

where \( \tau \) is the upper time limit of integration. During charge, \( \tau \) corresponds to the time when the current \( i(t) = 50 \mu A \) is reached. During discharge, \( \tau \) is the time when the voltage \( v(t) = 3.0 \) VDC is reached.

One of the most useful energy cell performance metrics is the Ragone plot [16], which correlates the specific energy (energy/mass) with the specific discharge power (power/mass), or energy density (energy/volume) with the discharge power density (power/volume). However, the multifunctional composite energy-structure application in the present work introduces another variable: mechanical loading. Therefore, the metric of choice for the present work was the charge/discharge capacity at different load levels.

Tensile tests were performed on CFRP specimens as follows:

1. Without any embedded energy cell to obtain the baseline laminate properties.
2. With an embedded energy cell to study the effect of an embedded cell.
3. With an embedded energy cell concurrently with a charge/discharge cycle at 150 MPa stress increments (see Fig. 2) to study the effect of mechanical loading on energy cell performance.

The [0/90]s CFRP coupons were laid up following the schematic in Fig. 1, and were fabricated in an autoclave with the recommended cure cycle for each prepreg used (see Fig. 4).

### 3. Results and discussion

The tensile test results are summarized in Table 1 for various configurations, where NE stands for non-embedded, and E for embedded with an energy cell. The energy cells embedded in the specimens listed in Table 1 were not tested for their charge/discharge performance. Rather, they were used only to investigate the effect of an embedded cell on the mechanical properties of the laminate. The pres-

<table>
<thead>
<tr>
<th>Lot no. – sample no.</th>
<th>CFRP type</th>
<th>E/NE</th>
<th>Thick (mm)</th>
<th>Width (mm)</th>
<th>Gage (mm)</th>
<th>Modulus (GPa)</th>
<th>Strength (MPa)</th>
<th>Strain (%)</th>
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</thead>
<tbody>
<tr>
<td>#1-1</td>
<td>AS4/3502</td>
<td>NE</td>
<td>0.64</td>
<td>51.5</td>
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<td>34,160</td>
<td>803.4</td>
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<td>AS4/3502</td>
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<td>1.902</td>
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<tr>
<td>#1-4</td>
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<td>49,440</td>
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<tr>
<td>#1-1</td>
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<td>NE</td>
<td>0.62</td>
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<td>96.75</td>
<td>44,740</td>
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</table>

NE stands for ‘non-embedded’, E means ‘embedded’
Fig. 3. Tensile stress–strain curves for laminate specimens with (E) and without (NE) embedded energy cell: (a) AS4/3502 CFRP and (b) T700SC/RS-30G CFRP.

Fig. 4. (a) AS4/3502 \([0/90]\) s CFRP test panel with an energy cell being charged after autoclave cure. (b) Three CFRP test coupons with embedded energy cell after autoclave cure. (c) AS4/3502 cure cycle. (d) T700SC/RS-30G cure cycle.

Fig. 5. (a) T700SC/RS-30G \([0/90]\) s CFRP specimen ready for charge/discharge testing under mechanical load. (b) Charge/discharge capacity results (1: as-received; 2–4: before embedding; 5–7: after embedding). (c) Charge/discharge capacity results under stress increments of 150 MPa.
ence of a thin-film energy cell embedded does not appear to significantly alter the quasi-static uniaxial mechanical properties of the CFRP laminate. The corresponding uniaxial tensile stress–strain plots are shown in Fig. 3a and b. They indicate a slight increase in modulus and strength when an energy cell is embedded. For AS4/3502 CFRPs, the average strength and modulus increased on average 13.5% and 29.2%, respectively, from non-embedded to embedded specimens. For T700SC/RS-30G CFRPs, the average strength and modulus increased on average 7.6% and 8.9%, respectively, from non-embedded to embedded specimens.

Fig. 4 shows CFRP panels with an embedded energy cell together with the curing cycles used. Fig. 4a and b depict the curing cycle for AS4/3502 and T700SC/RS-30G, respectively. Fig. 5 shows a T700SC/RS-30G [0/90] specimen with an embedded energy cell ready for charge/discharge testing under incremental tensile loads. The discharge cycle 1 is for as-received specimens, while cycles 2–4 are before embedding. Cycles 5–7 are after embedding but without any loading. Cycles 1–4 in Fig. 5b are under tensile stresses of 150, 300, 450, and 600 MPa, respectively. Typical charge/discharge curves for incremental stresses at 150, 300, and 450 MPa are shown in Fig. 6a and b, respectively. Up to a stress of 450 MPa, the charge/discharge curves compare favorably with the baseline curves obtained prior to embedding. At 600 MPa, the charge current remains asymptotically around 100 µA, never reaching the 50 µA level for the energy cell to be considered fully charged. This is a clear sign of leakage in the cell, presumably due to the damage caused by mechanical loading. However, the subsequent discharge behaviour does not appear too much different from the baseline behaviour.

Fig. 7 shows fractured composite specimens; one without embedded cell (a) and the other with an embedded cell (b). It is interesting to observe that Fig. 7a shows a clean fracture, whereas Fig. 7b shows a fairly extensive amount of longitudinal splitting. This was not typical of all frac-
tured specimens, either embedded or not. The opposite of what occurred with the two specimens shown in Fig. 7a and b was also observed. In other words, some embedded specimens broke cleanly, some broke in longitudinal splinters, and similarly for non-embedded specimens. What is true for all specimens that were tested is that they all broke suddenly and sharply at the last sampling point, and with no evidence of yielding.

4. Conclusions

This study has demonstrated the capability of the all-solid-state thin-film lithium-ion energy cells to successfully withstand both the temperature and pressure required for CFRP composite manufacturing in the autoclave at 120 °C. The charge/discharge rates of the embedded energy cells did not significantly deviate from prior standard charge/discharge baseline parameters energy established at standard conditions before embedding. Furthermore, the embedded cells did not show much deviation from the charge/discharge baseline performance when subjected to a uniaxial tensile loading up to 450 MPa. The maximum tensile load that can be applied without degrading the performance of the embedded energy cell was found to be about 50% of the tensile strength of the CFRP.

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References