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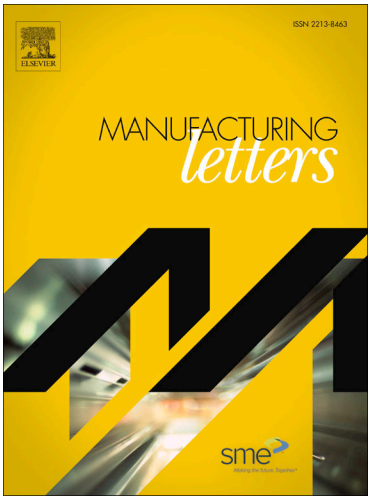

Letters

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Additive Manufacturing of 3D Structural Battery Composites with Coextrusion Deposition of Continuous Carbon Fibers

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Abstract

There is a growing interest in fabrication of structural battery composites to achieve mass-less energy storage. Additive manufacturing would allow customization of their battery form factor to fit specific needs. In this study, a multi-axis coextrusion deposition technique is proposed to fabricate a 3D structural battery composite with continuous carbon fibers coated by solid polymer electrolyte (SPE). The SPE-coated carbon fibers are coextruded with cathode doped matrix materials. All the printed complex structural battery composites successfully power up LEDs. Further mechanical and electrochemical characterization demonstrates the potentials of the additively manufactured composites in electrical energy storage and load bearing.

Keywords: Additive manufacturing; Structural battery composites; Lithium ion battery; Continuous carbon fiber; Solid polymer electrolyte.

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1. Introduction

Growing needs of electric technologies in aviation, automotive, and consumer electronics require further development of high energy storage systems [1,2]. One promising approach is to develop multifunctional composite structures and materials [3–5] to enable mass-less energy storage for electrically powered structural systems [6] in order to achieve improvement of energy and power densities at a system level. In particular, structural power composites are capable of simultaneously carrying mechanical loads and storing electrical energy, and thus have been extensively investigated [4,6–10]. Among them, carbon fiber composites, commonly used as structural materials, show great potentials of being used as structural power composites due to preferable electrochemical properties of carbon fibers [11–13]. A majority of multifunctional carbon fiber composites are based on a laminated composite structure and are fabricated through conventional lay-up processes [3,7], which involve high fabrication costs and long development cycles for components with complex geometries.

On the other hand, additive manufacturing (AM) methods allow flexible design of shape and size, which would further allow a battery form factor to be customized for improvement of energy storage or to fit a given product design [14–16]. In particular, AM techniques have been recently developed to fabricate carbon fiber reinforced thermoplastics based on extrusion deposition process [17–20]. However, their applications in multifunctional composites are limited [21–24]. Most of studies focused on optimization of their mechanical performance [25,26]. Thus, it will be necessary to develop AM techniques to explore applications of carbon fiber composites in structural power composites.

In this study, a multi-axis coextrusion deposition method is proposed to additively manufacture a 3D structural battery composite structure with continuous carbon fibers.

Electrocoating is first used to produce solid polymer electrolyte (SPE) onto each individual carbon fiber. Polylactic acid (PLA), a commonly used thermoplastic material for 3D printing, is infused with active and conductive materials to prepare cathode doped matrix materials that are further used to fabricate the structural battery composites with various geometries. It is worth noting that as previous studies [24] suggested the doped cathode materials would hinder the curing process of photopolymer binders, we propose a new 3D printing process using thermoplastics as feedstock in order to increase loadings of cathode materials. Both electrochemical and mechanical properties are characterized to demonstrate the potentials of the proposed AM method.

2. Experimental Procedure

2.1 3D structural battery architecture

A concentric 3D structural battery composite architecture in Figure 1A was implemented in this study. Carbon fiber works as both anode and current collector. A solid polymer electrolyte individually coated on each carbon fiber is used as electrolyte and separator. SPE-coated carbon fibers are embedded in cathode doped matrix materials that are further assembled with current collector. Dispersed in cathode doped matrix, individually SPE-coated carbon fibers formed a network of micro-battery cells. Due to high surface area between coated fibers and active materials, the obtained structural batteries have potentials of achieving high energy density [4,27].

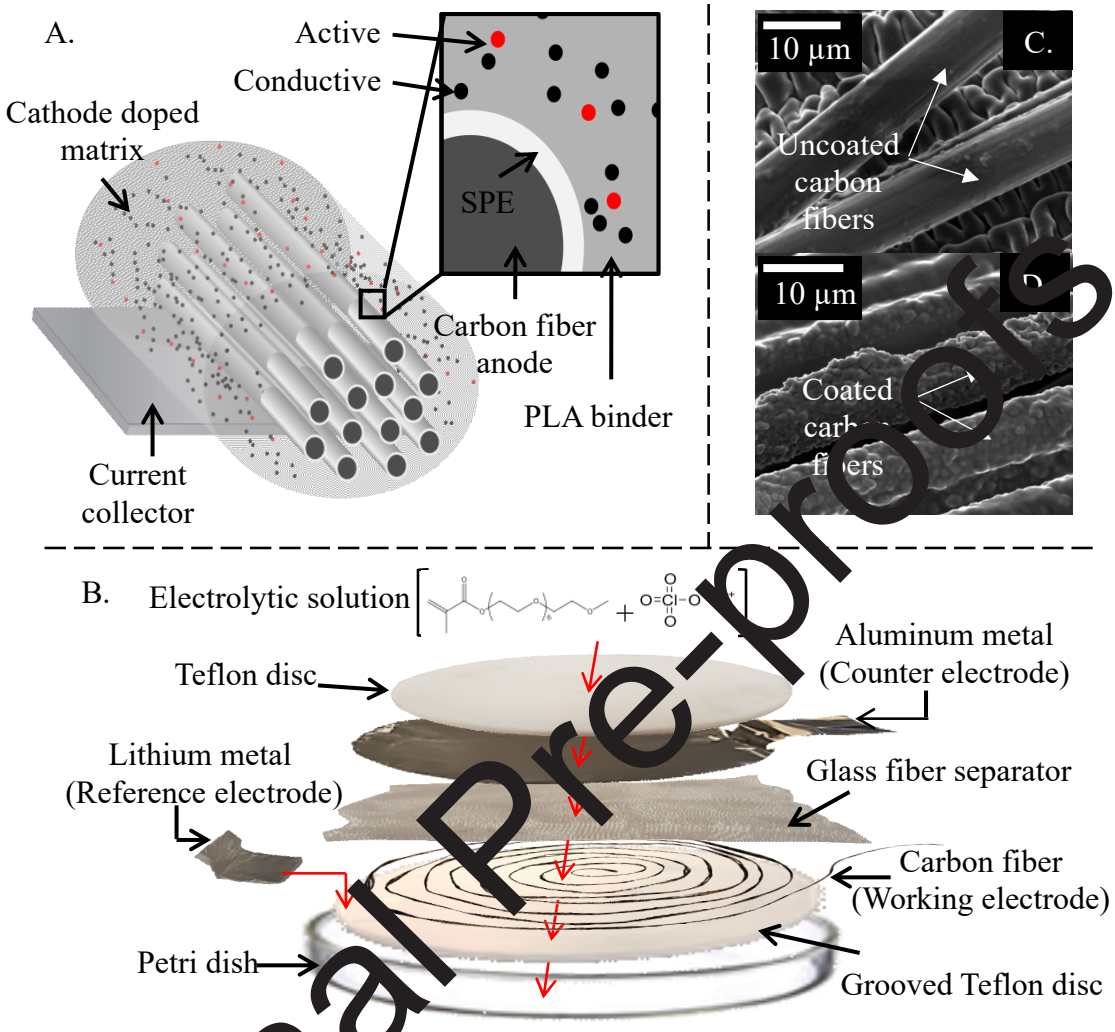

Figure 1. Schematics of the 3D structural battery composite architecture: A. shows the 3D structural battery design; B. shows the electrocoating process to produce solid polymer electrolyte onto continuous carbon fiber; C. and D. show a direct comparison of uncoated and SPE-coated carbon fibers.

SPE coatings [28] were prepared using a three-electrode electrocoating assembly in Figure 1B inside a glove box in an Argon atmosphere (<1 ppm oxygen content and moisture). A carbon fiber tow in Figure 1C with a total length of up to 300 mm could be electrocoated (Figure 1D) to

facilitate 3D printing of various structural battery composite samples. It should be noted that although longer coated carbon fiber length is possibly achieved, correspondingly increased heat generation and thermal induced stress during electrochemical cycling may lead to mechanical and electrical failure [29]. In this study, Polyacrylonitrile (PAN)-based carbon fibers (Toray T800HB, 12000 filaments per rowing) were selected (dried in a vacuum oven at 120 °C for at least four hours to remove moisture) to facilitate printing process for the structural battery composites, together with their favorable electrochemical and mechanical properties [13,30]. It is worth noting that the fiber bundle size may also affect structural battery performance. The solution with 1M $LiClO_4$ (less sensitive to the atmospheric moisture [27]) in methoxy polyethylene glycol (350) monomethacrylate (SR550) monomer was dissolved in Dimethylformamide (DMF by Sigma-Aldrich) with a monomer-to-solvent ratio of 1:2 (by volume) and used in the electrocoating process. The SPE coating was polymerized from the solution, leaving grafted polymer on each individual carbon fiber. A SPE coating of about 2 μm thickness in Figure 1D was obtained with a polarization time of 400 s. The SPE coating thickness was estimated via the scanning electron microscope (SEM) images of the uncoated and coated fibers, by characterizing their cross sections using the FIJI image analyses package.

The cathode doped matrix materials need to have a high electrical conductivity and a high ionic conductivity. Commercial graphene infused PLA pellets (by Blackmagic3D) with an electrical resistivity of 1 Ω·cm were used, where graphene worked as conductive materials, and PLA would serve as binder material to facilitate the proposed AM method. Lithium iron phosphate (by Sigma-Aldrich), commonly used for electrodes of lithium ion batteries, was selected as active material for its high theoretical specific capacity. The pelletized cathode doped matrix materials were then prepared following through dissolving, curing, and drying. While PLA is a commonly

used 3D printing material, a major challenge in the structural battery composites is its very poor ionic conductivity. It was thus converted into an ionically conductive matrix through post cure swelling of printed samples by infusion with liquid electrolytes. A 1:1 (by volume) solution of ethyl methyl carbonate (EMC) and propylene carbonate (PC) with 1 M $LiClO_4$ was used since it was shown to promote stable ionic conductivity and retain mechanical integrity of infused polymers over a long period of time [31]. In this study, all printed samples were infused at 50 ℃ for 24 h and aged for another 24 h prior to testing.

2.2 Experimental setup

To fabricate the proposed 3D structural battery architecture, a coextrusion deposition method in Figure 2A was proposed to additively manufacture the 3D structural battery composite materials. It included a single-screw extruder with its movement controlled by a multi-axis machine, thus allowing drawing toolpaths in three-dimensional space. The extruder rotation speed was used to control the material deposition rate during printing process. The cathode doped PLA pellets were fed through the extruder hopper and melted by the heater before being extruded out through the coextrusion nozzle (4 mm inner diameter). Meanwhile, a continuous SPE-coated carbon fiber bundle was impregnated through the extrusion nozzle [20] and coextruded with the cathode doped PLA melt before being deposited on the print bed layer-by-layer, in an ambient air pressure and temperature. It should be noted that drawing forces during the proposed printing process tend to place the SPE-coated carbon fibers near the top region of each deposition layer in Figure 2B. This would hinder the fiber impregnation into the cathode doped matrix materials. The resulting voids and fiber clumping would severely limit the electrochemical performance of the printed battery samples. Moreover, the coextrusion nozzle may scratch away the SPE coatings.

Any exposed carbon fiber would be in direct contact with the cathode matrix materials and cause short circuiting of the printed structural battery cells. Thus, a 5-axis printing process (with the extruder in Figure 2 mounted on a 5-axis machine) was implemented. The rotational A axis and B axis were adjusted to maintain a constant tilt angle (Figure 2C) between extruder and deposition bead following the printing toolpath. In this study, a tilt angle of 15° was used with a melting temperature of 175 °C, a print speed of 40 mm/min, and a layer thickness of 2.5 mm. A preheated temperature of 45 °C on the print bed was also used to facilitate deposition process. With an extruder rotation speed of 22 RPM, a material output rate of 280 mm³/min was achieved with a typical deposited sample shown in Figure 2D. It is worth noting further optimization of these printing parameters may help improve the performance of printed structural battery composites, the effects of which will be investigated in future studies.

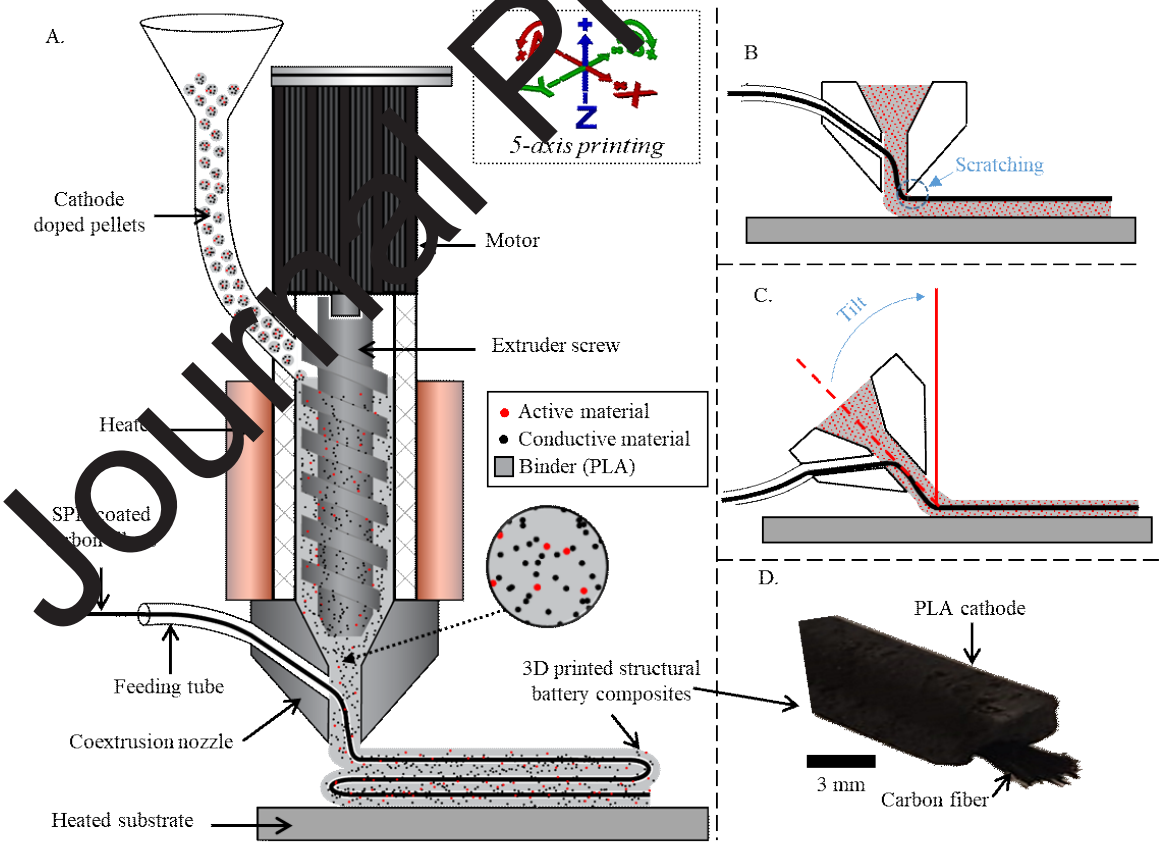

Figure 2. Schematics of the proposed AM method to print structural battery composites with SPE-coated continuous carbon fibers: A. shows the experimental setup, where the extruder is mounted on a 5-axis machine; B. and C. demonstrate the implemented multi-axis printing process; D. shows a typical printed structural battery composite sample.

3. Results and Discussion

To maximize energy capacities, the ratio of active material to conductive material was first optimized to achieve highest ionic conductivity in Figure 3A. Electrochemical Impedance Spectroscopy (EIS) measurements were performed using a Gamry Reference 600+ potentiostat over a frequency range of 1 MHz to 10 Hz at 100 mV pp. Electrical resistivity measurement was made using a Signatone Pro4-4000 Four Point Resistivity System with a Keithley 2400 Sourcemeter. At a fixed percentage of PLA binder, an active material to conductive material ratio of 20:80 yielded a highest ionic conductivity of 1.2 mS/cm. The need to use a relatively high amount of conductive materials was attributed to the presence of high volume of PLA binder, which hindered the electrical contact between active and conductive materials [31]. A corresponding electrical resistivity of 4 Ω·cm was measured for the cathode doped PLA matrix materials, much higher than the as-received graphene/PLA pellets. This was possibly attributed to the addition of active material as well as additional post processing in preparing cathode doped pellets.

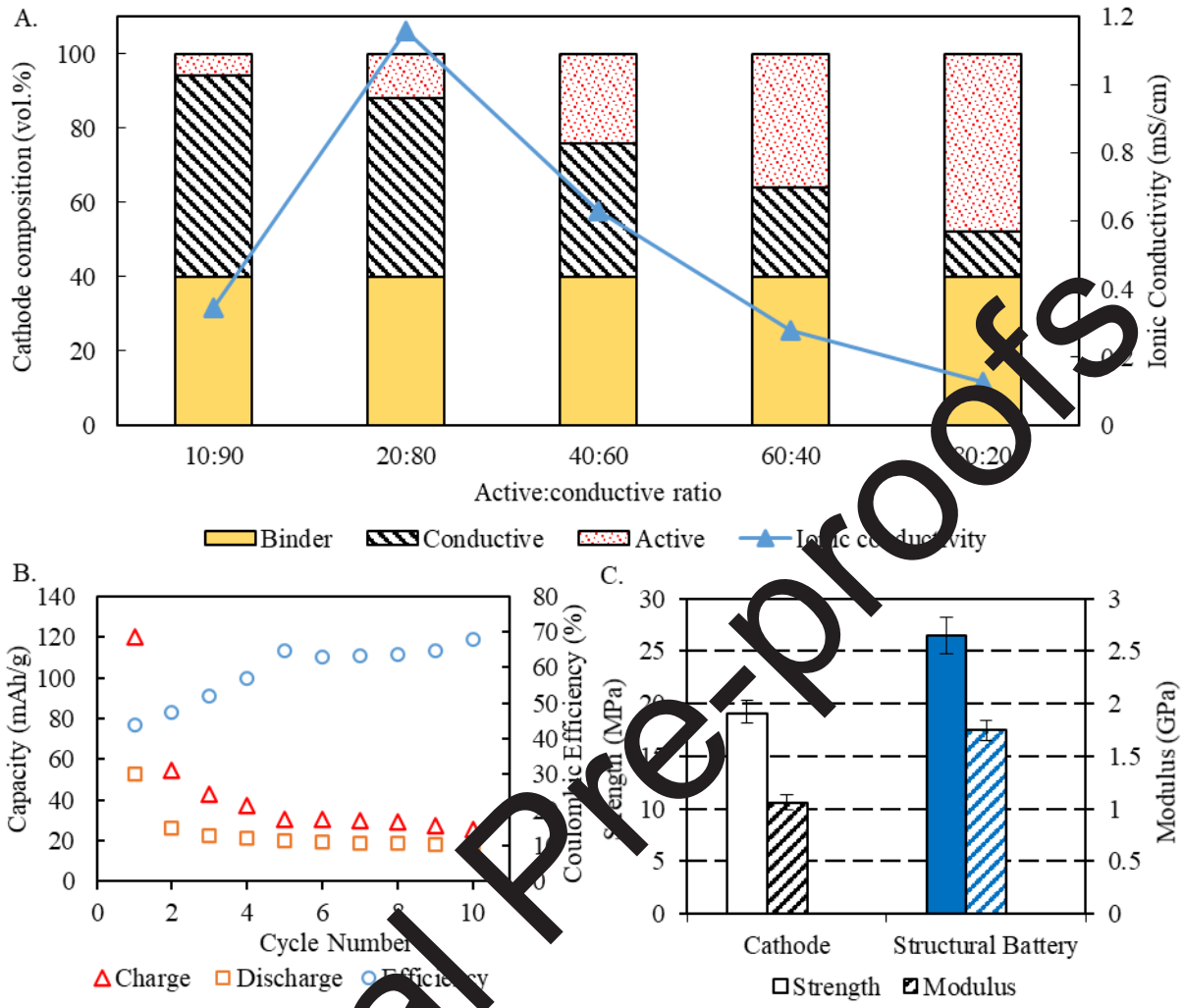

Figure 3. Characterization of the printed samples: A. shows optimization of cathode doped matrix materials; B. shows capacity and Coulombic efficiency of the printed structural battery at a current density of 10 mA/cm^3 at C/2 for 10 cycles; C. shows flexural strength and modulus measured through 4-point bending tests in comparison of printed cathode matrix and structural battery composite samples (80 mm × 10 mm × 5 mm).

The electrochemical performance was characterized through specific capacity measured by a Gamry Reference 600+ potentiostat. The electrochemical performance for full battery cells

was performed within a cutoff voltage range 6.0−1.0 V. The capacity was normalized to the mass of anode active material (i.e. carbon fiber). Figure 3B shows the charging-discharging capacities of rectangular structural battery samples (80 mm × 10 mm × 5 mm) for 10 consecutive cycles with a current density of 10 mA/cm^3 at C/2. The specific capacity of graphite (372 mAh/g) was used to calculate the C-rate. An obvious drop in charging capacity was observed, decreasing from 119.9 mAh/g to 25.5 mAh/g after 10 cycles when it tended to stabilize. The large irreversible capacity loss was attributed to the formation of solid electrolyte interphase [31–33] and trapped lithium in the carbon fiber structure [34]. The discharging capacity of the battery cell was also notably higher than that of a single print PLA battery by fused filament fabrication [31]. It is worth noting that this was mainly attributed to higher loadings of conductive and active materials in the cathode doped matrix materials as enabled by the proposed AM method. Pellet-based extrusion processes typically exhibit better printability for given compositions, which would otherwise lead to clogging or brittle filaments that become too brittle to handle based on filament fusion fabrication. Meanwhile, the improvement was expected to be related to the introduced SPE-coated carbon fibers, which showed high electrochemical performance [28] and would also promote the mechanical performance of the printed structural battery composite samples. On the other hand, for the 10 consecutive cycles, the battery cell yielded an average charging capacity of 42.9 mAh/g and discharging capacity of 23.4 mAh/g, showing an average Coulombic efficiency of nearly 68% after the 10 cycles. The energy density was 7.6 Wh/kg with an average battery cell voltage of 1.8 V calculated over the discharge cycle [31]. These values are substantially lower than energy densities of typical lithium-ion full battery cells [28,35]. The low values were attributed to the relative thick SPE coatings as well as high percentage of PLA binder used to maintain good

printability of the cathode matrix materials, which limited the contact between active and conductive materials.

The mechanical properties of both cathode doped matrix and structural battery composite samples were measured using 4-point bending tests with a support span of 40 mm and a load span of 20 mm at a cross-head speed of 1 mm/min. Three samples of each composition were used to measure the mechanical properties in Figure 3C with the error bars showing the variations in the measured strength and modulus. The transverse modulus of the composite samples was measured in this study. With the introduction of 15 vol.% continuous fiber reinforcements, 39% in flexural strength and 66% in flexural modulus were achieved compared to those of cathode doped matrix materials. These well demonstrated the potentials of the printed carbon fiber structural batteries in load bearings while working as batteries to store electrical energy. Meanwhile, the mechanical properties were lower than conventional carbon fiber composites, which are believed to be related to the proposed AM process. The doped cathode materials are expected to increase the viscosity of PLA matrix materials, thus lowering fiber impregnation quality and possibly leading to a higher void fraction, which will be examined in follow-up studies.

The capability of the proposed AM method was further demonstrated through printing structural battery composite samples of various geometries in Figure 4. As the AM method was able to fabricate a full structural battery cell in one print, the obtained samples just needed to be assembled with aluminum current collector before being charged to power up LEDs.

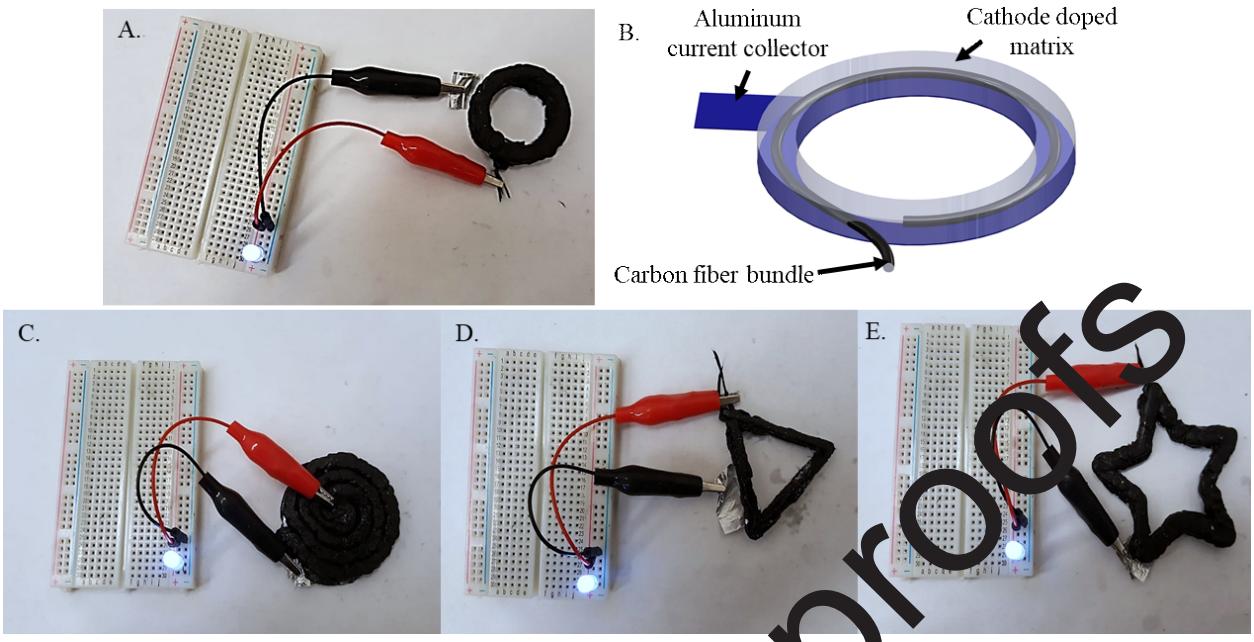

Figure 4. Printed structural battery composites illuminating LEDs with a ring-shaped structure shown in A and the schematics of its full battery assembly shown in B. A similar full battery assembly process has been used for a disc-shaped structure in C, a triangle structure in D, and a star-shaped structure in E.

4. Conclusion

A coextrusion deposition method was proposed to additively manufacture a 3D structural battery composite with continuous carbon fibers. Cathode doped matrix materials were coextruded with solid polymer electrolyte coated carbon fibers. The structural battery cells fabricated in single print were shown to successfully power up LEDs. The implemented pellet-based extrusion enabled high loadings of active and conductive materials and promoted the obtained electrochemical performance. The introduced SPE-coated carbon fibers not only enabled electrical energy storage but also promoted the mechanical performance of the printed structural battery composites. With individually SPE-coated carbon fibers dispersed in cathode matrix working as micro-battery cells,

further improvement of the proposed AM method will help explore their potentials of achieving high energy density.

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