

# Multifunctional Characterization of 3D Printed Structural Battery Composites for Battery Health Monitoring

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## ABSTRACT

As a promising lightweight multifunctional material, carbon fiber structural battery composites have great potentials to enable longer service life and operating distance for the rapidly increasing mobile electric technologies. While simultaneously carrying mechanical loads and storing electrical energy, the developed multifunctional composites can achieve “massless” energy storage and further extend to sensing and energy harvesting for self-powered structural health monitoring. However, it is still very challenging to predict the state-of-health of structural battery composites due to a lack of understanding of underlying coupled mechanical-electrochemical phenomena during operation. In this study, we first use a novel 3D printing method to fabricate and tailor microstructure of the multifunctional carbon fiber composites. With an optimal electrode layer thickness of 0.4 mm, the stable specific capacity at 1C reaches over 80% of the theoretical capacity of the electrode active materials (lithium iron phosphate) with an average energy density of 152 Wh/kg observed. The corresponding flexural modulus and flexural strength are 8.7 GPa and 69.6 MPa, respectively. The state-of-health of 3D printed structural battery composites under electrochemical cycling and external mechanical loadings are also investigated. The mechanical performance is not affected by the electrochemical charge-discharge processes. The structural battery composites under three-point bending testing show good capacity retention with rapid degradation of electrochemical performance observed near fracture point. The findings from this study not only provide insights for monitoring the state-of-health of structural battery but also show mechanical-electrochemical coupling as a potential way of self-powered structural health monitoring through the 3D printed multifunctional composites.

## INTRODUCTION

As a new type of energy storage device, structural battery composite materials have the advantages of high energy, simplified structure, long cycle life, and flexibility [1-4]. Its lightweight and high-strength characteristics are mainly used in new energy vehicles, aerospace, military, and other fields [5-9].

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The stacked structure battery technology prepared traditionally has good multifunctional performance. Structural batteries made of composite structures prepared from carbon fibers have made great progress in the manufacturing process and battery performance, but there are still some problems to be solved. ASP et al. designed a structural battery composite consisting of a CF negative electrode and a positive electrode supported by an Al film, separated by a glass fiber (GF) separator in a structural battery electrolyte (SBE) matrix material [1]. They compared GF fabric separators, Whatman GF/A, and GF plain weave fabrics were used as model materials to study the effect of separator thickness and structure, and the multifunctional performance of structured batteries. They obtained full cells with an energy density of  $24 \text{ Wh/kg}^{-1}$ , an elastic modulus of 25 GPa, and a tensile strength of over 300 MPa [1]. However, the energy density of structural batteries prepared by this method has not reached the energy density of current lithium-ion battery products [2]. Moyer's team designed current collectors utilizing carbon fibers for graphite/carbon fiber anodes and Lithium iron phosphate (LFP)/carbon fiber cathodes [3]. They used a conventional composite lamination process integrated directly into the carbon fiber panels to produce a full-cell lithium-ion battery that absorbs power and stores it in the CubeSat's structural walls [3]. Fabrication of structural batteries by conventional lamination processes has the disadvantages of high manufacturing costs, long development cycles for components with complex geometries [4], small batch production, poor surface finish and dimensional accuracy, and low mechanical strength [5].

3D printing techniques have gained growing interests in fabricating batteries. Wei et al. developed a design for a fully 3D printed LIB consisting of thick electrodes [6]. High-performance thick-electrode custom lithium-ion batteries were fabricated using functional inks and ultraviolet (UV) curable packaging. Their proposed additive manufacturing method simplifies the process steps such as drying, electrolyte filling, calendaring, clamping, and heat sealing required for conventional LIB fabrication [6]. However, their study only discussed the electrochemical performance of the prepared Li-ion batteries without considering the mechanical properties of the batteries.

Thakur and Dong proposed the use of continuous carbon fibers coated with solid polymer electrolytes coextruded with cathode-doped matrix materials to create 3D structural battery composites and demonstrate their versatility. They added the thermoplastic material polylactic acid (PLA) as a binder material to the solid polymer electrolyte (SPE) fibers. Active conductive materials are used to prepare cathode doped matrix materials, which can be used to manufacture structural battery composites of various geometric shapes [4]. At the same time, they also studied the effect of photopolymer resin as a matrix material on structural batteries [7]. They proposed a new method of impregnating continuous carbon fibers with photopolymers and curing them with a UV laser [7]. Structural batteries fabricated using 3D printing techniques were further studied by Pappas et al. [8]. They discussed the effect of additives on conductivity and printed and selected optimal parameters to prepare the structure of the battery composite. However, due to the high percentage of binder, the battery energy density and CE are lower than other LIBs [11,14-16]. Thakur and Dong also found that the electrochemical and mechanical properties of 3D printed structural battery composites can be effectively improved by changing the solid content and binder content of the cathode slurry [9]. They propose that residual voids play a key role in the multifunctional performance of 3D printed structural battery composites [9].

In this study, a novel drop-on-demand 3D printing method is used to fabricate and tailor microstructure of the multifunctional carbon fiber composites. With an optimal electrode layer thickness of 0.4 mm, the stable specific capacity at 1C reaches over 80% of the theoretical capacity of the electrode active materials (LFP) with an average energy density of 152 Wh/kg observed. The corresponding flexural modulus and flexural strength are 8.7 GPa and 69.6 MPa, respectively. The state-of-health of 3D printed structural battery composites under electrochemical cycling and external mechanical loadings are also investigated. The mechanical performance is not affected by the electrochemical charge-discharge processes. The structural battery composites under three-point bending testing show good capacity retention with rapid degradation of electrochemical performance observed near fracture point.

## EXPERIMENTAL PROCEDURE

### Material Preparation

The material of the samples consisted of glass fibers (Style 1080,10y glass fabric) and 6k carbon fiber fabric (Carbon Fiber Fabric Plain Weave Intermediate Modulus 6k 38"/96.52cm 5.6oz/191gsm Toray T830). The carbon fiber fabric needed desizing in a fume hood. After soaking the carbon fiber fabrics in a dish containing acetone for 8 hours at room temperature, they were submerged in a chloroform solution overnight (minimum 12 h). Desized carbon fiber fabric was dried for 2 hours and then placed in an oven at 80°C for at least 4 hours to remove excess moisture. A photopolymer resin (LOCTITE 3D 3955 HDT280 FST photopolymer black) was used in this study. Liquid electrolytes were composed of ethylene carbonate (EC), propylene carbonate (PC) and lithium perchlorate ( $LiClO_4$  by Sigma-Aldrich). A 1:1 (by volume) electrolyte solution of EC and PC with the addition of 1 M  $LiClO_4$  was found to have the highest electrical conductivity [10].  $LiClO_4$  is less sensitive to atmospheric humidity and is usually used as lithium salt [4, 11, 8]. The EC and PC solutions were mixed in a beaker, and  $LiClO_4$  was slowly added within 1 minutes using a 0.79-inch PTFE magnetic mixer stir bar on an 80 °C hot plate (four E'S Scientific 5 in magnetic hot plates) at 400 rpm until the solution was completely dissolved. The prepared electrolyte is stored in a centrifuge tube and used within 10 h for the best electrochemical performance. The volume of liquid electrolyte solution and photopolymer resin is used to prepare the SPE. Photopolymers mixed with liquid electrolyte solutions can cure rapidly under UV laser while maintaining high ionic conductivity [8, 12, 13].

### Cathode Coating Procedure

Desized carbon fiber fabric and aluminum foil (or copper foil) were bonded together using silver conductive epoxy adhesive (MGChemicals, #8330S-21G, 4 h Working Time). In many studies of the electrical properties of carbon fibers, a metal block or foil (copper, nickel, gold) was pressed onto the fiber, or another conductive layer (evaporated gold, silver filled paint or adhesive) was applied to the carbon fiber, it was beneficial to achieve good electrical contact of fibers [14]. The carbon fiber fabrics and foils were cured in a 65 °C oven for at least 2 h.

The cathode solution should be prepared in a fume hood.  $LiFePO_4$  (Lithium iron phosphate, LFP by Sigma) powder was added to a beaker containing Dimethylformamide (DMF) solution. Poly (diallyl dimethylammonium) chloride (PDDA) and ethanol were slowly dissolved in the LFP-DMF solution and stirred using a 24 V homogenizer for 20 min. Graphene, carbon black, and DMF solution were mixed with the previously prepared solution and mixed with a homogenizer for 20 min.

## Experimental setup

The preparation of the 3D printed structural battery composite is shown in Fig 1 through a drop-on-demand additive manufacturing method. The preparation of the shell, diaphragm, laminate, and curing is done simultaneously during the printing process. The Snapmaker 3D printer has a roller mounted below the middle linear module. The tilt angle of the laser is 45 degrees. The roller under the printer can exert external force during the printing process, which is conducive to a more uniform surface layer and can also increase the contact between layers. The structural battery composite consists of 6 layers of carbon fiber and 14 layers of glass fiber. The 3D diagram of structural battery composites is shown in Fig 2. Each seal has one layer of carbon fiber and two layers of fiberglass. Carbon and glass fibers were placed in the middle of the scanned area and pure resin was added for the preparation of the battery case (Fig. 1a). The third and fourth layers of the battery composite structure consist of SPE, negative electrode, and positive electrode. The negative electrode consists of copper foil and desized carbon fiber. The positive electrode was coated carbon fiber (Fig. 1b). The printer's heated bed was kept at 80 °C throughout the printing process. The roller rolled once over the resin-covered fiberglass (Fig.1c). This step removes excess resin and prevents large solids from damaging the surface of the material. At the same time, the cylinder exerts pressure on the material during printing, resulting in better contact between layers. Carbon and glass fibers were cured using 100% laser power (Snapmaker 3D printer) at a lateral speed of 500 mm/min and a hatch spacing of 0.5 mm (Fig.1d) with an optimal layer thickness of 0.4 mm [17].

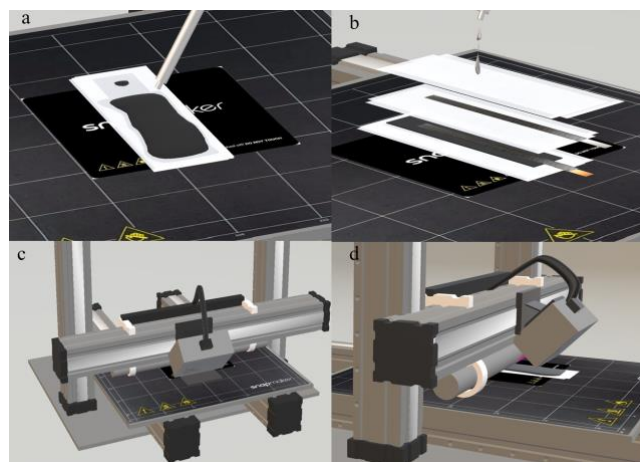


Figure 1. 3D printing process for structural battery composites (a) adding resin and glass fibers (b) layup (c) rolling (d) laser curing.

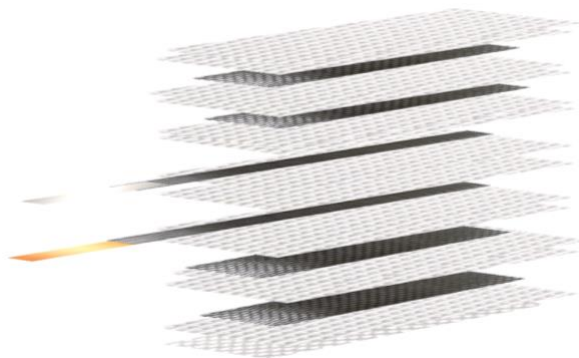


Figure 2. 3D diagram of structural battery composites.

### **Electrochemical Testing**

The electrochemical performance of 3D-printed structural battery samples was measured by galvanostatic charge and discharge cycles using the GAMRY Reference 600+. Before the electrochemical test, structural battery samples were charged/discharged between 2.0 V and 3.5 V at a 0.1C for 10 hours to precondition the battery. The cells were then subjected to charge/discharge cycles at 1C rate after completion of the pretreatment for electrochemical characterization. The capacities of the 3D printed structural batteries were normalized to the cathode active materials. The tests were conducted within cut-off range between 3.5 V and 0.5 V.

### **Mechanical Testing**

The mechanical properties of the samples were measured using an Instron 5965 tester. The sample was placed in the middle of the instrument. Experimental flexural properties were obtained by three-point flexural testing with a crosshead speed of 1 mm/min, according to the ASTM D7264/D7264M-21 standard. The support span for the three-point bending test of samples was 40 mm. The structural battery composite samples (60 mm in length and 13 mm in width) were prepared and used to measure the flexural strength and modulus.

## **RESULTS AND DISCUSSION**

The ionic conductivity of SPE with different resin content is shown in Fig. 3. SPEs with lower resin content yielded lower ionic conductivity. When the resin content was 15 vol.% and 10 vol.%, damage appeared on the sample's surface. The surface of the samples at 20 vol.% resin content is not uniform. 25 vol.% and 30 vol.% resins were used in this study. The average ionic conductivity of SPE with 25 vol.% resin content is 0.00196/(cm\*ohm).

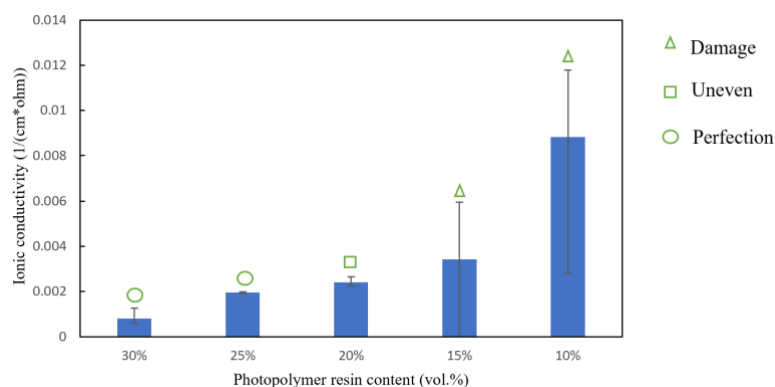


Figure 3. Ionic conductivity of SPE with different resin contents.

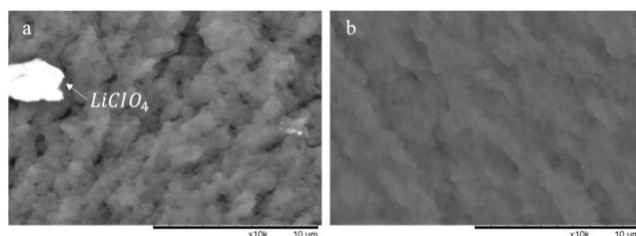


Figure 4. SEM images of samples with different electrolyte ratios (a) 25 vol.% resin, (b) 30 vol.% resin sample at 10k magnification.

Scanning electron microscopy (SEM) was used to analyze the effect of different resin ratios on the microstructure of the samples. The fractured samples were immersed in filtered water for 24 h to extract the liquid electrolytes ( $LiClO_4$ , EC, and PC) and excess resin. The samples were dried in a vacuum oven at 60 °C for 14 h. Fractured cross-sections were coated for 1 min using a Denton Au/Pd Coater in a vacuum atmosphere. The sputtering setpoint was set to 8 mA. SEM images were analyzed by Tabletop Microscope TM-1000 (HITACHI). Figs. 4a and 4b show the presence of nanoporous network polymers on the surface of the samples. This network structure allows liquid electrolytes to exist in the pores of the polymer. The white particles in Fig.4a were  $LiClO_4$ . The 25 vol.% resin sample had more nanopores than the 30 vol.% resin sample.

The measured flexural modulus and strength are shown in Fig. 5. Samples 1-3 are structural battery composites prepared without electrochemical testing. Samples 4-6 were subjected to a three-point bending test after 8 days after fabricating the structural battery. Samples 7-9 were subjected to electrochemical tests (90 cycles, about 8 days) after the structural battery was prepared, and mechanical performance tests were then performed after the test was completed. The average flexural modulus and flexural strength are 8.7 GPa and 69.6 MPa, respectively, for samples 1-3. The mechanical properties of samples 4-6 are similar to those of samples 7-9, and the battery cycling tests did not obviously affect the obtained mechanical properties.

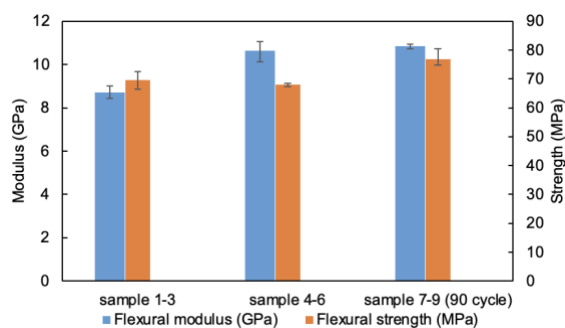


Figure 5. The average flexural modulus and strength of samples 1-9.

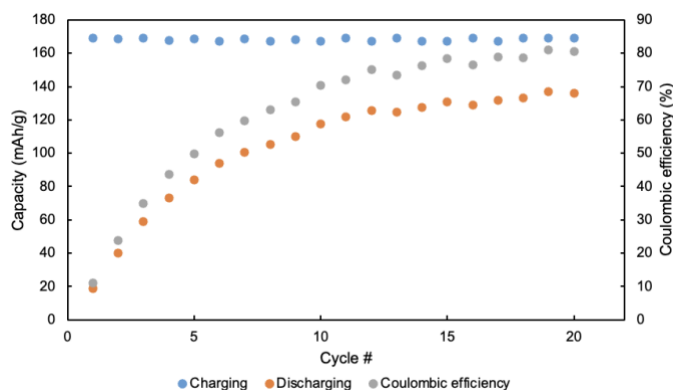


Figure 6. Capacity and CE of 3D printed structural battery samples at a current of 0.0004 Amp(s) for 20 cycles

The 3D printed samples showed stable electrochemical charge-discharge processes in Fig. 6 with no obvious capacity fading up to 20 cycles, demonstrating the potentials of the sealing layers. The discharge capacity and CE gradually stabilized after 15 cycles. An average specific capacity of 89.5 mAh/g at 1C was obtained, reaches over 80% of the LFP theoretical capacity. The average energy density was 152 Wh/kg with a nominal voltage of 1.55 V during discharge. Our further testing showed that the structural battery composites under three-point bending testing show good capacity retention with rapid degradation of electrochemical performance observed near fracture point.

## CONCLUSIONS

In this study, the 3D printed structural batteries achieved good electrochemical and mechanical performance. The measured average flexural modulus and flexural strength of the structural battery are 8.7 GPa and 69.6 MPa, respectively. The stable specific capacity reached over 80% of the LFP theoretical capacity with an average energy density of 152 Wh/kg observed. Further coupled mechanical-electrochemical testing showed that the mechanical performance was not obviously affected by electrochemical cycling. A good capacity retention was obtained until reaching fracture point. The findings provided insights in future design and fabrication of structural battery composites for multifunctional applications.

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