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Three-Dimensional Printing of a Complete Lithium Ion Battery with **Fused Filament Fabrication**

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Supporting Information

ABSTRACT: The ability to 3D print lithium ion batteries (LIBs) in an arbitrary geometry would not only allow the battery form factor to be customized to fit a given product design but also facilitate the use of the battery as a structural component. A major hurdle to achieving this goal is the low ionic conductivity of the polymers used for 3D printing. This article reports the development of anode, cathode, and separator materials that enable 3D printing of complete lithium ion batteries with low cost and widely available fused filament fabrication (FFF) 3D printers. Poly(lactic acid) (PLA) was



infused with a mixture of ethyl methyl carbonate, propylene carbonate, and $LiClO_4$ to obtain an ionic conductivity of 0.085 mS cm^{-1} , a value comparable to that of polymer and hybrid electrolytes. Different electrically conductive (Super P, graphene, multiwall carbon nanotubes) and active (lithium titanate, lithium manganese oxide) materials were blended into PLA to determine the relationships among filler loading, conductivity, charge storage capacity, and printability. Up to 30 vol % of solids could be mixed into PLA without degrading its printability, and an 80:20 ratio of conductive to active material maximized the charge storage capacity. The highest capacity was obtained with lithium titanate and graphene nanoplatelets in the anode, and lithium manganese oxide and multiwall carbon nanotubes in the cathode. We demonstrate the use of these novel materials in a fully 3D printed coin cell, as well as 3D printed wearable electronic devices with integrated batteries.

KEYWORDS: ionic conductivity, electrical conductivity, lithium electrolyte, anode and cathode, poly(lactic acid) (PLA), 3D printing

1. INTRODUCTION

A majority of consumer electronic devices, electric vehicles, and aerospace electronics are powered by lithium ion batteries (LIBs) because of their high energy and power densities.¹⁻³ Commercially available lithium ion batteries (LIB) consist of an anode, cathode, electrolyte, separator, and current collectors fabricated in multilayer rolls that are packaged in cylindrical or rectangular cases.¹ The size and shape of the package has a significant impact on the battery life and design of the products they power.⁴ For example, the battery life and shape of portable electronics such as cell phones or laptops are governed by the volume that is dedicated to the battery. The need to maximize energy storage while minimizing size and weight requires the development of approaches to rapidly design, prototype, and manufacture batteries in any desired shape.1

Previous work dedicated to creating batteries in unconventional form factors includes spray paintable batteries,¹ thin paper batteries,⁵ printable solid-state batteries,⁶ and stretchable wire-shaped batteries.⁷ Other approaches include 3D printing technologies such as electrodes printed from inks,⁸⁻¹³ 3D printed graphene electrodes,¹⁴⁻¹⁶ and 3D printed ceramic– polymer electrolytes.¹⁷ These manufacturing technologies

alleviate inherent form factor restrictions by creating small or thin batteries that can conform to the surface of an object.^{18,19} On the other hand, structural batteries increase the energy and power density of the entire system by serving as a multifunctional structural component.³ Examples of structural batteries include reinforced electrode composites for use as body panels for electric vehicles and unmanned aerial vehicles.^{2–4,20–22} Other structural battery work integrates commercially available LIBs into a cavity in a panel that is then used as a multifunctional, structural component of a spacecraft or satellite. $^{20,23-26}$ Although there have been many recent advances in the creation of unconventional battery form factors, most prototype fabrication methods are limited to curved or flat surfaces.^{8-16,24-29}

Three-dimensional printing enables the creation of complex 3D objects as well as rapid changes in the design without requiring modifications to the manufacturing process. Incorporating conductive materials into the 3D printing process can even enable the creation of structural devices with integrated

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Figure 1. (A) Log ionic conductivity versus percent volume change for PLA infused with various carbonate solvents. (B) Ionic conductivity of PLA infused with lithium salts after storage in air.

electronics.²⁷⁻³² For example, the Voxel8, a multimaterial 3D printer developed by a Lewis et al., is capable of producing functional electronic devices, such as guadcopters and watches, by using a combination of fused filament fabrication (FFF) and conductive inks to wire circuit components embedded in a 3D printed object.²⁸ However, these 3D printed electronics must still be designed around conventional batteries, restricting the ability of designers to create a product in any shape or form. Overcoming this limitation requires the ability to 3D print the battery, structural and electronic components concur-rently.³¹⁻³⁶ However, to enable rapid prototyping of custom battery form factors, all the components of the battery, including the anode, cathode, separator, current collector, and case, need to be 3D printable. To make this approach widely accessible, it would be beneficial if each part of the battery could be printed with low-cost FFF 3D printers. As a first step toward achieving FFF 3D printed batteries, Foster et al. recently used an FFF 3D printer and a commercially available graphene-based filament to print lithium ion anode disk electrodes. They tested these printed anodes with a lithium metal counter electrode in a coin cell and achieved a volumetric capacity in the range 1.36-35.8 mAh cm⁻³. This work did not include printing of the cathode, current collectors, and separators and, thus, was limited to 2D geometeries.

A major hurdle to creating 3D printable LIBs is that the polymers typically used for FFF 3D printing, such as poly(lactic acid) (PLA), are not ionic conductors. Typical hybrid, polymer, gel, and composite electrolytes exhibit ionic conductivities ranging from 0.01 to 1 mS cm⁻¹.^{33–38} Only a couple of papers have reported efforts toward increasing the ionic conductivity of PLA. The highest ionic conductivity reported to date (0.02 mS cm⁻¹) was for a composite consisting of PLA mixed with ethylene carbonate, aluminum oxide nanoparticles, and lithium perchlorate.^{39,40}

Here, we report the development of PLA-anode, cathode, and separator materials that enable 3D printing of complete lithium ion batteries with a low-cost FFF printer for the first time. This was achieved by (1) measuring the degree to which nine different solvents swell PLA and increase its ionic conductivity; (2) measuring how much the ionic conductivity of PLA was improved and retained after infusion with three different lithium salts; and (3) determining how the amount and morphology of the conductive carbon filler affect the printability, conductivity, and capacity of the anode and cathode. We hypothesized that PLA could be converted into an ionically conducting matrix by swelling the polymer with liquid electrolytes, thereby enabling the 3D printing of a lithium ion battery. By testing 9 combinations of carbonate solvents and 3 electrolytes typically used in commercial lithium ion batteries, we increased the ionic conductivity of PLA to 0.085 mS cm⁻¹, \sim 4 times higher than previous reports. Measuring the effect of conductive carbon filler loading on printablility revealed that PLA with 30 vol % of graphene could still be printed, whereas for Super P (a conductive carbon commonly used in lithium ion batteries) only 12 vol % could be loaded into PLA before it becomes too brittle to print. Suprisingly, the ratio of conductive: active material that optimized the capacity of the 3D printable anode and cathode materials was 80:20, very different from the 5:90 ratio of conductive: active material typically found in lithium ion batteries. Optimized 3D printed batteries were stable for at least 100 cycles but exhibited capacities ~100 times lower than their theoretical capacities. The low capacity of the batteries was due to the large amount of PLA necessary to make the anode and cathode 3D printable, which in turn resulted in poor electrical contact between the conductive and active materials in the composite, even at high ratios of conductive:active material. Nevertheless, we used these new composite filaments to demonstrate that a full 3D printed LIB can be made in a single print with no assembly required, and that integrated 3D printed batteries can be used to power electronic devices such as 3D printed LCD sunglasses and an LED bangle.

2. RESULTS AND DISCUSSION

2.1. Optimization of PLA Electrolyte. For pure PLA, we measured a very low ionic conductivity of 8.2×10^{-11} mS cm⁻¹, which is similar to previously reported values.³⁹⁻⁴² We hypothesized that the ionic conductivity of PLA could be improved by infusing the printed polymer with an electrolyte solution to create a 3D printed hybrid polymer electrolyte. Various solvents and solvent combinations commonly used for lithium ion battery electrolytes were tested to determine which would allow for the most electrolyte uptake while maintaining structural integrity. We also hypothesized that greater electrolyte uptake would correlate with higher ionic conductivity.^{33-38,43} Electrolyte uptake was determined by comparing changes in volume before and after PLA–solvent infusion. Electrochemical impedance spectroscopy (EIS) was used to



Figure 2. SEM images of the conductive carbons used in the printable composites: (A) graphene, (B) multiwalled carbon nanotubes (MWNTs), and (C) Super P. (D) The resistivity versus volume percent of Super P, graphene, and MWNTs loaded into PLA. The maximum volume % that was also printable is labeled for each material. (E, F) Average capacity versus ratio of conductive carbon to active material in PLA for the anode and cathode, respectively.

measure the ionic conductivity, and the results were plotted against the change in volume after infusion (Figure 1a). Negative values of volume change indicate polymer dissolution. Although diethyl carbonate (DEC) had the greatest volume increase (34%), this composite is brittle and has one of the lowest ionic conductivities. A 1:1 (by volume) solution of propylene carbonate (PC) and ethyl methyl carbonate (EMC) had the second highest volume change (29%) in PLA and had the highest ionic conductivity (0.031 mS cm⁻¹) (Figure 1d). Thus, the PC/EMC solvent was chosen for tests of ionic conductivity with lithium electrolytes.

PLA disks were printed and infused with solutions of 1 M lithium hexafluorophosphate (LiPF₆), lithium perchlorate (LiClO₄), or lithium trifluoromethanesulfonate (LiTFMS) in PC/EMC. The ionic conductivity for infused PLA was investigated with EIS and calculated using eq 1,

$$\sigma = \frac{l}{AR_{b}} \tag{1}$$

where *l* is the thickness of the sample, *A* is the cross-sectional area, and R_b is the bulk resistance which is extracted from a Nyquist plot.⁴⁰ The Nyquist plot for PLA infused with 1 M LiClO₄ in 50/50 vol EMC/PLA is shown in Figure S1. Each sample was tested twice: once 1 h after infusion, and again after storage on the lab bench open to air for 24 h (Figure 1b). The highest conductivity (1.7 mS cm⁻¹, 20 °C) was obtained for PLA infused with LiPF₆, but this electrolyte was not used in the final batteries because of its tendency to degrade upon exposure to moisture, causing it to lose ionic conductivity after 24 h (Figure 1b).^{44,45} Such sensitivity is not desirable for the production of 3D printing filament with reproducible and stable ionic conductivity. PLA infused with LiClO₄ had the second highest ionic conductivity (0.085 mS cm⁻¹, 20 °C) and retained its mechanical integrity and ionic conductivity after 24

h of exposure to ambient conditions. The mechanical integrity was determined qualitatively by examining the ability of the infused PLA to be handled without tearing or crumbling. LiTMFS had the lowest ionic conductivity (0.039 mS cm⁻¹, 20 °C). The ionic conductivity of the LiClO₄-infused-PLA is comparable to those of previously reported hybrid and polymer electrolytes utilizing LiClO₄ (0.01–1 mS cm⁻¹), enabling it to be used as a printed hybrid electrolyte in an LIB. 36,37,46

The anode and cathode need to have a high electrical conductivity in addition to a high ionic conductivity, so we next determined the maximum amount of conductive filler that could be added to the filament.⁴³ The total volume percents of active, conductive, and binder materials in a typical LIB electrode are in the ranges 70-90%, 5-10%, and 5-15%, respectively. However, if high volumes of solid (i.e., nonthermoplastic) fillers are loaded into PLA filament, the nozzle tends to clog during printing, or the filament becomes too brittle to print. To determine the optimal loading of filler, we prepared samples containing up to 40% of Super P, graphene, and multiwalled carbon nanotubes (MWNTs) (Figure 2a-c). We tested these conductive fillers because they are among the most conductive and commonly used fillers in LIB electrodes.^{47–50} These conductive fillers were mixed with solutions of PLA dissolved in dichloromethane. The solutions were then dried, pelletized, and extruded to create a conductive filament with a diameter of 1.75 mm. Figure S2 shows images of these experimental steps.

Figure 2d shows the resistivity of the filaments as a function of volume % of the conductive filler, as well as the maximum volume % of filler that could still be printed. As these materials were solids, we did not analyze their printability using their viscosity as has been done in previous work in which the printing material was an ink, gel, or paste.^{6,8,9,13} Instead, the



Figure 3. (A) Anode and (B) cathode composition and capacity comparison. 3D printed and molded samples both have carbon:active material ratios of 80:20. Volumetric discharge capacities are shown above each electrode type.

filament was determined to be not printable if the filament clogged during printing of 15–25 cm of filament through a 0.4 mm nozzle, or if the filament was too brittle to load into the FFF 3D printer. The graphene composite had the highest printable volume loading (30%), followed by MWNTs (20%) and Super P (12%). The graphene composite began to clog during printing at volume loadings above 30% while the MWNT composite became brittle as well as clogged during printing at volume loadings above 20%. The Super P composite did not clog but became too brittle to handle at volume loadings above 12%. The difference in the printability of these composites may be due to the different level of dispersion of the particles within the composite. As determined by dark field microsopy (Figure S3), graphene was welldispersed in PLA with $1-2 \mu m$ aggregates, which may explain its relatively good printability. In contrast, Super P, which consists primarily of particles with a diameter of ~100 nm and an aspect ratio of 1-10, formed aggregates with diameters between 20 and 30 μ m in the composite. MWNTs, which are 20–30 nm in diameter and 10–30 μ m in length, also formed aggregates 1–10 μ m in diameter, but to a lesser degree than Super P. The fact that Super P and the MWNTs did not disperse well within PLA may explain the relatively poor printability of these filaments.

After determining the maximum amount of filler that could be loaded into the filaments without degrading printability, we studied what ratio of active material to conductive filler resulted in the maximum energy capacity (Figure 2e,f). The total volume percent of filler was held constant for samples containing Super P (12%), graphene (30%), and MWNTs (20%). Lithium titanate (LTO) particles 100 nm in diameter and lithium manganese oxide (LMO) particles 500 nm in diameter were added into the anode and cathode material, respectively (see Figure S4 for SEM images). Active anode and cathode nanomaterials were mixed into PLA at different ratios to determine the effect of carbon material type and ratio on their capacity for energy storage. This was accomplished by mechanically stirring the conductive carbon and active nanomaterials sequentially into PLA dissolved in dichloromethane. LTO was chosen for the anode because of its excellent thermal stability, long cycling life span, low volume expansion, and high volumetric capacity. LMO was chosen for the cathode because it has good thermal stability, low volume expansion, and high power density when paired with $LTO.^{7,51-53}$ Anode and cathode disk electrodes were 3D printed to be 150 μ m thick and 14 mm in diameter. After printing, the disks were infused with 1 M LiClO₄ in 50/50 vol

EMC/PC and aged by allowing the samples to rest, undisturbed, for 24 h prior to cycling. Specific capacity measurements were performed in a coin cell using lithium metal as the counter electrode, a 25 μ m polypropylene disk as the separator, and 1 M LiClO₄ in 50/50 vol PC/EMC as the electrolyte.

The specific capacity of each sample increased as the ratio of active to conductive material decreased, demonstrating that achieving a high electrical conductivity in the composite was critical for achieving good capacity. All samples had the highest obtained capacities with a conductive carbon to active material ratio of 80:20. For the anode samples, LTO-graphene had the highest capacity at 7.48 mAh cm^{-3} (Figure 2e). For the cathode samples, LMO-MWNT had the highest capacity, 9.74 mAh cm^{-3} (Figure 2f). The anode capacity was in the same range as that achieved by Foster et al. $(1.36-35.8 \text{ mAh cm}^{-3})$ with a commercially available graphene-PLA composite for the FFF 3D printed anode.¹⁴ Although the MWNT composite is more conductive, it is curious that the MWNT composite outperformed the graphene composite in the cathode but not the anode. This may be because the LMO particles in the cathode are larger (500-750 nm) than the LTO particles in the anode (100-200 nm), which may in turn have improved the probability of the particles having one or more points of electrical contact with the relatively aggregated and lower volume percent MWNT network. In contrast, the smaller LTO particles may have a greater number of contacts with the more well-dispersed, though less conductive, graphene particle network.

Although the electrical resistivity (10² Ω cm) and ionic conductivity $(10^{-5} \text{ S cm}^{-1})$ of our 3D printable composites are comparable to those of conventional electrodes^{54,55} and polymer electrolytes,^{56–59} the specific capacities are only 1.1% and 1.63% of their theoretical capacities (600 and 596 mAh cm⁻³ for LTO and LMO, respectively). $\hat{s}_{1,52,60-62}$ We hypothesized that the large volume % of polymer (70-80%) in our composites was preventing the conductive filler from making electrical contact with the active material, thereby causing the capacity to be low. To test this hypothesis, we created half-cells with the same thickness and same ratio of conductive to active materials (80:20), but with only 10% PLA. The 10% PLA composites were blended in dichloromethane (DCM) in the same manner as was used for the composite filaments, but this solution was then dried in a mold 1.27 cm in diameter to form the samples for testing in the coin cell. As shown in Figure 3, the cast molded anode and cathode had a capacity much closer to that of a conventional electrode, which

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Figure 4. Half-cell testing of anode and cathode composites. Charge/discharge capacity and Coulombic efficiency of (A) anode and (B) cathode composites at a current density of 20 mA g^{-1} for 100 cycles. (C, D) Rate performance and (E, F) discharge voltage curves of anode and cathode composites.

contains 5% polymer. The capacity of the anode and cathode increased to 404 mAh cm⁻³ for LTO and 538 mAh cm⁻³ for LMO, an increase of 62 and 55 times, respectively, compared to the 3D printed versions. Achieving comparable capacities in 3D printable composites may necessitate wrapping the active materials with conductive fillers prior to mixing in the polymer to ensure there is good electrical contact to the active materials when they are present at low concentrations in the polymer.

2.2. 3D Printed Anode and Cathode Half-Cell Characterization. After maximizing the amount of filler in the polymer and optimizing the ratio of active to conductive material, approximately 3.0 m of anode and cathode filament was extruded. The final composition for each electrode was 6/24/70 vol % LTO/graphene/PLA and 4/16/80 vol % LMO/MWNT/PLA. Specific capacity calculations utilized the volume percent of active materials (4% for LMO cathode and 6% for LTO anode). PLA was stable in both anodic and cathodic conditions as each printed half-cell was capable of at least 100 charge–discharge cycles. The printed LTO anode had a charge and discharge capacity of 4.84 and 3.34 mAh cm⁻³, respectively, when averaged over 100 cycles (Figure 4a).

The printed LMO cathode had a charge and discharge capacity of 8.1 and 6.99 mAh cm⁻³, respectively, when averaged over 100 cycles (Figure 4b). The average discharge capacity for the entire printed anode and cathode (including polymer and conductive filler) is 0.34 and 0.71 mAh $\rm cm^{-3}$, respectively. Both samples experienced significant capacity loss during the first 10 cycles: 50% and 25% loss for anode and cathode, respectively. This loss is most likely due to the formation of the solid electrolyte interphase (SEI).43,63-65 Evidence of SEI formation can be seen in the XPS data taken before and after cycling (Figure S5). Pristine anodes and cathodes exhibit three distinct peaks for C=O, C-O, and CH in the 294-278 eV region which are associated with PLA (Figure S5A,B).⁶⁶⁻⁶⁸ This is due to the composite consisting of 70–80% polymer by volume. After cycling, both electrodes give spectra consistent with an SEI layer with peaks for $LiCO_3$, Li_2C_2 , ROCO₂Li, and ROLi (Figure S5C,D).^{69–72}

The electrodes were discharged at different current densities to investigate the effect of discharge rate on capacity and capacity recovery (Figure 4c,d). The printed LTO anode had a significant drop in capacity (from 3.81 to 1.10 mAh cm⁻³)



Figure 5. Cyclic voltammograms of (A) a 3D printed LMO cathode and (B) a 3D printed LTO anode. Both samples were tested in half-cell, twoelectrode configurations with lithium metal as the counter electrode. (C) Nyquist plot for 3D printed anode and cathode half-cells and 3D printed full-cell. The inset shows the region for the plot for the 3D printed anode and cathode. All EIS scans were performed at 100 mV pp from 1 MHz to 100 Hz.



Figure 6. (A) Individual components of the 3D printed coin cell. (B) Assembled 3D printed coin cell. (C) Capacity and Coulombic efficiency at a current density of 20 mA g^{-1} for 100 cycles. (D) Charge–discharge voltage curves for the full-cell with 1st, 10th, 50th, and 100th cycle shown.

when the current density was increased from 20 to 30 mA g⁻¹. The capacity recovered to 4.46 mAh cm⁻³ when the current density was decreased to 10 mA g⁻¹. The printed LMO cathode experienced similar capacity effects as the printed LTO anode except for a decrease in capacity (17.08 to 11.92 mAh cm⁻³) during the first 10 cycles at 10 mA g⁻¹. The cathode stabilized and recovered to 13.97 mAh cm⁻³ during the last 10 cycles at 10 mA g⁻¹. This stabilization may be due to the formation of the SEI layer and stabilization by the last set of cycling.⁷² Discharge voltage curves for current densities of 10, 20, 30, and 40 mA g⁻¹ reveal significant potential drops for the printed LTO anode (3.0–2.0 V) and the printed LMO cathode (4.0–3.3 V). This large potential drop can be attributed to the low conductivity and polarization caused by the large amount of polymer in our electrodes.⁴³

We performed cyclic voltammetry on the 3D printed anodes and cathodes to further analyze their electrochemical properties (Figure 5). Each sample was scanned at rate of 10 mV s⁻¹ in a two-electrode configuration with 1 M LiClO₄ in 50/50 by vol EMC/PC and a lithium metal counter electrode. The positions of the oxidative peaks for the 3D printed LMO cathode (Figure 5a) are at 4.01 and 4.20 V, and the reductive peaks are at 3.92 and 4.11 V. The 3D printed LTO anode's (Figure 5b) oxidative and reductive peaks are at 1.81 and 1.59 V. These values are comparable to literature results for conventional lithium ion anodes and cathodes utilizing LTO and LMO, respectively.^{73,74} The peaks for both anode and cathode CVs are broader and smaller in peak current compared to conventional LTO and LMO electrodes. Sharper redox peaks are associated with increased redox efficiency which is effected by ion diffusion and electronic conductivity.

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Figure 7. (A) A 3D printed battery was printed in a single print by exchanging the filament at predetermined layer heights. The battery was then vacuum filled with electrolyte. (B) Cross-sectional 10× microscope image showing the individual layers of the single print battery. (C) Image of 3D printed battery powering an LED. (D) Capacity and Coulombic efficiency of the single print battery at a current density of 20 mA g^{-1} for 10 cycles.

EIS was used to determine the charge transfer resistances of the 3D printed anodes and cathodes to be 59.2 and 43.1 Ω , respectively (Figure 5c, inset). These are comparable to conventional LTO anodes and LMO cathodes (43.8 and 42.2 Ω , respectively).^{75,76} The reduced current and peak broadening in our samples may be due to slower lithium ion diffusion in the PLA electrolyte, which is 2 orders of magnitude less conductive than the conventional liquid electrolye (1 M LiPF₆ in a carbonate solvent) used in lithium ion batteries.^{43,75,77}

2.3. 3D Printed Li Ion Battery Full-Cells. Following the electrochemical characterization of the anode and cathode composite, a 3D printed full-cell was tested. Printed current collectors, anode, cathode, and separator were encased in a printed coin cell (Figure 6a,b). All printed anodes, cathodes, and separators were 16 mm in diameter and 150 μ m thick, and were infused with 1 M LiClO₄ in 50/50 vol EMC/PLA prior to assembly. Electrifi filament was used for 3D printing the current collectors, as it has the highest conductivity of all commercially available conductive filaments. Pure PLA was used for printing the separators.

The electrochemical performance for full-cells was performed within a cutoff voltage range 3.0-2.0 V at a massnormalized current of 20 mA g⁻¹ (Figure 6c). For comparison with the half-cell results, the full-cell capacity was normalized to the active mass of the anode material. The full-cell experienced large irreversible capacity loss during the first 10 cycles (from 22.96 to 9.4 mAh cm⁻³) due to SEI formation which stabilizes near the 50th cycle (from 9.4 to 5.32 mAh cm⁻³). This fully printed cell reached an average discharge capacity of 3.91 mAh cm⁻³, and maintained an average Coulombic efficiency over 88.5% after the first 50 cycles. Electrochemical stabilization of the full-cell is reflected in the improvement of the discharge plateau as it broadens from the 1st to the 100th cycle (Figure 6d). This Coulombic efficiency is lower than a conventional lithium ion battery for which efficiencies range from 95% to 99%.⁷⁸ We believe the relatively low Coulombic efficiency of the 3D printed batteries may be due to the increased electrical resistivity of our anode and cathode, 538 and 252 Ω cm, respectively, relative to conventional electrodes, 0.16–1.0 Ω cm.⁵⁴ It is also possible that the ionic conductivity of the electrode layers may gradually increase during cycling due to increased infusion time, leading to an increase in the Coulombic efficiency. The capacity of the full-cell $(3.91 \text{ mAh cm}^{-3})$ is less than that of the half-cells (LTO anode 6.76 mAh cm⁻³, LMO cathode 6.99 mAh cm⁻³) possibly due to increased cell resistance created by contact resistances between printed components. Resistivity values extracted from EIS measurements (Figure 5C) showed that the use of two printed current collectors increased the resistivity from $10^2 \Omega$ cm for the half-cells to $10^4 \Omega$ cm for the printed full-cell. The volumetric capacity of the entire 3D printed coin cell (case, electrodes, current collectors, and separator) was 0.25 mAh cm $^{-3}$.

To create a completely printed electronic device with an integrated battery and no assembly required, we need a printer with the ability to print the current collectors, anode and cathode, separator, and case. Flowers and co-workers recently demonstrated the ability to create 3D printed electronics and circuits in one print using dual material FFF.⁷⁹ If this approach could be applied to four materials, fully printed LIBs could be integrated into electronic devices with FFF, but after testing several commercially available printers, we found we could not find a relatively low-cost (<\$10,000) 3D printer that could perform such printing reliably. To circumvent this limitation, we utilized a printing method in which the filament is



Figure 8. (A) Three-dimensional printed glasses with an electronic darkening LCD lens and 3D printed batteries integrated into the side temples. (B) Demonstration of the LCD transmitting and blocking an image of the Duke Chapel in the off and on state. (C) Separated view of the internal 3D printed components of a 3D printed bangle battery with an integrated LED. (D) Assembled 3D printed bangle battery powering an LED.

exchanged during printing, enabling the 3D printing of a LIB in a single print (Figure 7a,b) with a \$250 3D printer. The 3D printer instructions (i.e., the g-code file) were modified to pause the printer and change the nozzle temperature (if needed) at specific z-layer heights corresponding to each component of the battery, and the material was changed accordingly (see Figure S6 for images of the printing steps). After infusion and cycling, the battery was able to power an LED (Figure 7c). Cycling performance is shown in Figure 7d. The single print battery had a lower capacity (1.16 mAh cm⁻³) than the fully printed and assembled battery (3.91 mAh cm⁻³). The volumetric capacity of the entire single print battery is ~0.1 mAh cm⁻³. This lower capacity relative to the assembled battery may be caused by the inability to completely infuse the anode and cathode with electrolyte.

The volumetric energy and power densities of the 3D printed coin cell were calculated using data from the discharge voltage curves. Details regarding energy and power density calculations can be found in the Experimental Section. The assembled coin cell had energy and power densities of 0.14 Wh L^{-1} and 0.83 W L^{-1} , respectively. The energy and power density for the 3D printed coin cell were 0.28% and 0.02%, respectively, compared to energy and power densites of a conventional LTO-LMO full-cell.⁸⁰ We attribute the low energy and power densities mainly to the large volume percent of PLA polymer binder necessary for printability (see Figure 3). The increased polymer volume limits the contact of the active material with the conductive filler, decreasing the capacity performance. In addition, the larger polymer volume lowers the energy and power density by displacing active material.

2.4. 3D Printed Devices with Integrated 3D Printed Batteries. One of the key benefits of 3D printing is the ability to print arbitrary shapes and sizes. This ability may eventually enable the production of customizable wearable elec-

tronics.^{7,19,81-83} To demonstrate this capability, we 3D printed two wearable devices with integrated printed batteries. Figure 8a shows an example of 3D printed LCD sunglasses with 3D printed batteries integrated into the side temples (Figure 8a, inset). The batteries are connected in series to power an LCD panel that darkens when a voltage is applied by pressing the integrated switch (Figure 8b). The frames and temple arms of the sunglasses were designed as a snap-together case in which the components of the battery and electronics could be inserted. Each component of this battery (anode, cathode, and separator) was printed individually and infused with electrolyte prior to assembly into the printed casing. We also demonstrate an LED bangle with an integrated battery in Figure 8c,d. For this battery, the anode and cathode were printed as freestanding curved electrodes that matched the contour of the bangle (Figure 8c). A Celgard polymer separator (not shown) was used in this device to both improve the performance of the battery as well as demonstrate the ability to integrate 3D printed battery technology with existing materials. After infusion and assembly, the bangle battery could power a green LED for ~ 60 s. (Figure 8d).

3. CONCLUSION

This paper demonstrates that it is possible to 3D print full lithium ion batteries with low-cost fused filament fabrication 3D printers by (1) modifying the most commonly used 3D printing polymer, PLA, to have a similar ionic conductivity to previously reported polymer electrolytes, and (2) creating new polymer composites to enable 3D printing of LIB anodes and cathodes. We found the need to maintain printability limited the amount of conductive filler that could be loaded into the polymer to <30% by volume, and that a maximum battery capacity was achieved at a ratio of 80:20 conductive to active material. This is in contrast to a commercial lithium ion battery, in which the binder is <15% by volume, and the ratio of conductive to active material is \sim 1:10. As a result of the low active material loadings that could be achieved without degrading printability, the capacity of these first-generation 3D printed LIBs is about 2 orders of magnitude lower than lithium ion batteries using LTO and LMO as the active materials, which is too low for practical use.^{25,54,55,84,85} Future work may improve upon this initial demonstration by replacing the polymer-based anode and cathode materials with 3D printable pastes that can accommodate high loadings of active material and can be printed in tandem with a polymer separator and case. The use of alternative nanomaterials such as reduced graphene oxide may potentially serve as both the conductive filler and active material, eliminating the need for both an inactive conductive material and a low conductivity active material.^{86,87} Alternatively, wrapping the active materials, LTO and LMO, with conductive fillers prior to mixing in the polymer may improve electrical contact to the active materials when they are present at low concentrations in the polymer. These results should benefit those seeking to create energy storage materials and devices that can be 3D printed to create batteries in arbitrary shapes.

4. EXPERIMENTAL SECTION

4.1. Chemicals. Ingeo Biopolymer 4043D poly(lactic acid) (PLA) pellets were purchased from NatureWorks, LLC. Dichloromethane (DCM) (BDH113) was purchased from VWR. Ethylene carbonate (EC) anhydrous, 98% (676802); propylene carbonate (PC) anhydrous, 99.7% (310328); ethyl methyl carbonate (EMC), 98% (752002); diethyl carbonate (DEC) anhydrous, \geq 99% (517135); lithium hexafluorophosphate (LiPF₆) battery grade, \geq 99.99% (450227); lithium fluoromethanesulonate (LiTFMS), 99.995% (481548); lithium perchlorate (LiClO₄) battery grade, 99.99% (634565); lithium manganese (III, IV) oxide (LMO) spinel, <500 nm, >99% (702277), were all purchased from Sigma-Aldrich. Graphene nanoplatelets and multiwalled carbon nanotubes were purchased from Cheap Tubes Incorporated. TIMCAL graphite and carbon Super P conductive carbon black was purchased from the MTI Corporation.

4.2. Preparation of 3D Printable Electrode Filaments. Poly(lactic acid) (PLA) pellets were dried in an oven at 85 °C for at least 4 h prior to use in order to remove moisture. PLA was dissolved in dichloromethane (DCM) (Sigma-Aldrich) at 0.1 g/mL under vigorous stirring until completely dissolved. Active and conductive materials were then added, and the mixture was stirred vigorously for at least 12 h. The solution was then cast into a Teflon lined sheet and set in a fume hood at room temperature overnight to evaporate the remaining solvent. The cured composite sheets were then pelletized and dried in an oven at 85 °C. A polymer extruder (Filabot.com) was used for the extrusion of 1.75 mm composite filaments. The extruder was loaded with at least 25 g of dried anode or cathode pellets and preheated to 180 °C for 15 min. After preheating, the extruder motor was turned on to begin extrusion. Once the composite began to extrude, the temperature was lowered to 160 °C for the remaining extrusion time. After extrusion, the filament was stored in sealed plastic bags with desiccant to keep the PLA dry.

4.3. Single Print, 3D Printed Battery. A 3D model of the battery was designed with 123D (Autodesk 2016), exported as an STL file, and sliced using Cura (Ultimaker). The parameters for printing were 100 μ m layer height, 50 °C bed temperature, 210 °C extruder temperature, and 40 mm/s print speed for the cathode current collector, cathode, separator channel, and anode. A 160 °C extruder temperature and 20 mm/s print speed were used for the for the anode current collector. The GCODE file was also set to pause after printing each component layer so that the filament could be exchanged. After printing, the battery was allowed to cool to room temperature and filled with 1 M LiClO₄ in 50/50 vol EMC/PC. The battery was allowed to rest for 24 h prior to cycling.

4.4. Characterization. All printed samples were infused with 1 M LiClO₄ in PC/EMC 50/50 vol % at 50 °C for 4 h prior to cell assembly. After assembly, half- and full-cells were aged for 24 h prior to cycling. Galvanostatic cycling for coin cells was performed using an Arbin Instruments BT2043 using voltage ranges and mass-normalized currents as described in the text. For the full-cells, the cells were anode-limited on the basis of the mass of the active material within the cathode and anode and the specific capacities obtained from halfcell tests. The capacity of the full-cells was normalized to the active anode mass for comparison with half-cell test results. Electrical conductivity measurements were made using a Keithley 2400 series source meter unit. Electroimpedance spectroscopy measurements were performed using a Bio-Logic Science Instruments SP-200 potentiostat at 100 mV pp over a frequency range 1 MHz to 10 Hz. XPS experiments were perfrom using a Kratos Axis Ultra X-ray photoelectron spectrometer. Electrochemical measurements were performed with a CHI600D, CH Instruments, potentiostat. Each sample was scanned at rate of 10 mV s⁻¹ in a two-electrode configuration with 1 M LiClO₄ in 50/50 vol EMC/PC and a lithium metal counter electrode.

4.5. Energy and Power Density Calculations. Energy and power density were calculated using data discharge voltage experiments for the 3D printed coin cell and single print full-cell.^{88,89} Volumetric energy density was calculated using eq 2

$$E_{\rm Vol} = \frac{C_{\rm dc} \times V_{\rm ave}}{\rm Vol_{\rm cell}} \tag{2}$$

where $E_{\rm Vol}$ is volumetric energy density in Wh L⁻¹, $C_{\rm dc}$ is the dischage capacity in A h, $V_{\rm ave}$ is the voltage averaged over a given discharge cycle, and Vol_{cell} is the volume of the full-cell where half the thickness of both current collectors and full thickness of anode, cathode, and separators were taken into account and converted from cm³ to L.⁹⁰ Volumetric power density was calculated using eq 3

$$P_{\rm Vol} = \frac{E_{\rm Vol} \times 3600}{t_{\rm dc}} \tag{3}$$

where P_{Vol} is volumetric power density in W L⁻¹, E_{vol} is volumetric energy density multiplied by a factor of 3600 to convert hours to seconds, and t_{dc} is the dischargre time in seconds.⁹¹

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsaem.8b00885.

Additional characterization information including Nyquist plots, SEM images, and XPS data (PDF)

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Notes

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