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3D Printing of Lithium-Ion Battery Electrode Components

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Abstract

In this work, 3D printing of lithium-ion battery (LIB) components using the fused deposition modeling (FDM) process is presented. The filament's formulation, printability and material properties are characterized. Specifically, the graphite/polylactic acid (PLA) filaments were fabricated from a formulation process in literature [5]. In our LIB designs, the graphite/PLA serves as the anode, and high-performance cathode filament is explored as well. These filaments are studied and compared based on their printability, electrochemical performance, and mechanical characteristics. Through this study, printed electrodes and separator materials can be assembled to form a fully 3D printed battery of complex desired shapes with optimized energy density and sufficient mechanical strength. Additionally, this study can help expand the teaching of 3D printing technologies, as students may fabricate customized 3D printing materials (filaments) based on desired electrical or mechanical properties.

1. Introduction

Lithium-ion batteries are used in various applications ranging from consumer electronics, transportation and aerospace applications [1]. The growing number of industry applications for LIBs has led to an increased to develop clean and sustainable energy storage systems with higher storage capacity and power density. However, current design and manufacturing technologies presents restriction in the size and shape of batteries in different packages [1], [2]. In other words, there are limitations in the rapid design batteries of complex shapes and structures.

Several groups have reported on the use of additive manufacturing or 3D printing in the preparation and manufacturing of complex 3D objects for battery applications. It is reported that 3D printing, with its "low cost, quick and simple process," presents a "solution for improving battery performance" and "minimizing size and weight" of lithium-ion batteries [2], [4], [1]. 3D printing technologies work by "adding material layer-upon-layer" to build a complex 3D object of desired shape [5]. One extrusion-based 3D printing technology of primary interest in the current study is called Fused Deposition Modeling (FDM). As described by Maurel et al. [5], FDM uses a "thin filament of melted thermoplastic material" to build 3D object layer-upon-layer [5]. Liquid Deposition Method (LDM), which uses inks or pastes extruded through a syringe, has also been used extensively in the fabrication of 3D LIBs [5], [6], [7]. Challenges presented by LDM can be found in the necessity to conduct post-processing of the obtained 3D objects and in the adequate control of the ink viscosity [3], [5]. FDM can be used with minimal post-processing and offers the added advantage of higher resolution, thus the use of FDM in this study [5]. Moreover, at Indiana University – Purdue University Indianapolis (IUPUI), several undergraduate engineering capstone projects have involved the use of 3D printing for rapid prototyping and small-scale production of complex objects. This study can provide a framework to improve student adoption of additive manufacturing as an efficient design project technology.

2. Literature Review

Within the available reviewed literature for LIB applications, Maurel et al [3] uses lithium iron phosphate/polylactic acid (LFP/PLA), graphite/PLA and Silicon dioxide/PLA (SiO_2/PLA) 3D-printable filaments, respectively as positive electrode, negative electrode and separator in a Lithium-ion battery, to produce a "complete LFP/graphite battery cells" in "one-shot." Following the formulation steps shown in figure 1 below, Maurel et al. [3] reported on the fabrication of 3D electrodes and separators and properties characterizations (mechanical, morphological, electrical and electrochemical). Of great interest were the investigations of the "effect of carbon black as conductive additive" on the electrical conductivity and of the impact of plasticizers on the mechanical strength and printability of the filaments [3], [5].

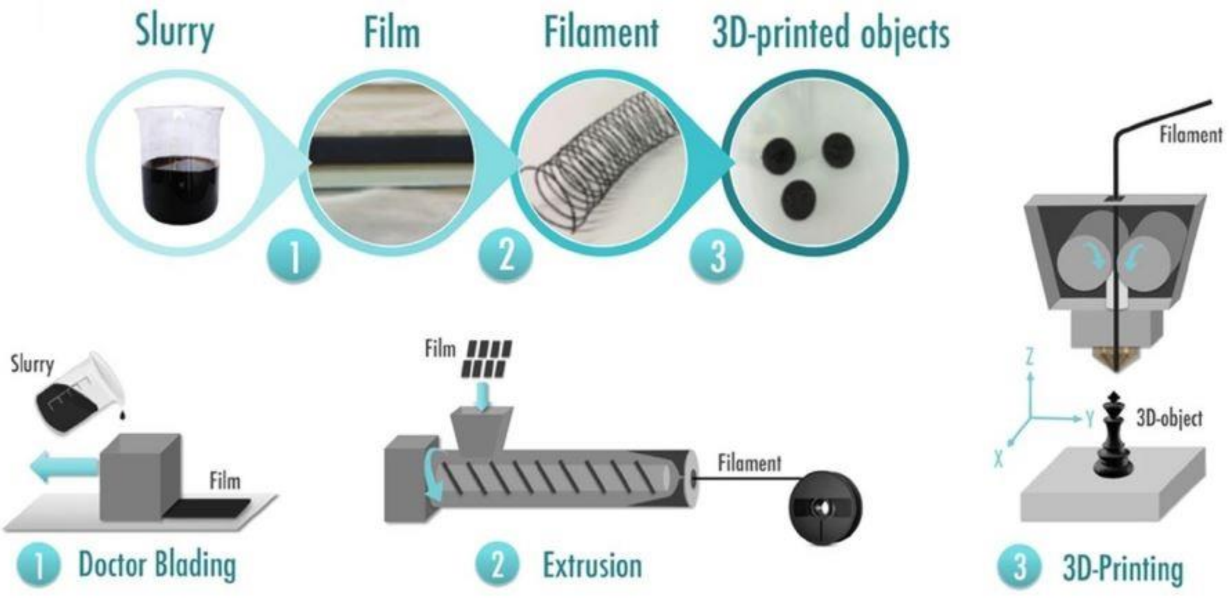

Figure 1: Formulation steps. This scheme was reproduced from Ref. [3].

Using poly (ethylene glycol) dimethyl ether average Mn ~ 500 (PEGDME500) as the plasticizer, it was demonstrated through experiments that filaments having a low content of plasticizers were too brittle and those will high content were too soft and flexible [5]. Maurel et al. used a 40 wt % of PEGDME500 which provided adequate mechanical strength for printing while allowing for graphite content within the filament to be "increased as high as possible" [5]. Additionally, the authors investigated the influence of conductive additives such as Carbon nanofibers (CNF) and Carbon black Timcal Super-P (CSP) on the electrical conductivity of the filaments [5]. It was demonstrated that "higher conductive values" and "higher specific capacity" can be achieved with increasing CSP and CNF contents [3], [5].

Other groups such as Reyes et al. [1] have demonstrated the complete 3D printing of lithium-ion battery using Fused Filament Fabrication, another term for FDM. In this study, Lithium Manganese Oxide (LMO) and Lithium Titanium Oxide (LTO), respectively used for the cathode and the anode, were formulated with PLA and other conductive additives such as graphene and multiwalled carbon nanotubes (MWNT). Pure PLA infused in electrolyte solution was used as the separator [1]. However, the electrical and electrochemical performances of the printed batteries were "2 orders of magnitude lower than lithium-ion batteries due to the high PLA content necessary to enable printability through FDM [1]. Dimensions of 3D printed cathode, anode and separator disks were 150 μm in thickness and 16 mm in diameter [1].

Wei et al. [8] reported the complete 3D printing of LIBs with "thick semi-solid electrodes" using Direct Ink Writing (DIW). In total, four inks are developed for (cathode, separator, anode, and packaging) and used to fully 3D print LIBs [8]. Similar to ref. [3], LFP is as active material in the cathode LTO is used in the anode due to their "exceptional thermal stability" and "low volumetric change upon cycling" [8]. Ketjen Black (KB) was used as conductive additives [8]. The 3D printing process involved the use separate syringes for all four inks in a customized 3D printer [8].

Similarly, Zhang et al. [6] have reported the fabrication of 3D printable graphite negative electrode based on the DIW technology. In this study, Acetylene black (AB) was used as a conductive agent and polyvinylidene fluoride as a binder for the graphite slurry [6]. Additionally, Celgard polypropylene was used as a separator during testing [6]. It was also shown that electrodes made fully of graphite displayed higher performances than coated graphite electrodes [6].

In this paper, Lithium Nickel Manganese Cobalt Oxide (LNMC) and Lithium Cobalt Oxide as two distinct positive active materials, graphite as negative active materials, Carbon black super P as conductive additives and PEGDME500 as plasticizer are used to make positive and negative 3D printable electrode filaments in combination with PLA. All three composite filaments, namely PLA-Graphite, PLA-LNMC, and PLA-LCO, are fabricated following the formulation steps from figure 1 [3]. This study aims to provide preliminary results for the formulation and printability testing of the electrode filaments. Moreover, subsequent future steps will involve the formulation of PLA/Lithium Manganese Oxide (LMO) and PLA/LFP for positive electrodes. Additional work on the fully assembled lithium-ion batteries will thoroughly investigate the electrical and electrochemical properties as well as key mechanical properties of the printable filaments.

3. Methods

3.1. Materials

Table 1 below list all the chemicals and their suppliers. Dichloromethane or methylene chloride is a colorless organic solvent widely used for fast dissolution of the PLA because it produces very small particles [5], [9]. LCO has been widely used in lithium-ion batteries due to its "easy preparation, excellent conductivity and high energy density" [10]. LNMC or NMC is increasingly being used in LIBs for its high-performance values and lower cost compared to LCO [11]. PEGDME500 was chosen for its high-performance characteristics and improvement in "the thermal behavior and compatibility with the composite film" [5]. CSP was shown to greatly improve the electrical and electrochemical properties of printable filaments [3], [5].

Table 1: Material List

Materials	Suppliers
Luminy LX175 PLA pellets	Filabot
Dichloromethane (DCM)	Cole-Palmer
Timcal TIMREX SLS graphite	MSE supplies
Lithium cobalt (III) oxide (LCO)	Sigma Aldrich
Lithium nickel manganese cobalt oxide (LNMC)	Sigma Aldrich
Poly (ethylene glycol) dimethyl ether average Mn ~ 500 (PEGDME500)	Sigma Aldrich
Carbon black Timcal Super-P (CSP) (62 m2 g−1)	Alfa Aesar

3.2. Filament preparation and 3D printing

3.2.1. Slurry formulation steps

1. PLA particles were dried for 4-6 hours at 85°C to remove moisture as per manufacturer's recommendations [12].

2. The PLA pellets were then dissolved into DCM in a fume hood for an hour and under magnetic stirring with a weight ratio of PLA/DCM 1:10 [3].

3. PEGDME500 was added to the solution and magnetically stirred for 30 minutes.

4. Pre-mixed amount of active material (graphite for negative electrode and LNMC or LCO for positive electrode) and CSP were added to the slurry and magnetically stirred for about 1h to 3h until evaporation of DCM prevents adequate stirring.

5. The solution was spread on an aluminum plate and left to rest overnight at room temperature.

3.2.2. Extrusion and 3D printing

1. The resulting film was cut into small pellets and fed to a Filabot EX2 Filament Extruder (Filabot.com), as seen in figure 2, to produce filament of approximately 1.75 mm diameter. Extrusion temperature varied between 150 and 175 °C. The obtained filament was then stored in a plastic bag. The extruder was cleaned with pure PLA.

2. A LONGER LK4 3D Printer (longer3d.com) and a Makerbot Replicator Mini (makerbot.com) were used with nozzle size of 0.4 mm. The nozzle temperature varied between 200 and 210 °C based on the filament while the bed temperature was fixed to 65 °C. Cura and Makerbot Desktop were used to slice 3D CAD models.

Figure 2: Filabot EX2 Filament Extruder

3.3. Curriculum Incorporation of 3D printing of batteries

As detailed by Pinger et al., 3D printing has been used in several applications such as chemistry education to enable “students to create and compare several models” [14]. From this approach, students were able to use 3D printing as “tactile-learning” tool in the design and fabrication of 3D models of complex protein structures and understand “the protein−protein interactions” [14]. A similar approach to incorporate the present study of 3D printing in battery fabrication will include providing students with detailed instructions for fabricating customized filaments, later fed to 3D printers to produce 3D printed electrodes. With the assistance of trained supervisors, the fabricated electrodes can be assembled into battery coin cells and tested for their electrochemical performances. The obtained electrochemical results will allow for comparison and understanding of the influence of different material contents on the performances of fabricated battery cells.

4. Preliminary Results and Discussion

4.1. Negative electrode filaments

Four PLA-Graphite solutions were attempted, and their weight ratios can be found in table 2. The graphite test 1-1 was developed with a weight ratio PLA/graphite of 60/40. In this test, the weight ratio of PEGDME500/PLA and CSP/graphite were kept at the same values as the optimized filament ratios in ref. [5]. The graphite tests 2-1, 2-2 and 2-3 used a CSP/graphite weight ratio of 1:100, which was shown to provide significant improvement in electrical conductivity compared to samples without CSP [5]. Those last three tests had different weight ratios of PLA/Graphite to study the influence of PLA content on extrusion and printability.

Table 2: Weight ratios for 4 graphite tests

Weight Ratios	**Graphite test 1-1**	**Graphite test 2-1**	**Graphite test 2-2**	**Graphite test 2-3**
PLA/Graphite	60/40	40/60	50/50	60/40
PLA/DCM	1:10	1:10	1:10	1:10
PEGDME500 / PLA	40:100	40:100	40:100	40:100
CSP/Graphite	10:100	1:100	1:100	1:100

In the graphite test 1-1, the obtained slurry was magnetically stirred, left to rest overnight, and pelletized as can be seen in figure 3. The pellets were then fed to the Filabot Extruder, heated at

150 °C which is slightly below the melting temperature of 155 °C for PLA [12]. The obtained filament became flexible and soft, making it unsuited for printing. This could be due to an incorrectly high plasticizer content during formulation. It was also hypothesized that the low extrusion temperature used in this test may have led to a nonhomogeneous filament.

The graphite test 2-1 failed during the slurry step. This could be due to fast evaporation of DCM and incomplete dissolution of PLA pellets. Samples in test 2-2 and test 2-3 were successfully formulated and extruded into filaments. For the graphite test 2-2, extrusion temperature was set at 165 °C, 10 degrees higher than PLA melting temperature. The obtained filament demonstrated adequate brittleness and relatively consistent and smooth surface finish. The diameter of the obtained filament however, the diameter of the obtained filament was lower than 1.75 mm. 3D printing testing will be used with slightly smaller filament diameter parameter. Figure 4 shows the information for the graphite test 2-2.

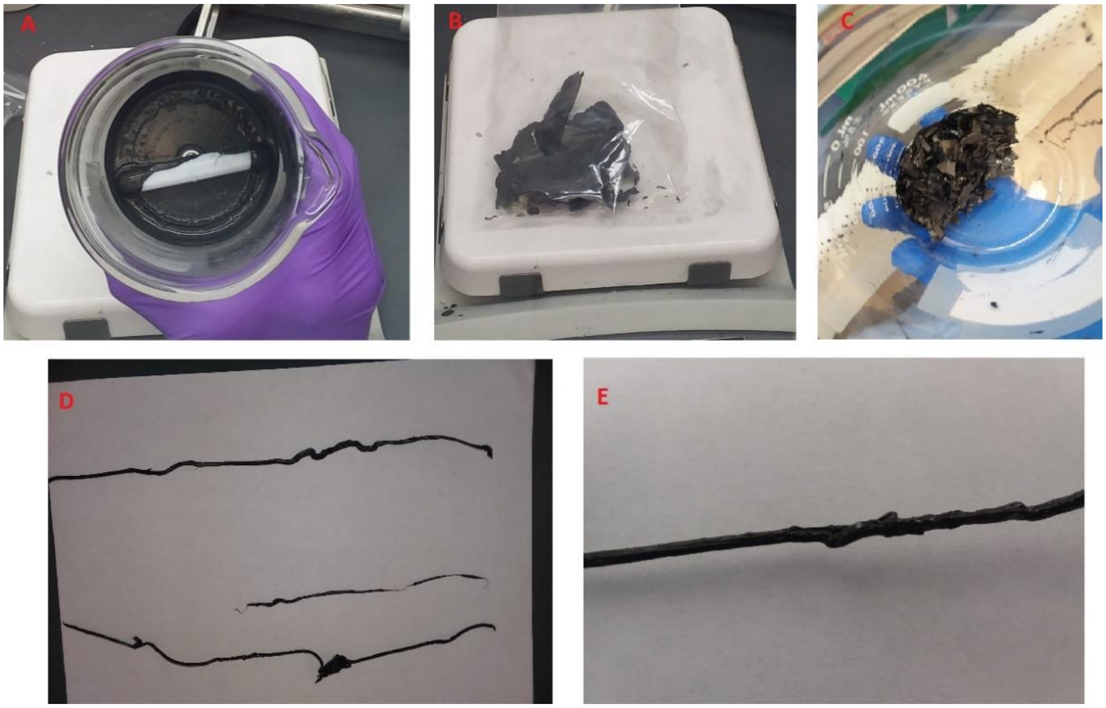

Figure 3: (A) Magnetically stirred slurry. (B) Obtained film stored in plastic bag. (C) Small PLA/Graphite pellets to be fed to extruder. (C) Top view of obtained filament after extrusion showing inconsistent surface (D) Close-up view of filament showing rough surface finish.

Similarly for the graphite test 2-3, extrusion temperature was set at 165 °C. The obtained filament also demonstrated adequate brittleness and relatively smooth surface finish, though with a diameter lower than 1.75 mm. Despite the difference in the PLA content between test 2-2 and test 2-3, there was no significant difference in their apparent brittleness. Figure 5 shows the information for the graphite test 2-3.

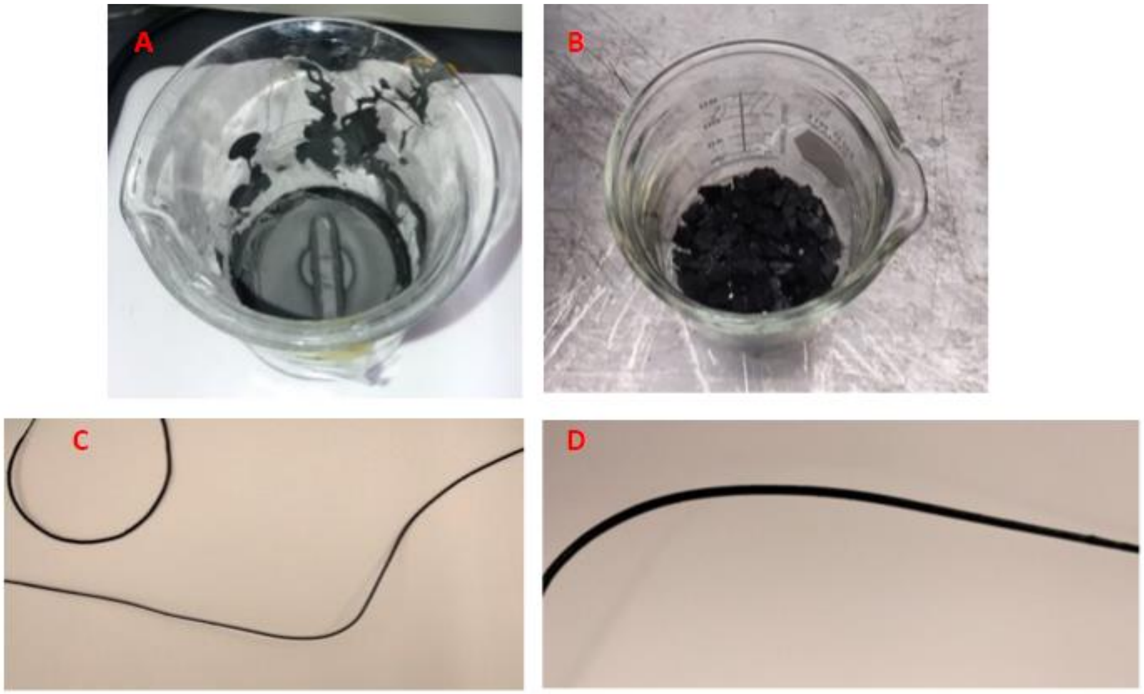

Figure 4: (A) Magnetically stirred slurry for the graphite test 2-2. (B) PLA/Graphite pellets for test 2-2. (C) Obtained filaments (D) Close-up view of the obtained filament showing smooth surface

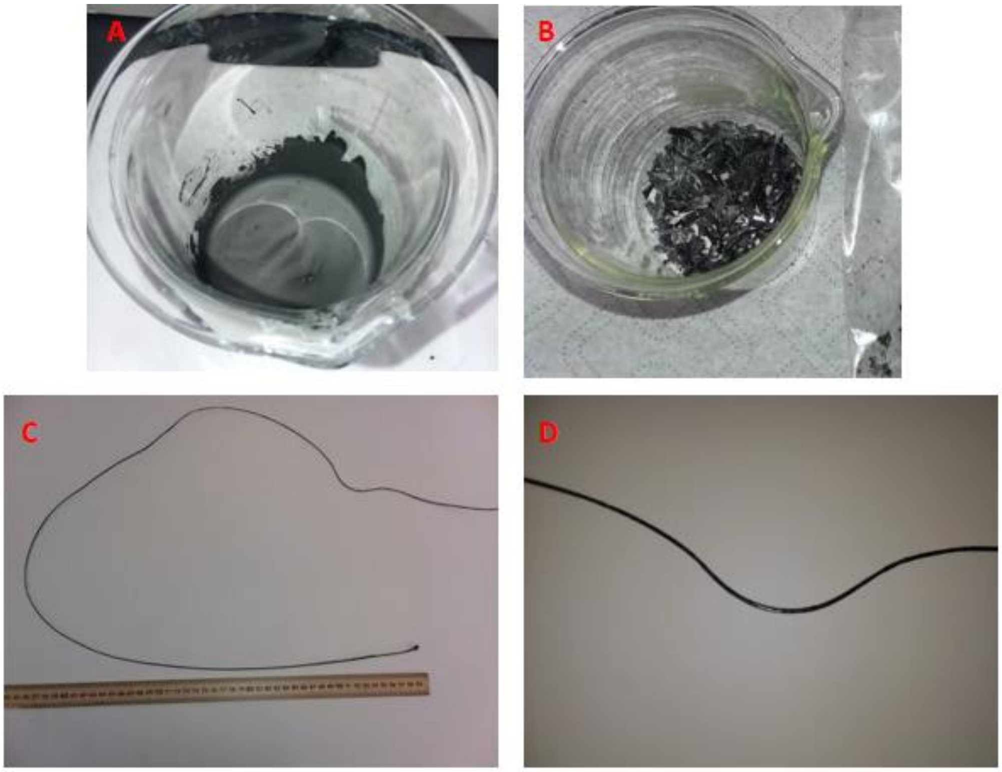

Figure 5: (A) Slurry for the graphite test 2-3. (B) PLA/Graphite pellets for test 2-3. (C) Obtained filaments (D) Close-up view of the obtained filament

Further studies will focus on assembling half-cell batteries using a CR2032 coin cell with a Graphite/PLA as the anode and Lithium metal as counter electrode [13].

4.2. Positive electrode filaments

Two slurries were developed for cathode filaments, one made of LNMC-PLA and the other of LCO-PLA, and their weight ratios can be found in table 3. The weight ratio of PLA / Active material was kept constant at 40/60 from literature [5]. In this test, the weight ratio of PEGDME500/PLA and CSP/graphite were kept at the same values as the optimized filament ratios in ref. [5].

Table 3: Weight ratios for positive electrode formulation

Weight Ratios	Ratios
PLA/Active Material	40/60
PLA/DCM	1:10
PEGDME500 / PLA	40:100
CSP/Active Material	10:100

Both slurries were magnetically stirred, then samples of each were spread on an aluminum plate and left to rest overnight (figure 6). The LNMC-PLA film was cut into small pieces and fed to the Filabot Extruder heated at 160 °C. During extrusion, about 5 g of pure PLA were added after introducing the electrode slurry. This ensured that most of the LNMC-PLA would be extruded without difficulty.

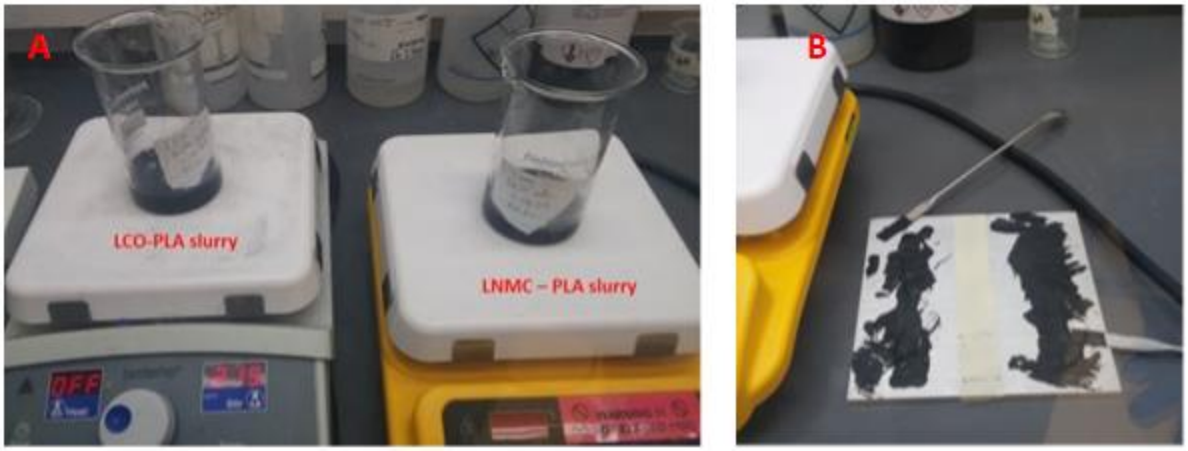

Figure 6: (A) LCO-PLA and LNMC-PLA slurries under magnetic stirring(B) Samples of LCO-PLA (left) and LNMC-PLA (right) spread on ¼” aluminum plate

The obtained filament (figure 7) was displayed similar brittleness as regular commercial PLA filaments with a diameter around 1.75 mm, though not fully uniform along the entire length.

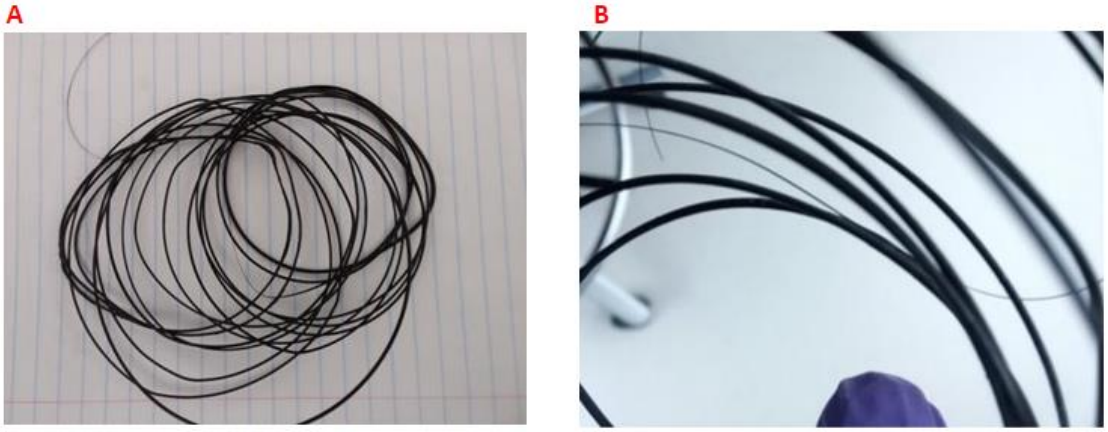

Figure 7: (A) Top view of LNMC-PLA filaments (B) Close-up view of the obtained filament

Only the LNMC-PLA was used to 3D print two 3D objects. Printing dimensions as well as resulting 3D objects for those two tests can be found in figures 8 and 9. The first print had a layer height of 0.12 mm with a shell thickness of 1.2 mm. Print speed was set at 70 mm/s, printing temperature at 200 °C and bed temperature at 65 °C to improve adhesion of the first layer. The fill density was set at 20%. It was observed that the first layer stayed mainly intact, while subsequent layers degraded in quality and became very porous. For this reason, height of the 3D object for the second print was reduced to 1 mm, the fill density was increased to 30% and print speed slightly reduced to 65 mm/s. While the first layer remained intact, the obtained 3D object could benefit from an increase in fill density to 100 % in order to remove pores. Further 3D printing tests will focus on obtaining 3D electrodes adequately dimensioned for coin cell testing [5], [13].

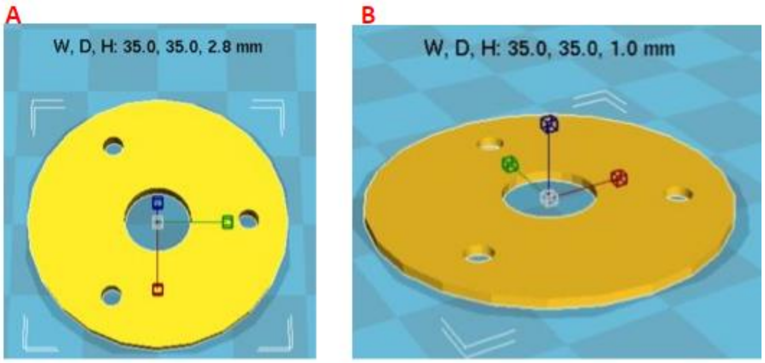

Figure 8: (A) 3D CAD model for the first and (B) second print using Cura slicer

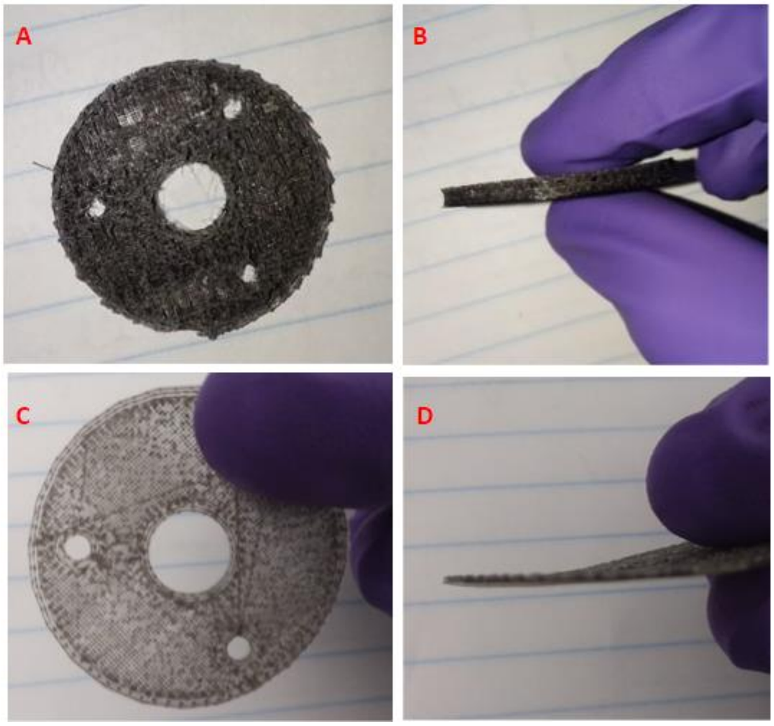

Figure 9: (A) First 3D printing object using LNMC-PLA (top view). (B) Side view of first 3D object. (C) Top view of second 3D object. (D) Side view of second 3D object.

5. Summary

- This study shows the production of 3D printable electrode filaments to form a fully 3D printed battery of complex desired shapes via FDM.
- Graphite/PLA filaments and LNMC/PLA were developed and demonstrated adequate brittleness to be used in a 3D printer.
- This works serves as a preliminary report in the design of optimized 3D printable electrodes via FDM.
- Future work will focus electrochemical and electrical characterizations as well as some mechanical testing. Further work to optimize electrode formulation, 3D printing, and performances will enhance our understand of 3D printable lithium-ion batteries.
- Moreover, this study provides a framework for the production of customized filaments tailored to specific applications in an engineering curriculum.

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Conflict of Interest

No conflicts of interest declared.

Keywords
3D printing; Fused Deposition Modeling; battery

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