Preface

Additive manufacturing (AM), commonly known as 3D printing, has transformed material fabrication by enabling design flexibility, precision, and efficiency. Unlike traditional manufacturing methods, AM builds complex geometries layer by layer directly from a .stl file. This approach allows the creation of intricate structures with superior properties, making it a vital tool across diverse applications such as aerospace, automotive, healthcare, and energy storage systems. Additionally, it minimizes material waste and facilitates rapid prototyping, thereby accelerating product development cycles and enhancing overall efficiency.

One field where AM shows remarkable potential is electrochemical energy storage. The rising demand for efficient batteries, driven by the growth of green energy systems and portable electronic devices, has intensified research into advanced battery technologies. Among these, lithium metal batteries (LMBs) stand out due to their exceptional energy density and potential to surpass conventional batteries. However, practical implementation of LMBs faces significant hurdles, including dendrite growth that can cause short-circuiting and reduced efficiency. Overcoming these challenges requires innovative approaches to the design of electrodes and current collectors, where additive manufacturing can play a transformative role.

The current collector plays a vital role in LMBs, acting as the conductive substrate that enables electron transfer between the external circuit and the electrochemical reactions within the battery. Traditionally, copper (Cu) foil is used as the current collector in LMBs. The flat surface of traditional Cu current collectors presents a low surface area, leading to uneven lithium deposition and the formation of dendrites. These dendrites can cause short-circuiting, severely compromising the performance and safety of LMBs. An effective solution to address this challenge is the implementation of porous current collectors.

Porous current collectors provide a significantly higher surface area, which helps suppress dendrite growth while improving the overall performance of LMBs. Their advantages include enhanced ion transport, increased active surface area, improved mechanical stability, and better accommodation of volume changes during cycling. By facilitating uniform lithium deposition and minimizing the risk of dendrite formation, porous current collectors represent a pivotal advancement in enhancing the efficiency, safety, and durability of LMBs.

AM of complex porous Cu electrodes for energy storage systems (ESS), such as LMBs, has garnered significant interest in recent years. AM technologies present innovative solutions to the limitations of traditional manufacturing methods, including restricted design flexibility, excessive material waste, multi-step production processes, and inefficiencies.

Various AM techniques, such as direct energy deposition (DED), electron beam melting (EBM), binder jet printing (BJP), direct ink writing (DIW), and selective laser melting (SLM), have been utilized to fabricate intricate porous Cu electrodes. Among these, DIW has emerged as the most extensively explored method, largely due to the challenges encountered by alternative techniques.

For instance, laser-based AM methods like SLM struggle with Cu high reflectivity and thermal conductivity, making processing difficult. EBM, on the other hand, often results in excessive thermal damage and elevated costs. BJP, while capable of producing complex Cu components, faces drawbacks such as high dimensional inaccuracies, difficulties in powder handling, and limited self-supporting capabilities. These limitations position DIW as the optimal approach for fabricating intricate Cu structures, offering superior precision, versatility, and efficiency.

This study centres on the fabrication of hierarchically porous Cu current collectors using DIW. By harnessing the design flexibility and precision of AM, this approach enables the creation of porous architectures that effectively address critical challenges in LMBs. The research investigates the relationship between structural design, fabrication parameters, and electrochemical performance, with the goal of developing a scalable and efficient method for producing high-performance current collectors. The findings of this work have the potential to significantly advance battery technology, contributing to the development of safer, longer-lasting, and higher-capacity energy storage solutions.

The thesis has been structured into the following eight chapters.

Chapter 1 emphasizes the technological significance and addresses the key challenges in LMBs, a critical area of energy storage research. As the demand for high-capacity, long-lasting, and safe energy storage solutions continues to grow, the development of innovative electrode designs has become increasingly important. Hierarchically porous Cu (HP-Cu) current collectors offer a promising pathway to overcome limitations such as dendrite formation, uneven lithium deposition, and volume expansion during cycling. By utilizing DIW to fabricate these advanced structures, this work seeks to bridge the gap between innovative design and practical application, paving the way for transformative advancements in battery technology and energy storage systems.

Chapter 2 begins with a brief overview of LMBs, followed by a detailed examination of various processing routes for developing porous Cu structures using AM techniques. It includes a summary of different AM methods and highlights their relevance for fabricating porous Cu structures. The chapter also presents a comprehensive review of conventional fabrication techniques along with an in-depth analysis of the latest research on AM-based approaches for creating 3D porous Cu current collectors. The chapter also highlights the research gaps and concludes with the objectives of the present work.

Chapter 3 outlines the details of materials and the experimental procedures undertaken starting from preparation of high particle-loaded Cu ink to the fabrication of porous Cu current collector. Cu powder (99% purity) from Nano Matrix, India, was selected for its high performance. The ink was prepared using PLA 4060 D binder (NatureWorks, USA) and solvents Dichloromethane, Dibutyl Phthalate, and 2-Butoxyethanol (Thermo Fisher Scientific) to achieve a high Cu particle loading. The ink preparation begins by mixing Dichloromethane (DCM), Dibutyl Phthalate, and 2-Butoxyethanol to form a homogeneous solvent. PLA is dissolved in DCM, and Cu powder is gradually added to create a uniform suspension. Vortex mixing ensures even dispersion of particles. Ultrasonic sonication for 1 hour further breaks down aggregates, resulting in a stable, homogeneous Cu ink. This carefully controlled process ensures that the ink is ready for high-quality printing applications. Viscosity is measured using the ARES G_2 rheometer, with 25 mm plates and a 500 µm gap. Temperature control is achieved via Forced Convection Oven, with a range of 25°C to 80°C. A shear rate sweep (0.01 to 1000 s^{-1}) analyses the material's flow behavior, identifying shear thinning or thickening. For viscoelastic materials, a frequency sweep (0.1 to 100 Hz) measures storage modulus and rheological properties within the linear viscoelastic region (0.1% to 5% strain). These tests ensure accurate, reliable viscosity and flow property analysis for inks and other materials. The spherical Cu powder has been chosen for its optimal mobility and uniform distribution, ensuring smooth extrusion and consistent printing. This shape enhances surface finish, reduces defects, and increases the printed material's apparent density, improving mechanical properties and structural integrity. Cu inks with optimal rheological properties has been used to fabricate parts through DIW using a multimaterial extrusion-based 3D printer (Hyrel 3D). A CAD model was converted to STL format, then printed with a micro nozzle at different speeds. The ink was extruded uniformly, layer by layer, to form precise 3D structures. After printing, the green Cu samples were dried at room temperature for 24 hours to evaporate excess solvent before further processing. The sintering was performed after 3D printing of green samples. The furnace tube was vacuumed to 10^{-3} Torr to remove air, then purged with Ar gas at 121 mm^3/min to maintain a stable atmosphere. This continuous gas flow ensured a controlled environment, preventing undesirable reactions during debinding and sintering.

Coulombic efficiency tests were performed on the half coin cells using the Arbin 20084 battery tester to assess their charge-discharge cycles, providing key insights into their electrochemical performance and stability.

Chapter 4 delves upon the development of Cu ink with ideal rheological properties for fabricating a porous electrode for the LMBs. High particle loading is necessary for the fabrication of high-strength porous Cu current collector. However, to date, no work focusing on systematic Cu ink development with Cu particle loading more than 95 $wt\%$ has been reported. Hence, in the present work, a novel Cu ink with a particle high particle loading and PLA as a binder has been developed. The rheological behaviour of the Cu ink with different amounts of Cu loading i.e. 91, 93, 95 and 97 $wt\%$, respectively, were investigated. Moreover, the modelling using the Herschel-Bulkley equation was done to establish the rheology. All the prepared inks showed viscoelastic and shear-thinning behaviour. Moreover, the ink having 97 $wt\%$ Cu loading exhibited optimum rheology with a shear elastic modulus of around 10^5 Pa in the linear viscoelastic area. The morphological study of the 3D printed Cu green samples was performed, and it was found that the variation in Cu particle loading significantly affected the density and volumetric shrinkage.

Chapter 5 deals with the processing routes for accurate design of the porous Cu current collector. In this chapter, process parameters such as Cu loading, layer height, nozzle diameter, and print speed were optimized for achieving minimum dimension deviation. The optimized set of process parameters was obtained as Cu loading= 97 $wt\%$, print speed =

10mm/s, nozzle diameter = 0.2 mm and layer height = 70% of nozzle diameter. Using the optimized parameters, HP-Cu parts having honeycomb and cubic structures along with a cylindrical green part were printed subsequently followed by three-step sintering in an argon atmosphere. To evaluate the efficacy of DIW 3D printed green samples, sintering of the samples was subsequently performed. The morphological analysis of the sintered samples revealed proper inter-particle bonding along with the presence of some micropores. Hence, successful fabrication of HP- Cu samples was achieved.

Chapter 6 focuses on the fabrication of high-performance porous Cu current collector. A novel approach to fabricate thin, HP-Cu current collector to withstand the crimping load during the cell assembly, using DIW and post-sintering optimization has been presented in this chapter. A systematic study of sintering parameters i.e., temperature (T), heating rate (HR), and soaking time (ST) was conducted to maximize relative density, minimize volumetric shrinkage, and enhance compressive strength. Optimized sintering conditions (938°C, 2°C/min heating rate, and 80-minute soaking time) led to significant improvements in properties. A proper inter-particle bonding with 91% relative density and 215 MPa ultimate compressive strength was achieved. Finally, a proof-of-concept study targeting the fabrication of thin HP-Cu current collector was performed and the pore size of 154±10 μm with a thickness of 200 μm was achieved successfully using the optimized set of DIW and sintering parameters. The resulting HP-Cu current collector demonstrated remarkable mechanical robustness, withstanding compressive stress of 35 MPa without fracture.

Chapter 7 describes the in-depth morphological characterization of Li-ion deposition and the investigation of coulombic efficiency with varying current density. Comprehensive morphological and electrochemical characterization has been conducted to assess dendrite suppression at the lithium anode. The performance of the 3D-printed porous Cu current collector was compared to that of traditional Cu foil. Moreover, coulombic efficiency tests have been conducted at current densities of 1 mA/cm² and 3 mA/cm², with a plating capacity of 5 mAh/cm². The results showed that the 3D-printed Cu current collector achieved an average coulombic efficiency of more than 95 % at current densities of 1 mA/cm² and 3 mA/cm², with a plating capacity of 5 mAh/cm², low charge resistance of 169 Ω, and superior impedance profiles when compared to traditional Cu foil. The microstructural analysis confirmed uniform Li deposition with no dendritic growth, indicating the reliability and stability of the 3D-printed HP-Cu in LMB applications. Additionally, a comparative study with the relevant literatures has been done to showcase the benchmarking achieved in the present work. The results of the comparative study with existing literature underscore the satisfactory electrochemical performance of the LMB system using the HP- Cu current collector. Furthermore, it offers valuable insights into the fabrication of durable, high-strength current collectors, which is crucial for the next generation of high-energy-density batteries.

Chapter 8 presents the major conclusions of the current investigation pertaining to the 3D printed porous Cu current collector.

This research makes significant scientific contributions by developing a novel high-particle-loaded $\boldsymbol{Cu}$ ink for DIW, for 3D printing of porous structures. A comprehensive optimization of printing and sintering parameters led to the successful fabrication of self-standing, HP- $\boldsymbol{Cu}$ current collectors with high relative density and enhanced compressive strength. These architected current collectors demonstrated superior electrochemical performance, including improved Coulombic efficiency, suppressed dendrite formation, and stable lithium deposition behavior when used in LMBs.