Chapter 2: Review of literature

This chapter begins with a concise introduction to LMBs, emphasizing their significance in the next generation of high-energy-density energy storage systems. Following this, the chapter delves into an in-depth exploration of various processing routes for the fabrication of porous Cu current collectors, with a particular focus on AM techniques.

A brief yet informative overview of different AM techniques is presented to establish their potential and suitability for fabricating 3D porous Cu current collectors. The discussion outlines the advantages of AM, such as design flexibility, material efficiency, and the ability to engineer complex architectures with tailored porosity features that are especially valuable for enhancing the electrochemical performance of current collectors in LMBs.

Subsequently, a comprehensive review of conventional fabrication methods for porous Cu structures is conducted. These traditional methods, including chemical etching, powder metallurgy, and templating techniques, are evaluated in terms of their capabilities, limitations, and scalability.

The chapter then transitions to an extensive literature review of state-of-the-art AM techniques applied specifically to the development of 3D porous Cu current collectors. Through this critical evaluation of both conventional and AM approaches, key research gaps are identified. These include limitations in structural integrity, challenges in achieving high-particle-loading inks, and inadequate understanding of the relationship between microstructural features and battery performance.

The chapter concludes with a precise problem formulation, laying the foundation for the current research. It articulates the major objectives that guide the investigation, which aim to address the identified gaps by optimizing AM-based processes for the fabrication of high-performance, porous Cu current collectors tailored for use in LMBs.

2.1 Ink Development

AM techniques have revolutionized the fabrication of metallic components, particularly for applications requiring complex geometries and tailored properties. Among AM technologies, DIW has gained increasing attention for the fabrication of metallic structures due to its simplicity, room-temperature operation, and lower cost compared to laser-based techniques. In DIW, a highly loaded ink, typically composed of metallic fillers, binders, solvents, and additives, is extruded through a nozzle to form a three-dimensional structure which is subsequently sintered to achieve densification.

Cu, owing to its high electrical conductivity, low cost compared to silver, and widespread availability, represents a highly attractive candidate for ink formulation in printed electronics, flexible devices, and structural components. However, the development of Cu inks suitable for DIW is challenging due to the need for high filler loading, stable dispersion, control of rheological properties, and mitigation of oxidation during processing. Despite numerous studies on ceramic and metallic ink systems, there remains a gap in developing Cu-based inks with high filler loading for achieving high-density final parts.

This review systematically explores the historical development, formulation strategies, challenges, and recent advances in Cu ink development for DIW, synthesizing findings from contemporary research efforts including the works of Park et al.[29], Mooraj et al. [30], Biasetto et al.[31], and others.

2.1.1 Fundamentals of Ink formulation for DIW

The formulation of inks suitable for DIW involves careful balancing between solid content, binder system, solvent selection, and the inclusion of functional additives. The primary components are:

- **Filler Material (Metallic Particles):** The major component providing the final functional properties. For metallic inks, the filler typically consists of sinterable metal powders such as titanium alloys, steel, tungsten, Cu, and Aluminum alloys [32].
- **Binder:** Provides mechanical strength to the 'green body' (pre-sintered structure) by holding the filler particles together. Binders also influence ink viscosity and shear-thinning behavior [33].
- **Solvent:** Facilitates the uniform dispersion of fillers and binders, impacting ink rheology, evaporation rate, and particle-particle interactions.
- **Additives:** Include surfactants, dispersants, plasticizers, and rheology modifiers to fine-tune the ink's flow behavior and stability.

The inks must exhibit Herschel–Bulkley flow behavior, characterized by a yield stress (to maintain shape post-extrusion), shear thinning (to enable extrusion at reasonable pressures), and rapid recovery [34].

For metallic inks, particularly Cu, high filler loading is crucial to minimize shrinkage during sintering, maximize final density, and optimize mechanical and electrical performance. However, as filler content increases, the ink's viscosity rises sharply, posing challenges for extrusion and nozzle clogging.

2.1.2 Development of Cu ink

The development of Cu inks for DIW has attracted considerable attention in the AM field due to Cu's excellent electrical conductivity, high thermal stability, and economic advantage over precious metals like silver and gold. However, the formulation of Cu inks faces unique challenges, including high oxidation susceptibility, the difficulty of achieving high solid loading without sacrificing rheology, and maintaining structural stability post-sintering. Park et al. [29] addressed early issues in Cu ink development by formulating a Cu nanoparticle-based ink using Polyvinylpyrrolidone (PVP) as a binder and Diethylene glycol as a solvent, achieving a particle loading of around 20 $wt\%$. Their work demonstrated good dispersion and moderate viscosity, but such low solid content limited the applicability for DIW, which requires higher viscosities and yield stresses to maintain structure after extrusion. Mooraj et al. [30] advanced this by developing a Mn– Cu bimetallic ink using Poly(methyl methacrylate)-b-poly(butyl acrylate) (PMMA-b-PBA) as the binder and Tetrahydrofuran (THF) as the solvent, achieving 70 $wt\%$ solid loading. Their work illustrated that higher filler loading significantly improved the mechanical integrity of the green parts, but the focus on a bimetallic system restricted its direct application for pure Cu ink development. In a significant leap forward, Biasetto et al. [31] focused on maximizing Cu particle loading using a water-based binder system composed of Polyvinyl alcohol (PVA) and Polyethylene glycol (PEG), with distilled water as the solvent. They successfully prepared Cu inks with a solid loading up to 94 $wt\%$, carefully tuning the powder-to-binder volume ratio and optimizing particle size distribution to achieve acceptable rheological behavior. Biasetto et al. [31] emphasized that powder size distribution had a greater impact on rheological properties and printability than the chemical composition of the powder itself, an important insight for future ink design strategies.

Zeng et al. [35] provided a comprehensive review in "Nanoscale" on various methods for Cu ink formulation, oxidation resistance strategies, and sintering techniques for printed electronics. They categorized Cu inks into four types: Cu particle inks, Cu nanowire inks,

Cu precursor inks, and mixed Cu inks. According to Zeng et al. [35], Cu particle inks, despite being relatively easier to formulate via chemical reduction methods, suffered from severe oxidation problems that increased the sintering temperature requirements due to the formation of CuO and Cu_2O. To counteract these effects, surface capping agents like PVP, oleic acid, lactic acid, and thiols were investigated to stabilize Cu nanoparticles against oxidation without inhibiting their sinterability. For example, lactic acid was identified as a highly effective capping agent capable of producing 10 nm Cu nanoparticles that could sinter at low temperatures (around 150°C) while maintaining high electrical conductivity. Zeng et al. [35] also discussed advanced sintering methods such as intense pulsed light (IPL) sintering and microwave-assisted sintering, which could significantly lower the thermal budget and enable processing on flexible substrates. These findings are crucial, considering that high filler loading and oxidation control must be achieved simultaneously for effective DIW of Cu inks. Similarly, Taylor et al. [36] explored ink preparation for metallic systems using iron and nickel particles, focusing on the synthesis of inks using polylactic-co-glycolic acid (PLGA) binders and graded volatility solvents such as dichloromethane. Although their study was directed towards oxide and metallic particle systems for cellular structures, the underlying principles of solvent selection, particle packing, and green body stability directly apply to Cu ink formulation for DIW [37].

Binders such as Polyvidone, Poly(methyl methacrylate)-b-poly(butyl acrylate), and 2, 4, 6-trimethylbenzoyldiphenylphosphine oxide have been used to date for the preparation of metallic ink [38]. Moreover, solvents such as diethylene glycol, Tetrahydrofuran, 2-butoxyethanol, 1,6-hexanediol diacrylate, and 1,1,1-Trimethylolpropanetriacrylate have been used [39]. Compared to metallic ink, the rheology of ceramic ink is far better established. Ceramic ink with filler materials such as aluminum oxide, titanium oxide, silicon dioxide, tungsten oxide, and zirconia, along with binders such as Poly(lactic-co-glycolic acid), Polyvinylpyrrolidone, Sodium alginate, Methylcellulose, Polyvinyl alcohol, and Polyethylene glycol has been developed successfully. To achieve optimum ink rheology, most of the aforementioned work focuses on testing the different combinations of filler and binder materials, the major outcome of most of the research in this direction showcased the importance of maximizing the amount of filler content and minimizing the proportion of additives [36]. A high proportion of additives in ink results in more porosity and crack formation that ultimately leads to reduced storage modulus, mechanical strength and performance. Hence, it is important to develop a metallic ink with a high proportion of metallic filler particles. It is hypothesized that high particle-loading metallic ink results in a higher storage modulus that ultimately leads to the fabrication of extremely fine intricate shapes for LMB applications.

Moreover, it has been reported in previous studies [21,22] that as the particle loading increases, the viscosity of the ink also increases which results in a higher force to extrude the material and the problem of clogging of the nozzle may occur. Thus, the development of Cu ink with high particle loading i.e. above 95 $wt\%$ remains a challenging task. To date maximum 94 $wt\%$ Cu loading has been achieved in the DIW of Cu. Additionally, related to the development of Cu ink for LMB applications, only few works have been reported. It has been also reported that fine micron-sized pores strongly support the plating and stripping behavior in LMB thereby improving its efficiency [23]. A 3D porous Cu current collector was fabricated using prepared ink and it was reported that a higher-resolution porous structure results in an overall increase in the LMB performance in terms of suppression in dendritic growth, improvement in coulombic efficiency and improved plating/stripping behavior. Callegari et al. [82] prepared HP-Cu samples using a Cu ink consisting of Cu, CuO and Pluronic F127. It was concluded from their work that a highly porous interconnected network in Cu current collectors significantly increases the active surface area for the deposition of lithium. Thus, it could be inferred that for LMB applications, an extremely dense fine HP-Cu structure results in an overall increase in its performance [42]. However, to fabricate such structures, it is essential to develop a suitable 3D printable Cu ink capable of retaining such a complex fine shape [43].

2.1.3 Comparative Summary of Cu Inks

The research on Cu-based inks, as presented in Table 2.1, reflects the intensive development efforts aimed at optimizing Cu inks for use in printed electronics.

Table 2.1 Comparison of Cu Inks Prepared Using Different Reducing Agents [35]

Material	Capping/Reducing Agent	Substrate	Printing Method	Post-Treatment Method	Resistivity (μΩ·cm)
Cu nanoparticles (CuNPs)	PVP	Glass/PI	Spin-coating	Thermal sintering (225 °C in Ar)	44.7
CuNPs	Lactic acid	Glass	Spin-coating	Thermal sintering (150 °C in N_2)	21.0 ± 7.0
Cu flakes	Phenol resin/Triethanolamine	PI	Screen printing	Thermal sintering (170 °C in air)	74.6
CuNPs	Oleic acid	PI	Air-brush	Intense Pulsed Light (IPL)	6.7
CuNPs + Ag	Oleylamine	Glass	Spin-coating	Thermal sintering (350 °C in vacuum)	12.0
CuNPs + Ni	PVP/EC	PET	Screen printing	IPL	—
Cu formate/CuNPs	AMP	PET	Screen printing	Thermal sintering (140 °C in N_2)	11.3
CuNPs	1-Octanethiol	PI	Inkjet	IPL	24
CuNPs	PVP/$NaH_2PO_2 \cdot H_2O$	Glass	Inkjet	Thermal sintering (325 °C in vacuum)	17.2
CuNPs + Cu nanowires	PVP	PI	Spin-coating	Thermal sintering (250 °C in Ar)	31.5

Copper-based inks are highly promising for energy storage and printed electronics due to copper's excellent electrical conductivity, which rivals that of costly noble metals like silver and gold. This ensures efficient charge transport in electrochemical systems. In addition to its high conductivity, copper is abundant and significantly more cost-effective, making it a practical choice for large-scale manufacturing. Its compatibility with additive manufacturing methods like Direct Ink Writing further enhances its appeal, enabling precise structural control and efficient material usage. These attributes position copper as an ideal material for scalable, high-performance applications. However, a major challenge limiting the broader use of copper-based inks is their strong tendency to oxidize upon exposure to air. This oxidation leads to the formation of insulating copper oxides, significantly reducing electrical conductivity and compromising the performance and reliability of printed devices. The issue is further exacerbated during thermal processing, making oxidation control essential for practical application in printed electronics and energy systems. As a result, considerable research efforts have been directed toward developing effective stabilization strategies to prevent or minimize oxidation. These include the use of protective ligands, core-shell nanoparticles, and reducing atmospheres during processing. From the above literature it can be concluded that Cu nanoparticle (CuNP) inks, stabilized with agents like PVP, resist oxidation and agglomeration while maintaining good dispersion. Low-temperature sintering (<250 °C) is essential for flexible substrates (e.g., PET, PI), using methods like thermal or intense pulsed light sintering. To boost conductivity and sintering, additives like AgNPs, Ni, Cu nanowires, or Cu formate are often included. These hybrids improve particle bonding and oxidation resistance.

Overall, advanced formulations and processing make Cu inks a cost-effective, scalable alternative for flexible electronics.

2.2 Printing Parameter Optimization

2.2.1 Role of Printing Parameters for 3D Printing of Parts

In DIW, the ability to fabricate high-resolution, dimensionally accurate, and structurally sound components depends not only on the formulation of the ink but also on the careful selection and optimization of key printing parameters. These parameters, particularly nozzle diameter, layer height, printing speed, and extrusion pressure directly affect the accuracy, surface finish, and internal integrity of the printed parts [44]. For a material to be reliably deposited in layer-by-layer fashion without defects such as collapse, distortion, or delamination, there must be a balanced relationship between the rheological behavior of the ink and the kinematics of the printer. An ink with suitable shear-thinning properties and a yield stress that enables shape retention post-extrusion is a baseline requirement; however, even a well-designed ink may produce poor results if printing parameters are not appropriately calibrated [45]. For instance, a mismatch between the nozzle diameter and extrusion pressure may lead to inconsistent filament width or clogging. Similarly, an improper layer height can cause gaps between printed layers or smearing of deposited material. Thus, parameter optimization is essential for achieving high-resolution, defect-free structures, especially in complex geometries or thin-walled porous structures like those used in battery current collectors or heat exchangers. Moreover, in the case of high-particle-loading metallic inks such as those involving Cu, the elevated viscosity introduces additional constraints on flow dynamics, making optimization even more critical [46]. This is particularly relevant for performance of HP-Cu structures, where layer precision and internal porosity directly impact the functional performance in applications like current collectors for batteries or thermal spreaders. The optimization of printing parameters, therefore, is not an auxiliary step but a core requirement for translating promising ink formulations into functional, high-precision DIW-printed parts.

2.2.2 Literature Review on Printing Parameter Optimization in DIW

Numerous studies have examined the role of DIW process parameters in controlling print quality, with a majority of early efforts focused on ink base systems due to their well-established rheological profiles and sintering behavior. Shao et al. [47] investigated the influence of various DIW parameters on the print quality of zirconia structures. They reported that a nozzle diameter of 0.5 mm, layer height of 0.4 mm, and a printing speed of 20 mm/s resulted in optimum fidelity for ceramic parts, demonstrating that relatively low speed and moderate nozzle diameter for stable filament deposition. Their work emphasized that maintaining the layer height at ~80% of the nozzle diameter improved interlayer adhesion and minimized deformation.

Building on this, Wu et al. [48] conducted an orthogonal optimization experiment to study the combined influence of parameters such as nozzle diameter, layer height, and print speed. They concluded that the optimal setup for ceramic inks was a nozzle diameter of 0.41 mm, 50% - layer height relative to the nozzle, and a print speed of 15 mm/s, indicating the necessity of fine-tuning each factor individually due to their interdependent effects. Their data-driven approach confirmed that layer height was the most sensitive parameter in determining surface smoothness and feature definition.

Chu et al. [49] focused on zeolite-based ink and employed single-factor testing to isolate the effects of process variables. They found that smaller nozzle diameters, while improving resolution, increased the likelihood of clogging in high-viscosity inks. Layer height also played a significant role in shaping fidelity, particularly for porous structures where over-or under-extrusion could compromise the connectivity and mechanical robustness of the framework. They emphasized the importance of synchronizing print speed and extrusion rate to maintain accurate deposition, especially in designs with varying wall thicknesses.

When moving from ceramics to metals, particularly Cu, the challenge becomes more complex due to higher ink viscosity and greater sensitivity to extrusion pressure. Kolli et al. [50] performed one of the few systematic DIW parameter studies on Cu inks. They used nozzle diameters of 400 µm and 580 µm, printing speed of 20 mm/s, and an extrusion pressure range of 0.139-0.152 MPa. Their findings suggested that while higher pressures enabled smoother flow in high-particle-loading Cu inks, they also increased the risk of filament swelling and dimensional inconsistency if not balanced with travel speed and retraction settings. Importantly, their study highlighted the necessity of parameter tuning in tandem with ink rheology—a theme consistently echoed across other materials as well.

In contrast, Biasetto et al. [31] developed a Cu ink with 94 wt% Cu loading and demonstrated successful DIW printing followed by sintering. However, their study concentrated more on ink formulation and flow behavior rather than a full optimization of DIW process parameters. Although they achieved reliable structures, the lack of systematic testing across variables like speed, layer height, and pressure left a gap in understanding how these factors could further improve resolution and density. Notably, their work employed relatively standard parameters, showing the robustness of their ink but also hinting at potential improvements through parameter fine-tuning.

The broader literature review indicates that although extensive DIW process optimization exists for ceramic systems, its application to metallic and high-loading Cu inks remains limited. For instance, several works like those of Chu et al. [49] and Wu et al. [48] confirm that layer height must generally range between 40–60% of the nozzle diameter to balance print quality and structural cohesion. Similarly, print speed is often optimized within the 10–25 mm/s range, though this varies depending on ink viscosity and thixotropy. In the metallic domain, only Kolli et al. [50] appear to have rigorously optimized parameters for Cu DIW. Most others, including Biasetto et al.,[31] report successful prints without isolating the influence of each parameter, which limits reproducibility and scalability.

In the specific context of HP-Cu porous current collectors, printing accuracy is particularly important. Previous studies [51] shows that the achieved pore sizes above 200 µm, which, while acceptable, may be suboptimal for maximizing battery performance where smaller, uniform pores are preferred. The reason for these larger pores could lie in low particle loading, inadequate extrusion control, or inappropriately selected printing parameters, all of which could distort the microstructure during deposition or drying. As a result, the current state of literature reveals a critical gap in the systematic development of Cu-based DIW processes that simultaneously optimize both ink properties and printing parameters for thin-walled, high-porosity structures with precise dimensional control.

In summary, while DIW has proven itself as a powerful tool for 3D printing ceramic and metallic parts, the optimization of printing parameters remains a crucial and underexplored step, especially for high-particle-loading Cu inks. Only a handful of studies, most notably by Kolli et al., have attempted detailed parameter optimization for Cu systems. The lack of such optimization in recent high-loading ink studies like Biasetto et al. [31], highlights a clear opportunity for future work. Moreover, as application demands for miniaturized and porous Cu structures (such as current collectors or heat exchangers) grow, the importance of combining optimized material formulation with rigorous process control will be paramount to realize the full potential of DIW in functional device fabrication.

2.3 Sintering Parameter Optimization

2.3.1 Role of Sintering Parameters for 3D Printing of Parts

Sintering plays a pivotal role in determining the mechanical strength, structural integrity, and microstructure of Cu electrodes fabricated using DIW, particularly when intended for advanced energy storage applications such as LMBs. In DIW, sintering is not merely a densification step but a transformative post-process that consolidates printed green parts into strong, electrically conductive, and mechanically stable metallic structures [52]. The mechanical strength of the Cu electrode is especially critical in LMBs due to its dual requirement for thin, porous geometries (which improve ion transport and reduce dendritic growth) and sufficient structural robustness to withstand repeated charging, discharging, and mechanical stresses during operation. Porous structures, while beneficial for surface area and electrochemical performance, inherently compromise mechanical strength due to reduced cross-sectional material continuity. Therefore, optimizing sintering parameters such as temperature, duration, atmosphere, and heating rate becomes essential for balancing porosity with strength. At elevated sintering temperatures, particle necking and diffusion-driven bonding improve, leading to higher density and strength [53]. However, excessive sintering may lead to undesired grain growth or pore collapse, which can reduce surface area and limit the functional benefits of porosity. In the context of Cu, achieving metallurgical bonding at sintering temperatures between 950°C to 1050°C has been shown to significantly affect final properties like relative density, shrinkage, and microstructural stability, directly influencing the electrode’s ability to resist deformation, cracking, or delamination under electrochemical cycling or mechanical stress [54]. As LMB electrodes are subject to static and cyclic mechanical loading, as well as diffusion-induced stresses during lithiation/delithiation, sintering optimization emerges as a central strategy for ensuring both performance and safety in battery operation. Thus, sintering parameter optimization is not only necessary for improving densification but also critical for achieving mechanically robust porous Cu structures suitable for long-life, high-efficiency LMBs.

2.3.2 Review on Sintering Parameter Optimization for Electrodes

The significance of mechanical strength in the performance and reliability of electrodes, especially in energy storage systems, has been established across multiple studies. In the context of traditional flat Cu foils used as current collectors in LMBs, their inherently low surface area has been associated with the formation of lithium dendrites during charging cycles, which ultimately causes short-circuiting and capacity fading [55]. To overcome this, porous Cu current collectors have been proposed and explored as a solution, owing to their high surface area, which promotes uniform lithium deposition and suppresses dendrite growth [56]. However, fabrication of thin and porous Cu structures inherently compromises mechanical strength. This issue has been highlighted in several studies: Haiping et al. [57] emphasized that porous silicon structures in LIB suffer from low strength, which limits their energy density and long-term cycling stability. Similarly, Yoshinao et al.[58] showed that negative electrodes in lithium-ion batteries face substantial static and cyclic loads during use and manufacturing (including vibrations and pressure during assembly, which can cause electrode fracture and short-circuiting. Zang et al. [59] further reinforced the idea that mechanical failure is a major risk in safe lithium battery design. Zhu et al.[60] explained that during lithiation, the diffusion of lithium ions causes stress build-up within electrode materials, often leading to mechanical damage, while Wenbin Zhou [6] reported that stresses can be introduced during assembly and cycling, particularly due to ongoing diffusion and ion deposition, which accumulates over time and contributes to structural fatigue and breakdown.

From these findings, it becomes evident that mechanical strength of porous Cu electrodes is as critical as their electrochemical performance. In the context of DIW-fabricated Cu structures, sintering directly affects the necking between particles, grain boundaries, and the overall density, which together govern the mechanical resilience of the final part [61]. It is reported that amongst the three major stages in DIW ink formulation, printing, and post-processing, sintering has the most pronounced influence on mechanical strength, density, and internal microstructure [62]. In ceramic DIW systems, post-sintering optimization has been extensively studied. For instance, materials like alumina, optimized sintering parameters such as temperature and dwell time led to significant improvements in mechanical properties including fracture toughness and compressive strength. Moreover, previous studies [63] on Cu also show that sintering temperatures ranging from 950°C to 1050°C yield significant differences in shrinkage (~13.1%) and relative density (~94.5%). Importantly, Cu sintered at 1050°C for 3 h exhibited a more homogenous microstructure with improved inter-particle bonding, leading to better mechanical strength. In a related study, sintered Cu structures with thin wall dimensions of ~340 μm exhibited excellent metallurgical bonding, highlighting the potential of DIW-sintered Cu for fine-featured, yet robust designs.

Despite these advancements, the literature still lacks a systematic study that directly links variations in sintering parameters to the mechanical properties of DIW-printed Cu parts. Many works have focused either on achieving higher particle loading in the ink or optimizing printing fidelity, while sintering parameters have often been kept constant or inadequately explored. This represents a critical knowledge gap, especially when targeting demanding applications such as LMBs, where the electrode not only needs to exhibit tailored porosity and high conductivity but also withstand cyclic loading, vibration, and thermal stresses over extended usage cycles [64]. The importance of such optimization becomes even more pronounced when considering requirements like pore sizes below 200 µm, which are difficult to achieve with traditional extrusion or powder metallurgy techniques due to limitations in flowability and structural retention. Often, failure to achieve fine, consistent porosity can be traced to suboptimal sintering, which leads to either underdeveloped necks or excessive grain growth.

Therefore, to address these dual challenges, fabricating highly porous, thin Cu electrodes while ensuring sufficient mechanical strength, a detailed, quantitative investigation into sintering parameters is required. Parameters such as heating rate, soaking time, sintering temperature, sintering atmosphere (e.g., inert or reducing), and cooling profile all influence grain boundary formation, residual stresses, and densification kinetics. For example, rapid heating can trap volatile decomposition products from the binder phase, leading to pore formation or internal cracking. A reducing atmosphere can mitigate oxidation, but excessive reduction may cause structural collapse if not controlled. Similarly, longer soak times enhance diffusion but risk grain coarsening [52]. All these effects are interdependent and must be optimized carefully for the specific geometry and scale of the printed Cu electrode.

In conclusion, while porous Cu current collectors offer significant performance advantages for LMBs by suppressing dendrite growth and improving surface area, their structural fragility remains a major bottleneck. Mechanical strength, influenced strongly by post-processing sintering conditions, is a critical yet underexplored variable in current DIW research on Cu. Literature to date provides evidence of sintering affecting density and bonding quality, but does not systematically connect these changes to mechanical performance metrics such as yield strength, fracture resistance, or fatigue life under realistic battery operating conditions.

2.4 Fabrication of porous Cu Current Collector

The fabrication of porous Cu current collectors is critically important for LMBs due to their ability to enhance electrochemical performance and improve safety. Porous structures provide a high surface area that facilitates uniform lithium-ion flux and homogeneous lithium deposition, which helps mitigate dendrite formation, a major challenge in LMBs that can lead to short circuits and capacity loss [65]. Additionally, the porous framework can accommodate the volume changes associated with lithium plating and stripping, thereby improving structural stability and cycling performance [66]. This design also promotes better electrolyte infiltration and ion transport, further contributing to enhanced battery efficiency and longevity [67]. As a result, porous Cu current collectors are seen as a promising strategy to enable the practical use of lithium metal anodes in next-generation high-energy-density batteries [68].

2.4.1 Characteristics of Current Collectors for Lithium Metal Batteries

The term "characteristics of current collectors for LMBs" refers to the specific physical, chemical, and electrochemical properties that make a material suitable to function as a current collector in LMBs systems. Current collectors are essential, though electrochemically inactive, components of a battery that play a key role in supporting the electrode materials and enabling efficient electron flow between the electrodes and the external circuit [69]. In LMBs, these characteristics become even more critical due to the highly reactive nature of lithium metal and the challenges associated with its cycling behavior [70].

One of the most important characteristics is high electrical conductivity, which allows the current collector to collect and transport electrons with minimal energy loss efficiently [71]. Chemical and electrochemical stability is also crucial, particularly on the anode side, where materials like Cu must resist unwanted reactions with Li and electrolyte components [72]. Mechanical properties, such as strength and flexibility, help the current collector accommodate the significant volume changes that occur during lithium plating and stripping [46]. If the collector lacks sufficient durability, it may crack, delaminate, or deform, leading to reduced performance or even safety risks [57]. Furthermore, low weight and thin structure are desirable to improve the battery's energy density, especially for portable or automotive applications where weight and volume are critical constraints.

The importance of these characteristics in LMBs arises from the unique challenges posed by the lithium metal anode [73]. Lithium tends to form dendrites, needle-like structures that can grow through the electrolyte and separator, leading to internal short circuits and battery failure. A well-designed current collector with good surface properties can promote uniform lithium nucleation and suppress dendritic growth, thus improving both performance and safety. Additionally, the current collector influences the formation of the SEI, a protective layer that forms on lithium metal during initial cycling. A SEI when supported by a suitably compatible current collector surface, plays a pivotal role in enhancing the electrochemical performance of lithium metal batteries. The formation of a uniform and robust SEI not only provides a protective barrier that inhibits continuous side reactions between lithium metal and the electrolyte but also ensures efficient Li transport during repeated cycling. A current collector with compatible surface chemistry promotes homogeneous SEI formation. Table 2.2 shows the classification and characteristics of current collectors for LMBs. It has been reported in the previous studies that Aluminum is the most used cathode current collector in lithium-ion and lithium metal batteries due to its high conductivity, lightweight, and low cost. It works well with Li-containing cathode materials like $\mathrm{LiFePO_4}$ and NCMA natural $\mathrm{Al_2O_3}$ layer on its surface provides corrosion resistance. However, it reacts with lithium at low potentials, making it unsuitable as an anode current collector.

Table 2.2 Classification and Characteristics of Current Collectors for LMBs[73]

Material	Use as Cathode Collector	Use as Anode Collector	Remarks
Aluminum	Commonly used with various cathode materials	Reacts with lithium at low potential	High electrical conductivity, lightweight, and low cost. The naturally forming surface oxide layer (Al_2O_3) offers good corrosion resistance.
Cu	Oxidizes at high potential, thus not ideal for cathodes	Commonly used with various anode materials	High electrical conductivity, lightweight, and cost-effective. Susceptible to surface oxidation at high voltage.
Nickel	Often used with $LiFePO_4$ cathodes	Used with nickel oxide and silicon/carbon anodes	Chemically stable in acidic and basic environments. May react with electrolyte at high voltage, limiting its stability as a collector.
Stainless Steel	Used for $LiMnO_4$ cathode materials	Suitable for MnO_2 and Fe_3O_4 anodes	Possesses a surface passivation film (e.g., Cr_2O_3) that gives high corrosion resistance. Stability can vary with electrode/electrolyte pairing.
Carbon-Based	Used in forms like carbon fibers, nanotubes, and cloth	Not limited to one anode type	Offers high conductivity, flexibility, and low density—suitable for flexible or lightweight battery designs.

Cu is widely used as an anode current collector because of its excellent conductivity, good mechanical properties, and stability at low potentials. It supports materials like graphite and Li metal [74]. However, it cannot be used as a cathode collector due to oxidation at high voltage and its lithiophobic nature, which leads to uneven lithium deposition and dendrite formation [75].

Nickel is used as a current collector for both cathodes and anodes, especially with $\mathrm{LiFePO_4}$ and Si/C anodes. It offers good stability in harsh environments, but it may react with electrolytes at high voltage, limiting its long-term use on the cathode side.

Stainless steel is a corrosion-resistant collector, often used with $\mathrm{LiMnO_4}$ cathodes and $\mathrm{MnO_2}$ or $\mathrm{Fe_3O_4}$ anodes. It has good mechanical strength but is heavier than Al or Cu, which can reduce the cell's energy density. Its performance also depends on compatibility with specific electrode and electrolyte combinations.

Carbon-based materials like CNTs, carbon cloth, and graphene are lightweight, flexible, and conductive, making them ideal for flexible and next-generation batteries. However, their lithiophobic nature can hinder uniform lithium deposition, often requiring surface modifications to improve compatibility with lithium metal.

2.4.2 Modification Techniques of Cu-Based Current Collectors for Enhanced Lithium Deposition

The modification of Cu current collectors for LMBs is a crucial area of research aimed at overcoming challenges such as dendritic lithium growth and unstable SEIs. The expanded Table 2.3 outlines two major categories of Cu collector modifications: structural and chemical. Structural modifications are primarily concerned with altering the physical form of Cu, such as changing it from a flat foil into a three-dimensional structure, while chemical modifications involve altering its surface chemistry to improve interaction with lithium. Each modification strategy aims to address specific performance limitations and improve parameters like lithium plating uniformity, Coulombic efficiency (CE), and cycle life.

In the realm of structural modifications, various template methods have been developed. Organic templates and inorganic are used to fabricate porous Cu structures with high surface areas [22]. These 3D architectures reduce local current density and provide more sites for lithium nucleation, which helps prevent dendrite formation [76]. However, fabrication using organic templates can be time-consuming and costly, whereas inorganic templates offer more scalable and energy-efficient routes. Additionally, dealloying methods, where Cu-Zn alloys are chemically or thermally treated to remove zinc-can produce porous Cu frameworks [77]. These frameworks enhance lithium deposition by offering a larger surface area and roughness that supports uniform nucleation [78].

Another approach under structural modification involves oxidation–reduction techniques, where Cu is first oxidized into compounds like $\mathrm{Cu(OH)_2}$ or CuO and then thermally reduced to form a porous, mossy structure [79]. These methods yield Cu surfaces with enhanced Li ion flux distribution but typically require high energy input due to the heating steps involved. More advanced physical structuring methods, such as laser etching and 3D printing, allow precise design of microchannels and pores. Researchers have also found that the crystallographic orientation of Cu - whether Cu (100) or Cu (111) - can influence Li deposition behavior [86]. Such orientation engineering can guide lithium plating more uniformly, although results vary across studies, indicating a need for further exploration.

Table 2.3 -Modification Strategies for Cu Current Collectors in Lithium Metal Batteries [6], [80-85]

Modification Category	**Specific Technique**	**Description & Mechanism**	**Main Objective**	**Performance Impact & Observations**
Structural Modification	Organic Template Method	Uses organic materials like PMMA, polystyrene microspheres, cotton, etc., as sacrificial templates to create porous 3D Cu structures via electrodeposition and subsequent template removal.	Increase specific surface area (SSA), reduce local current density, guide Li plating into pores.	Enhances Li nucleation uniformity; lowers overpotential; pore size affects plating behavior; smaller pores can misguide lithium growth.
	Inorganic Template Method	Uses hydrogen or oxygen bubbles, or NaCl crystals as templates to form 3D macroporous Cu skeletons via electrodeposition or sintering.	Simplify 3D structure fabrication and improve porosity.	Provides good cycling performance and CE; gas bubble templates are scalable and easy; NaCl-based method shows over 700 cycles with CE > 95%.
	Dealloying (Vacuum or Chemical)	Cu is alloyed with Zn (e.g., brass foil), then Zn is selectively removed via vacuum distillation,	Create hierarchical pores and increase nucleation sites.	Porous CCs improve lithium accommodation and cycling stability; CE up to 100% at 300 cycles in full

		acid etching, or electrochemical dissolution, leaving porous Cu.		cells; high-temperature and acid use are concerns.
	Oxidation-Reduction Method	Flat Cu foil is oxidized (e.g., with ammonia or NaOH), then reduced thermally to generate Cu nanofibers or mossy structures.	Promote lithium diffusion and control nucleation sites.	Reduces dendrite formation; protuberant fiber tips distribute charge evenly; energy-intensive process due to heat treatment.
	Advanced Physical Structuring	Includes laser etching for vertical microchannels, 3D printing for Cu frameworks, or controlling crystal orientation (e.g., Cu(100) vs. Cu(111)).	Guide Li-ion flux; modify electric field; suppress vertical dendrite growth.	Micropores promote deep Li infusion; orientation-specific deposition improves cycling; $Cu(100)$ and $Cu(111)$ both show benefits depending on conditions.
Chemical Modification	Alloying (Cu-Zn, Cu-Ag, Cu-Sn)	Cu is alloyed with metals like Zn, Ag, or Sn using sintering, sputtering, or dealloying to reduce Li nucleation barriers.	Improve lithiophilicity and reduce overpotential.	Enhances uniform lithium plating and CE; Zn-alloyed CCs are low-cost and effective; up to 98% CE over 160 cycles reported.

Oxidation (CuO, $\mathrm{Cu_2O}$)	Forms Cu oxides on the Cu surface via water bath, thermal, plasma, or electrochemical methods; oxides convert to $\mathrm{Li_2O}$ in situ.	Stabilize SEI and distribute Li evenly.	CuO and $\mathrm{Cu_2O}$ layers guide Li nucleation; $\mathrm{Li_2O}$ acts as stable SEI component; possible lithium loss in early cycles.
Functional Spot Coating	Depositing particles (Ag, ZnO, LiF, etc.) on Cu surface to create localized lithiophilic sites.	Control lithium nucleation and suppress dendrites.	Lowers nucleation overpotential; enhances SEI quality; Cu-Ag layers show CE ~97.5% over 400 cycles; LiF allows aligned Li growth.
Protective Layer Coating	Applies a buffer/interfacial layer such as ZnO, TiO_2, LiF, Al_2O_3, Cu_3P, InN, or polymer films on Cu surface.	Block dendrite growth, buffer volume change, guide ion flux.	Provides mechanical and electrochemical stability; coatings must balance ion conductivity and structural compliance; some require complex fabrication.

For instance, Zn-alloyed Cu current collectors have demonstrated high CE and long cycle life, and Zn is both abundant and affordable. Oxidation techniques that generate CuO or $\mathrm{Cu_2O}$ layers on the surface also improve lithium nucleation. These oxides convert into beneficial SEI components (like $\mathrm{Li_2O}$) during initial cycling, though they can consume active lithium in the process [87]. The goal here is to balance surface reactivity with long-term cycling stability.

Finally, functional coatings and protective layers are added to Cu current collectors to regulate lithium-ion flux and physically suppress dendrite formation. Materials like Ag, ZnO, and LiF serve as preferential nucleation sites, reducing overpotential and helping to form stable SEI layers [88]. Other coatings, including metal oxides (like $\mathrm{Al_2O_3}$) and conductive polymers, act as buffer layers that isolate Li from direct contact with the electrolyte, preventing excessive reactions. These coatings must be mechanically robust and ionically conductive, while still being thin enough to avoid poor performance. Although highly promising, such protective strategies often require sophisticated fabrication and must be optimized for commercial scalability.

2.4.3 Electrochemical performance of the current collector fabricated using ordered and random pores

It has been reported in previous studies that ordered porous structures offer superior performance in LMBs compared to disordered pores because they enable a more uniform distribution of current density and lithium-ion flux [89]. This uniformity minimizes localized hotspots that typically initiate lithium dendrite growth, a common cause of battery failure [90]. In ordered architectures, such as vertically aligned pores, Li tends to deposit uniformly within the pores, guided by the consistent geometric framework [91]. This results in compact, dense Li layers rather than irregular, mossy, or dendritic formations often seen in disordered structures. The ordered layout also facilitates efficient ion transport and electrolyte access, improving rate capability and Coulombic efficiency [92].

Moreover, the structural regularity of ordered pores contributes to better mechanical stability and stress management during lithium plating and stripping. These architectures can more effectively accommodate volume changes and support the formation of a uniform and robust SEI, which is crucial for long-term cycling stability [93]. In contrast, disordered pores, with their random shapes and uneven pore distribution, often suffer from uneven lithium deposition and SEI breakdown, leading to poor reversibility and faster capacity fade [94]. Therefore, ordered porous current collectors provide a well-balanced platform for safe, high-performance, and durable LMBs operation. The comprehensive Table 2.4 outlines various porous metal current collectors (PMCCs) designed for LMBs, focusing on their pore structures, materials, fabrication techniques, electrolytes, and performance. These PMCCs play a pivotal role in regulating Li deposition, mitigating dendrite formation, and improving cycling stability. Among the most fundamental distinctions in design are between disordered and ordered pore structures. Disordered pores, typically produced through chemical etching or sintering, are easier to fabricate and scalable but offer less precision in controlling ion flux distribution [95]. In contrast, ordered pore designs, achieved through templating, 3D printing, or mesh pressing, allow better control of Li-ion movement and uniform deposition, enhancing battery safety and efficiency. Materials like Cu foam, Cu mesh, and nanowire-based structures dominate due to their high conductivity and compatibility with Li. For example, the use of 3D Cu foam via chemical etching allows for efficient lithium loading and enhanced electrolyte wettability, while nanowire-assembled freestanding PMCCs offer superior flexibility and mechanical stability [96]. Ordered designs like inverse opal templates enable extremely uniform Li plating, minimizing local current concentration and reducing dendritic growth. The choice of fabrication method often balances cost, structural precision, and scalability, with techniques such as slurry casting and electrochemical deposition showing promise for commercial use. Electrolyte compatibility is another essential factor. Most PMCCs tested with ether-based electrolytes (e.g., LiTFSI in DOL/DME with $LiNO_3$) exhibit higher Coulombic efficiency and longer cycling life due to the stable SEI formation and lower reactivity with lithium metal. Additionally, functional coatings like ZnO or Au layers further improve lithiophilicity and interfacial stability, demonstrating that surface chemistry modifications are just as important as structural design. These coatings help reduce overpotential, suppress SEI breakdown, and promote uniform nucleation [106].

More recent innovations include gradient pore structures, elastic matrices, and bidirectional designs. These advanced architectures not only manage lithium's volumetric changes during charge/discharge cycles but also extend cell lifespan and energy density. The bidirectional PMCCs, in particular, allow lithium plating/stripping on both sides of the collector, effectively doubling the capacity and opening doors for high-loading commercial applications. Similarly, elastic and freestanding PMCCs, built from materials like Cu nanowires or Cu-polymer composites, accommodate stress and prevent electrode cracking or delamination.

In conclusion, PMCCs offer a transformative approach to stabilizing lithium metal anodes in next-generation batteries. Their effectiveness lies in combining optimal pore structure, material selection, fabrication method, and electrolyte compatibility. While disordered PMCCs are beneficial for large-scale manufacturing, ordered and functionalized designs offer superior performance and longevity. The future of PMCC research will likely focus on integrating these strategies combining structural design with chemical surface tuning to produce lightweight, durable, and high-performance lithium metal batteries suitable for practical and commercial use.

Table-2.4 Porous Metal Current Collectors (PMCCs) for Lithium Metal Anodes [8], [70], [97-105]

Pore Type	**Material**	**Fabrication Method**	**Electrolyte**	**Max. Li Loading**	**Performance (Half-cell / Symmetric)**	**Key Features & Notes**
Disordered	3D Cu Foam	Chemical Etching (Cu–Zn alloy)	$LiPF_6$ in EC/DEC	5–6 mAh/cm²	Half-cell: 0.5 mA/cm², >250 cycles, CE > 97%	Good wettability; irregular pores; scalable method but limited structure control.
Disordered	Cu–CNT Composite	Slurry Casting	1 M LiTFSI in DOL/DME + $LiNO_3$	6–7 mAh/cm²	Symmetric cell: 1 mA/cm², >800 h, stable voltage profile	Stress relief via elastic CNT matrix; good mechanical stability.
Ordered	3DOM Cu (Inverse Opal)	Electrodeposition + PMMA Templating	1 M LiTFSI in DOL/DME + $LiNO_3$	4 mAh/cm²	Half-cell: 0.2 mA/cm², >750 h, CE > 93%	Highly regular pores; uniform Li-ion flux; low overpotential (<30 mV).
Mesh (Ordered)	Cu Mesh	Mechanical Pressing of Metal Grid	1 M $LiPF_6$ in EC/DEC	3–4 mAh/cm²	Half-cell: 0.5 mA/cm², CE ~94%, low hysteresis	Simple and scalable; enhances contact and ion transport.

Elastic	Cu Nanowire Felt	Self-Assembly of Cu Nanowires	1 M LiTFSI in DOL/DME + $LiNO_3$	7.5 mAh/cm^2	Symmetric cell: 0.5 mA/cm^2, CE > 98.5%, low voltage drop	Freestanding; excellent flexibility; long-term cycling capability.
Gradient Pore	Al_2O_3–Ni–Au/PMCC	Layered Sputtering + Electroplating	1 M $LiPF_6$ in DME	~5 mAh/cm^2	Symmetric: 1 mA/cm^2, 1000+ h cycling, stable interface	Enhances directional Li deposition; buffers stress via pore gradient.
Bidirectional	Cu–Polymer Hybrid	3D Printing + Polymer Mixing	1 M $LiPF_6$ in EC/DEC	20 mAh/cm^2	Full cell: Extended life, high CE, reduced dendrite growth	Double-sided active Li plating; enables high areal capacity.
Oxidation–Reduction	Porous Cu	Oxidized $Cu(OH)_2$, then thermally reduced	1 M LiTFSI in DOL/DME + $LiNO_3$	3–5 mAh/cm^2	Half-cell: 1 mA/cm^2, CE ~98.5%, ~600 h stability	High nucleation sites; thermal steps increase energy cost.
Electroplated	Cu Pillar Array	Electrochemical Deposition + ZnO Coating	1 M LiTFSI in DOL/DME + $LiNO_3$	6 mAh/cm^2	Half-cell: 0.5 mA/cm^2, CE > 98%, >400 h cycling	Aligned vertical growth; lithiophilic coating improves Li affinity.

3D Printed	Cu–PVDF Composite	Direct Ink Writing (extrusion-based 3D print)	1 M $\mathrm{LiPF_6}$ in EC/DMC	20 mAh/cm^2	Full cell: 3 mA/cm^2, stable for 145 h, minimal polarization	Customizable pore size (100–300 µm); precise structural control; scalable.

2.5 Research Gaps

The advancement of high-performance LMBs is closely tied to the design and effectiveness of current collectors. Cu remains the material of choice for anode current collectors due to its superior electrical conductivity, chemical stability, and compatibility with lithium. To improve electrochemical performance, porous Cu architectures have emerged as a promising solution, offering benefits such as uniform lithium deposition, suppression of dendrite growth, and effective accommodation of volume fluctuations during cycling. However, despite notable progress, key challenges remain in the fabrication, structural control, and long-term reliability of porous Cu current collectors. Addressing these critical research gaps is essential to unlock their full potential in next-generation energy storage technologies.

2.5.1 Identified Research gaps

1. **Lack of Controlled Porosity for Optimal Ion Transport**
   Current fabrication techniques offer limited precision in tailoring pore size, distribution, and interconnectivity. This hinders the optimization of ion diffusion pathways and lithium deposition behavior, affecting the battery's overall performance and safety.
2. **Need for Economically Feasible and Scalable Fabrication Approaches**
   Conventional fabrication methods are often labour-intensive, expensive, and difficult to scale. There is a need for AM techniques or hybrid methods that can reliably produce hierarchically porous Cu structures at industrial scales with consistent quality.
3. **Insufficient Understanding of Electrochemical Behavior of Hierarchical Cu Structures**

   Although hierarchical porous structures are known to improve electrochemical performance, systematic studies evaluating their behavior under realistic operating conditions remain scarce. More research is required to correlate structural features with lithium plating/stripping behavior and long-term cycling stability.

4. **Mechanical Integrity Challenges of Porous Structures** Increasing porosity often compromises mechanical strength, making the current collector susceptible to deformation or failure during prolonged cycling. Achieving a balance between porosity for electrochemical benefit and structural robustness is a key challenge yet to be fully addressed.

2.6 Research Objectives

The primary objective of this research is to develop and fabricate HP-Cu current collectors using the DIW technique, specifically engineered for high-performance LMB applications. The study focuses on establishing a comprehensive material and process framework that achieves controlled porosity, robust mechanical strength, and enhanced electrochemical performance. The main research objectives were as follows:

1. **To formulate a high-particle-loading Cu ink using polylactic acid (PLA) as a binder**, enabling the extrusion and structural stability necessary for DIW-based fabrication of porous architectures.
2. **To establish a robust processing route combining DIW and sintering**, for the reliable fabrication of three-dimensional porous Cu structures.
3. **To optimize the sintering parameters** in order to enhance the microstructural and mechanical properties of the hierarchical porous Cu electrodes.
4. **To perform comprehensive electrochemical characterization** of the fabricated hierarchical porous Cu structures to evaluate their suitability and performance as current collectors in lithium metal batteries.

2.7 Motivation for the present study

LMBs have garnered significant interest due to their superior theoretical energy density and potential to outperform conventional lithium-ion systems. However, their practical deployment remains constrained by critical issues such as lithium dendrite formation, low coulombic efficiency, and associated safety hazards. One of the most promising strategies to address these limitations involves the implementation of 3D architected porous Cu current collectors. Despite their potential, the fabrication of such hierarchically porous architectures through conventional manufacturing techniques is limited by a lack of precision, poor control over structural features, and scalability challenges. AM, particularly DIW, has emerged as a transformative solution by enabling the fabrication of complex geometries with tailored porosity, reduced material waste, and compatibility with a diverse range of material systems.

Nevertheless, the practical realization of DIW-fabricated Cu current collectors is hindered by several technical barriers, including the development of stable, high particle loading inks; precise control of printing and post-processing parameters; and the absence of comprehensive validation under relevant electrochemical conditions.

This thesis aims to bridge these critical gaps by (i) formulating a high-solids-loading Cu ink with optimal rheological characteristics, (ii) establishing an optimized DIW and sintering workflow for fabricating mechanically robust, hierarchically porous Cu structures, and (iii) evaluating their electrochemical performance in LMB configurations. The overarching motivation is to develop a scalable, cost-effective, and high-fidelity manufacturing route for next-generation current collectors, thereby contributing to the advancement of high-performance energy storage technologies.