

Chapter 8: Conclusions

A novel *Cu* ink with a particle loading of more than 95 wt% and polylactic acid (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, 97 and 99 wt% ,respectively, were investigated. Moreover, process parameters such as *Cu* loading, layer height, nozzle diameter, and print speed were optimized for achieving minimum dimension deviation. A systematic study of sintering parameters—temperature (T), heating rate (HR), and soaking time (ST)—was conducted to maximize relative density, minimize volumetric shrinkage, and enhance compressive strength. A porous *Cu* current collector with pore sizes under 200 μm was fabricated using direct ink writing and sintering techniques. The salient conclusions of the research are as follows:

8.1 Development of high particle loaded copper ink

This study developed PLA-based *Cu* inks (93–97 wt%) for DIW 3D printing of complex HP-*Cu* structures, targeting advanced applications like LMBs. Comprehensive analysis of their rheological, morphological, and microstructural properties confirmed the inks' suitability for fabricating high-quality, intricately shaped *Cu* components. The brief conclusions are as follows:

- 1. Rheological Properties:** All developed *Cu* inks demonstrated shear-thinning and linear viscoelastic behaviour, enabling smooth extrusion, stable flow, and accurate deposition. These rheological properties are crucial for achieving high-resolution, defect-free structures essential for achieving high-quality prints.
- 2. Optimization of Ink Composition:** Among all formulations, the ink with 97 wt% *Cu* showed optimal performance, combining the highest storage modulus (0.90×10^5 Pa) for shape retention and the lowest shear-thinning exponent ($n = 0.54$) for

stable, consistent extrusion making it ideal for high-quality DIW 3D printing of *Cu* structures.

- 3. Successful DIW Printing of *Cu* Green Samples:** The developed inks enabled successful printing of *Cu* green samples with well-interconnected particles and uniform PLA binder coverage, ensuring structural integrity and shape retention prior to sintering.

8.2 Optimization of printing parameters for fabrication of porous copper current collector

This study established an advanced DIW-sintering route to fabricate thin, self-standing HP-*Cu* structures with pore sizes below 200 μm for EES applications, especially LMBs. Through systematic optimization of ink rheology, printing, and sintering parameters, high-quality HP-*Cu* samples were successfully achieved. The brief conclusions are as follows:

- **Optimum Parameters Identified:** The optimal printing parameters 97 wt% *Cu* ink, 0.2 mm nozzle, 70% layer height, and 10 mm/s speed achieved the highest dimensional accuracy and consistent structural features in the printed *Cu* samples.

1. Printing of Complex HP-*Cu* Structures:

- Using optimized parameters, complex HP-*Cu* structures with diverse pore shapes, honeycomb, cubic and solid cylindrical forms were successfully printed with high precision.
- **Self-Standing and Shape-Retaining Properties:** All printed samples showed excellent self-standing and shape-retention, maintaining structural stability throughout and after printing, crucial for pre-sintering integrity.

2. Debinding and Sintering Process:

- **Sintering Results:** The sintered samples achieved a high relative density of 91% and an ultimate compressive strength of 215 MPa, confirming effective sintering and excellent mechanical robustness.

8.3 Optimization of sintering parameters of the high strength 3D printed porous *Cu* current collector

The main objective was to examine the effects of sintering parameters on the material properties of the 3D-printed *Cu* current collectors, with a particular focus on improving their performance for energy storage applications, such as LMBs. Below is a detailed, point-by-point breakdown of the study's methodology and results:

1. Systematic Statistical Modelling and Multi-Objective Optimization:

- A systematic statistical modelling approach effectively analyzed the combined influence of sintering temperature, heating rate, and soaking time on the final properties of printed *Cu* samples.
- **Multi-objective Optimization:** Optimizing sintering parameters enabled a balanced achievement of high relative density, strong compressive strength, and minimal shrinkage key for high-performance *Cu* current collectors in electrochemical applications.

2. Impact of Sintering Temperature on Material Properties:

- Optimization revealed that sintering at 950°C–1050°C yields maximum relative density, driven by dominant grain boundary and volume diffusion at elevated temperatures.
- **Sintering Mechanism:** Elevated temperatures enhance copper atom diffusion, promoting densification and higher relative density (RD), which in turn improves the compressive strength of the *Cu* current collector.

- Lower heating rates and longer soaking times led to higher RD by ensuring uniform temperature distribution, enhancing densification and mechanical strength.
- Longer soaking at high temperatures boosts diffusion, enhancing *Cu* particle bonding, RD, and strength, while short soaking causes poor densification and weaker performance.
- Slower heating, longer soaking, and higher temperatures boost RD but also increase shrinkage, requiring a careful balance to optimize material properties.
- Higher temperatures, slower heating, and longer soaking intensify diffusion and expansion, increasing shrinkage. Careful control is essential to balance densification and shrinkage.
- Optimal post-sintering for 3D-printed *Cu* electrodes is 938°C, 2°C/min heating rate, and 80 min soaking time, maximizing RD while minimizing shrinkage and strength.
- A proof-of-concept LMBs with the optimized 3D-printed HP-*Cu* current collector showed excellent mechanical strength (35 MPa) and superior electrochemical performance, achieving 90% coulombic efficiency over 100 hours at 5 mA/cm².

8.4 Electrochemical performance of 3D printed hierarchically porous Cu current collector for advanced lithium metal battery

1. Fabrication of Thin HP-Cu Electrode:

- Using optimized *Cu* ink, a thin HP-*Cu* electrode (16 mm diameter, 200 μm thick) with pores of $154 \pm 10 \mu\text{m}$ was fabricated, ideal for lithium deposition. Precise pore control ensured a stable, high-performance electrode for lithium metal batteries.

2. Electrochemical Performance of the HP-Cu Electrode:

- The HP-Cu electrodes showed excellent electrochemical performance in LMBs, with >95% coulombic efficiency over 400 hours at 1 mA/cm², low charge resistance (169 Ω), and superior impedance compared to traditional copper foil indicating better stability, conductivity, and long-term reliability.

3. Microstructural Analysis of the HP-Cu Electrode:

- Microstructural analysis showed uniform lithium deposition on the HP-Cu electrode with no dendrites, ensuring safe, stable cycling and reliable battery performance over time.

4. Comparative Study with Existing Literature:

- The 3D-printed HP-Cu current collector outperformed traditional Cu foil in coulombic efficiency, impedance, and charge resistance, proving to be a superior and promising alternative for LMBs and next-gen energy storage.
- This research highlights the fabrication of durable, high-strength 3D-printed porous Cu current collectors, enabling tailored design for improved lithium metal batteries. Such advances promise more efficient, long-lasting energy storage solutions.

8.5 Major Scientific Contribution-

- **High Particle Loading Cu Ink:** Developed a DIW-compatible copper ink with 97 wt% loading, exceeding previous benchmarks, to enable fabrication of dense, high-strength structures.
- **Rheology Characterization and Modeling:** Established ink flow behavior using the Herschel-Bulkley model, ensuring optimal printability and extrusion control.
- **Printing Parameter Optimization:** Fine-tuned DIW parameters (layer height, print speed, nozzle diameter) for high structural accuracy in complex geometries.

- **Optimized Sintering Process:** Identified ideal sintering conditions (938 °C, 2 °C/min, 80 min) achieving 91% density and 215 MPa strength, suitable for battery integration.
- **Electrochemical Performance:** Demonstrated >95% coulombic efficiency and dendrite-free lithium deposition in 3D-printed HP-*Cu* current collectors.
- **Scalable Manufacturing Demonstration:** Successfully fabricated thin (~200 μm) HP-*Cu* collectors with ~154 μm pores, validating the scalability of the DIW approach.

These outcomes advance the design, fabrication, and application of architected *Cu* structures for next-generation lithium metal batteries.

Future scope

The important studies mentioned may also be undertaken in the future.

1. Fabrication of copper electrodes with ordered porosity below 50 microns can increase the effective surface area, which helps distribute the current more evenly and lowers the local current density. This reduces lithium nucleation overpotential, leading to more stable and dendrite-free lithium plating/stripping. Future studies may investigate scalable and controllable fabrication techniques such as templated electrodeposition or 3D printing to achieve desired porosity and mechanical integrity.
2. Introducing lithiophilic interlayers such as *Cu*-Li alloys at the copper interface can promote uniform Li nucleation and reduce interfacial resistance. Future work can focus on controlled alloy formation and stability during cycling.
3. Future studies could explore the impact of varying the pore shape of the *Cu* electrode as a novel approach to enhancing the performance and stability of LMBs.
4. Another promising direction for future research involves the incorporation of conductive materials into copper such as graphene, CNT etc. to form composite *Cu* electrodes. Such modifications could enhance electrical conductivity, structural stability, and lithium affinity, potentially improving the overall performance and safety of LMBs. Moreover, The DIW-based strategy can be adapted for other conductive materials or composite systems such as Ni, Ag, or carbon-based hybrids to develop multifunctional electrodes. This opens avenues for applications not only in LMBs but also in supercapacitors, Li-S batteries, and flexible energy devices.
5. While electrochemical testing was performed using half-coin cells, further work should involve incorporation of the HP-Cu collectors into full-cell configurations, such as pouch or cylindrical cells.