Table of Contents

Contents **Page No.**

List of Figures xi - xiv

List of Tables xv

List of Abbreviations/Symbols xvi - xvii

Preface xviii- xxiv

CHAPTER 1: INTRODUCTION 1

1.1 Introduction 1

1.1.1 Lithium Ion Battery 1

1.1.2 Lithium Metal Batteries 3

1.1.3 Fabrication of Porous Cu Current Collector 4

1.1.4 Additive Manufacturing 8

CHAPTER 2: REVIEW OF LITERATURE 16

2.1 Ink Development 17

2.1.1 Fundamentals of Ink Formulation for DIW 18

2.1.2 Development of Cu Ink 18

2.1.3 Comparative Summary of Ink 22

2.2 Printing Parameter Optimization 24

2.2.1 Role of Printing Parameters for 3D Printing of Parts 24

2.2.2 Literature Review on Printing Parameter Optimization in DIW 25

2.3 Sintering Parameter Optimization- 28

2.3.1 Role of Sintering Parameters for 3D Printing of Parts 28

2.3.2 Review on Sintering Parameter Optimization for Cu Electrodes 29

2.4 Fabrication of Porous Cu Current Collector **32**

2.4.1 Characteristics of Current Collectors for Lithium Metal Batteries 32

2.4.2 Modification Techniques of Cu-Based Current Collectors for Enhanced Lithium Deposition 35

2.4.3 Electrochemical Performance of the Current Collector Fabricated Using Ordered and Random Pores 40

2.5 Research Gaps- **46**

2.5.1 Identified Research Gaps 46

2.6 Research Objectives- **47**

2.7 Motivation of the present study **48**

CHAPTER 3: SYNTHESIS OF MATERIALS AND EXPERIMENTAL PROCEDURE **49**

3.1 Material Synthesis **49**

3.1.1 Material Selection 49

3.1.2 Ink Preparation 51

3.2 Experimental Procedure **53**

3.2.1 Viscosity Measurement 53

3.2.2 Direct Ink Writing 55

3.2.3 Sintering Process 57

3.2.4 Compression Test 63

3.2.5 Electrochemistry & Characterization 65

CHAPTER 4: DEVELOPMENT OF A HIGH PARTICLE LOADING NOVEL CU INK FOR THE FABRICATION OF A THREE-DIMENSIONAL HIERARCHICAL POROUS STRUCTURE 70

4.1 Results and Discussion 71

4.1.1 Development of High Particle Loaded Cu Ink 71

4.1.2 Rheological Properties of Cu Ink with Variation of Binder and Filler Content 72

4.1.3 Rheological Characterization of the Optimized Cu Ink 76

4.1.4 DIW of Green Cu Parts 80

4.1.5 Morphological Characterization 82

CHAPTER 5: DEVELOPMENT OF A PROCESSING ROUTE FOR THE FABRICATION OF THIN HIERARCHICALLY POROUS COPPER SELF-STANDING STRUCTURE USING DIRECT INK WRITING AND SINTERING FOR ELECTROCHEMICAL ENERGY STORAGE APPLICATION 87

5.1 Results and Discussion 87

5.1.1 Process Parameter Optimization 88

5.1.2 Case Study 100

CHAPTER 6: OPTIMIZATION OF POST SINTERING PARAMETERS FOR FABRICATING ADVANCED HP-CU CURRENT COLLECTORS 105

6.1 Results and Discussion 106

6.1.1 Sintering Mechanism 106

6.1.2 Process Parameters Effects on Relative Density 108

6.1.3 Effect of Process Parameters on Compressive Strength 112

6.1.4 Effect of Process Parameters on Volumetric Shrinkage 114

6.1.5 Multi -Objective Function 117

6.1.6 Proof of Concept 118

6.1.7 Compression Analysis 119

CHAPTER 7: ADVANCED LITHIUM METAL BATTERY: ENHANCING ELECTROCHEMICAL PERFORMANCE WITH 3D-PRINTED HIERARCHICALLY POROUS COPPER COLLECTORS 125

7.1 Results and Discussion 126

7.1.1 Fabrication of Coin Cell 126

7.1.2 Electrochemical Performance 127

7.1.3 Morphological Characterization 133

7.1.4 XRD Analysis 138

7.1.5 Impedance Analysis 140

7.1.6 Comparison Study 143

CHAPTER 8: CONCLUSIONS 149

8.1 Development of High Particle Loaded Copper Ink 149

8.2 Optimization of Printing Parameters for Fabrication of Porous Copper Current Collector 150

8.3 Optimization of Sintering Parameters of the High Strength 3D Printed Porous Cu Current Collector 151

8.4 Electrochemical Performance of 3D Printed Hierarchically Porous Cu Current Collector for Advanced Lithium Metal Battery 152

8.5 Major Scientific Contributions 153

FUTURE SCOPE 155

REFERENCES 156

LIST OF PUBLICATIONS 173

List of Figures

Fig. 3.1: (a) SEM showing spherical Cu particle (b) Distribution curve of the spherical Cu particles 50

Fig. 3.2: Schematic for the preparation of the ink 51

Fig. 3.3: (a) Ultrasonicator (b) Vortex mixture 52

Fig. 3.4: ARES G_2 advanced rotational rheometer 54

Fig. 3.5: Flow chart for the 3D printing of the green sample 56

Fig. 3.6: Hyrel 3D ceramic printer 57

Fig. 3.7: Tube sintering furnace 58

Fig. 3.8: Schematic of the complete process for the preparation of the final component 59

Fig. 3.9: Compression test of 3D printed cylinder 64

Fig. 3.10: Procedure for the fabrication of 3D printed HP-Cu current collector for LMB 66

Fig. 4.1: Effect of particle loading on a) viscosity b) storage modulus for the prepared Cu ink 72

Fig. 4.2: Variation of a) Viscosity vs Shear rate for increased binder loading b) Storage modulus vs Shear stress for increased binder loading c) Viscosity vs Shear rate for increased Cu loading and d) Storage modulus vs shear stress for increased Cu loading 73

Fig. 4.3: a) Viscosity vs Shear rate b) Storage modulus vs Shear stress for the prepared Cu ink with 97 $wt\%$ particle loading 76

Fig. 4.4: Fitting curve for a) 93 $wt\%$ b) 95 $wt\%$ c) 97 $wt\%$ Cu -loaded inks with values of $n = 0.81, 0.69, 0.54,$ respectively 78

Fig. 4.5: Printed green samples with a) 93 $wt\%$ b) 95 $wt\%$ and c) 97 $wt\%$ Cu loading 81

Fig. 4.6: Printed green samples with 97 $wt\ \%\ \ Cu$ loading a) Rectangular Mesh; b) Honeycomb structure and c) Cylinder 81

Fig. 4.7: SEM image of a, b) Prepared ink with 97 $wt\%\ Cu$ loading & c, d) Green samples printed with 97 $wt\%\ Cu$ loading 82

Fig. 4.8: Variations of volumetric shrinkage and sintered density with Cu loading 82

Fig.4.9: Micrograph of a) 93 $wt\%$ b) 95 $wt\%$ c) 97 $wt\%\ Cu$ loaded sintered sample 84

Fig. 5.1: Main effect plots of selected printing parameter 92

Fig. 5.2: SEM image of prepared ink showing wetting of Cu particles 92

Fig. 5.3: Green Cu samples printed using layer height a) 60%; b) 70 % and c) 80 % and SEM images of the cross-section of green Cu samples printed using layer height d) 60%; e) 70 % and f) 80 % 92

Fig. 5.4: Schematic of the DIW process with variation in the layer height. a) $\triangle h \ll d$ b) $\triangle h < d$ c) $\triangle h \le d$ where $\triangle h$ is the layer height and d is the nozzle diameter 97

Fig. 5.5: Green HP-Cu samples fabricated using printing speeds of a) 5mm/s b) 10 mm/s and c)15mm/s 99

Fig. 5.6: a) Image of sintered honeycomb Cu sample fabricated using optimized printing parameters; b) SEM image of sintered sample, c) magnified view of strut (at 500 X) and d) SEM image (at 1000 X) showing interparticle bonding 101

Fig. 5.7: (a) Porous Cu current collector green sample (b)SEM image of fabricated HP-Cu current collector 102

Fig. 6.1: SEM images of Cu samples prepared at different sintering temperature i.e. (a) $650℃$ (b) $750℃$ (c) $850℃$ (d) $950℃$ and (e) $1050℃$ 107

Fig. 6.2: a) Main effect plot and (b-c) Interaction plot for relative density 108

Fig. 6.3: a) Main effect plot and (b-c) Interaction plot for compressive strength 112

Fig. 6.4: a) Main effect plot and (b-c) Interaction plot for volumetric Shrinkage 114

Fig. 6.5: SEM images of the samples sintered at the sintering temperature of $950℃$, soaking time of 60 min with heating rate a) $2\ ℃/min$ and b) $6\ ℃/min$ 115

Fig. 6.6: SEM images of sintered samples at the sintering temperature of $950\ ℃$, a heating rate of $4\ ℃\ /min$ and soaking time of a) 30 min b) 90 min 116

Fig. 6.7: Green sample of the porous Cu current collector with 97 $wt\%\ Cu$ loading 119

Fig. 6.8: Porous Cu current collector sintered sample printed with optimized printing parameters 119

Fig. 6.9: a) Compression test of 3D printed porous Cu electrode b) Stress-strain plot for Cu electrode under compression (c) SEM image of the porous copper electrode after 80 % of straining 120

Fig. 6.10: a) Schematic of 3D printed porous Cu current collector b) Comparison of coulombic efficiency of fabricated coin cell and Cu foil at current density of 5 $mAcm^{-2}$ for the plating capacity of $5\ mAhcm^{-2}$ 122

Fig. 7.1: - (a) Green sample (b-c) SEM of the green sample (d) Sintered sample of the (e-f) SEM after debinding and sintering of HP-Cu current collector 127

Fig. 7.2: Discharge profile of Li plating at current density of a) 1 mAcm^{-2},b) 3 mAcm^{-2} and (c) 5 mAcm^{-2} at a plated capacity of 5 mAhcm^{-2} 128

Fig. 7.3: Comparison of Coulombic efficiency of 3D printed HP-Cu current collector and 3D printed Cu coin at a) current density of 1 $mAcm^{-2}$ and b) current density of 3 $mAcm^{-2}$ at a plated capacity of 5 $mAhcm^{-2}$. 131

Fig. 7.4: Comparison of coulombic efficiency of 3D printed HP-Cu and the Cu foil at current density of (a) $1mAcm^{-2}$ and (b) $3mAcm^{-2}$ at capacity of 5 $\mathrm{mAhcm^{-2}}$ 132

Fig. 7.5: shows SEM images of Lithium deposition at current density of 3 $\mathrm{mAcm^{-2}}$ at a plated capacity of 5 $\mathrm{mAhcm^{-2}}$ (a-b) After 10 cycles (c-d) After 20 cycles 133

Fig. 7.6: SEM images of Li deposition at current density of 1 $\mathrm{mAcm^{-2}}$ at a plated capacity of 5 $\mathrm{mAhcm^{-2}}$ (a) After 200 h (b)After 400 h 135

Fig. 7.7: BSE images of Li deposition at current density of (a-c) 1 $\mathrm{mAcm^{-2}}$ (b-d) 3 $\mathrm{mAcm^{-2}}$plated capacity of 5 $\mathrm{mAhcm^{-2}}$ (a-b) porous HP-Cu (c-d) Cu foil 136

Fig. 7.8: XRD pattern of (a) As-sintered porous Cu; (b) Li deposited Cu foil after 10 cycles and (c) Li deposited 3D printed HP-Cu after 10 cycles 139

Fig. 7.9: (a) Impedance circuit diagram (b-c) Impedance plot for planar Cu foil and 3D printed Cu (b) zero cycle (c) After 5 cycles 141

List of Tables

Table- 1.1 Various methods used for improving the coulombic efficiency of lithium metal batteries 4

Table 1.2 Comparison of fabrication Methods 5

Table 1.3 Comparison of various additive manufacturing techniques 14

Table 2.1 Comparison of Cu inks prepared using different types of reducing agents 22

Table-2.2 Classification and characteristics of current collectors for lithium metal batteries 34

Table-2.3 Modification strategies for Cu current collectors in lithium metal batteries 37

Table-2.4 Porous Metal Current Collectors (PMCCs) for lithium metal anodes 43

Table-3.1 Process parameters ranges and levels 61

Table-3.2 Input parameters and responses 63

Table-4.1 Values of parameters obtained after fitting using HB equation 78

Table-4.2 Sintered Cu sample density with 93 $wt\,\%$, 95 $wt\,\%$ and 97 $wt\,\%$ loading 83

Table-5.1 Experimental Matrix Based on Orthogonal Array Design 89

Table-5.2 Response table for S/N ratio 90

Table-5.3 Comparison of ordered porous Copper structures produced by the additive manufacturing process 103

Table-6.1 Optimized set of sintering parameters 118

Table-7.1 Comparison of porous electrodes for LMB fabricated by various techniques 144

List of abbreviations & symbols

% : Percentage

°C : Degree Celsius

△h : Layer height

AM : Additive Manufacturing

BJ : Binder jetting

CE : Coulombic Efficiency

Cu : Copper

DIW : Direct ink writing

EES : Energy storage systems

FDM : Fused deposition modelling

h : Hour

HB : Herschel-Bulkley

HP-Cu : Hierarchically porous copper

HR : Heating rate

LIB : Lithium-ion battery

Li : Lithium

LMB : Lithium metal battery

MPa : Mega Pascal

PMCC : Porous metal current collectors

PBF : Powder Bed Fusion

RD : Relative density

ρ : Sintered density

s : Second

SEI : Stable electrolyte interface

SEM : Scanning electron microscopy

SLA : Stereolithography

SLM : Selective Laser Melting

τ : Shear Stress

v : Printing speed

V : Volumetric shrinkage

wt% : Weight percentage

XPS : X-ray photoelectron spectroscopy

XRD : X-ray diffraction

μm : Micrometer