

# Chapter 1: Introduction

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## 1.1 Introduction

The Government of India's (GOI) key initiative such as Make in India, aims at making India as the centre for global manufacturing. Such initiatives from GOI have facilitated industries like pharmaceuticals and apparel to excel. However, when it comes to intermediate industries such as batteries, specifically Lithium-ion battery (LIB), India is still relying on imports. Considering the huge demand of LIB in several applications such as consumer electronics (such as mobile phones, laptops, etc.), electric vehicles, and stationary energy storage applications, the manufacturing of the LIB system needs immediate attention. As per the key findings of the report published by The Council on Energy, Environment, and Water (CEEW), indigenizing the manufacturing of the battery cell contributes to around 11-25% of the final cell value, with 22-61% coming from upstream component manufacturing and material processing. Therefore, to cater to the Indian market's need for the LIB system, critical measures in the direction of LIB manufacturing are required to be taken. Around 13 – 35 % of the total cost of LIB manufacturing comes from the manufacturing of the active cathode and anode materials only. Hence, development of a sustainable and innovative processing route for the fabrication of an advanced LIB system in India is the need of the hour.

### 1.1.1 Lithium Ion Battery

Li based battery technologies have revolutionized portable energy storage, driving advancements in consumer electronics, electric vehicles (EVs), and renewable energy systems. Among these, LIBs have long dominated the market due to their high energy density, long cycle life, and reliable performance. A LIB consists of four primary components: the cathode, anode, electrolyte, and separator. During discharge, lithium ions

move from the anode (typically made of graphite) to the cathode (commonly composed of lithium metal oxides) through the electrolyte. This movement generates an electric current that powers devices. During charging, the ions reverse direction, moving from the cathode to the anode, thus storing energy for future use. The reversible nature of this ion movement is what makes lithium-ion batteries rechargeable.

LIBs can store a significant amount of energy relative to their size and weight, making them ideal for portable devices and electric vehicles. These batteries can endure hundreds to thousands of charge-discharge cycles, providing years of reliable performance. Key benefits include low self-discharge, fast charging, high efficiency, and low maintenance. They support renewable energy storage, making them vital for sustainable energy systems. Despite of the above advantages LIB have limited energy density due to limited capacity of graphite to store Li ions [1]. Each Li ion inserted into the graphite anode during charging only contributes a small amount of energy because the intercalation sites (spaces between the graphite layers) are limited. This restricts the amount of energy the battery can store per unit of mass or volume. LIBs store energy by inserting Li ions into the crystal lattice of the anode and cathode materials. However, these materials do not have the high-density atomic structure that pure Li metal does. Thus, the energy stored per unit volume and mass is limited by the chemistry and crystal structures of the materials involved. Hence, various studies are being conducted to improve the efficiency of the Li ion batteries such as fabrication of silicon electrodes, Lithium metal anode, using solid electrolytes, using the sulphur cathode etc. Amongst the above mentioned, using Li metal anode is the advanced technology which has been found to be efficient in increasing the energy density of the electrode.

### 1.1.2 Lithium Metal Batteries

Li is the lightest element within the alkali metal group and is notable for having the smallest atomic radius among all metals [2]. This diminutive size endows Li with an exceptional capacity and facilitates rapid transfer processes, making it highly effective in applications that demand swift charge or ion movement [3]. While Li shares the high reactivity characteristic of other alkali metals, it behaves somewhat differently depending on the environment [4]. Li has the most negative standard electrode potential ( $-3.04\text{ V}$ ), making it an ideal anode material [5]. This property allows Li based batteries to achieve high voltages, which directly contributes to their high energy density. *Li* possesses a low density ( $0.59\text{ g/cm}^3$ ), which makes these batteries very light in comparison to LIBs [6]. Li has a high theoretical specific capacity ( $3860\text{ mAh/g}$ ) [7]. This means it can store a significant amount of charge relative to its weight, which enhances battery performance and thereby making it an attractive candidate to be used for next-generation high-energy LMBs.

Even LMB have high value of energy density, but it has several limitations which restricts its use. During charging and discharging of batteries, Li metal forms the mussy zone and the needle like structure called dendrite [8]. These dendrites may penetrate the separator and problem of short circuiting occurs resulting in poor battery performance [9]. Moreover, during the charging and discharging cycle infinite volume changes occur, which results in repetitive formation of SEI (stable electrolyte interface) layer. Due to formation of SEI layers and chemical reactions loss of active Li takes place which leads to low coulombic efficiency of the battery[10,11]. Hence, there exist a need to supress the formation of dendrites to increase the coulombic efficiency. The suppression of dendrite growth in LMBs is critical for improving their safety as well as efficiency [11]. Various methods have been used to improve the coulombic efficiency of the LMBs and the same are listed in Table 1.1.

**Table 1.1 Various methods used for improving the coulombic efficiency of lithium metal batteries [16]**

S. No.	Method	Description	Mechanism for improving coulombic efficiency
1.	Using Advanced Electrolytes	Using high-concentration electrolytes and use of electrolyte additive such as lithium nitrate.	Use of high concentrated electrolytes stabilize the SEI and forms a more robust SEI that reduces continuous electrolyte decomposition.
2.	Solid-State Electrolytes	Replacing the liquid electrolyte with the solid electrolyte.	Suppresses dendrite growth and side reactions due to the physical barrier and improved ion transport.
3.	Artificial SEI Layers	Coating of lithium metal anode with pre-formed layers such as (e.g., polymer, ceramic, or hybrid).	Protects the lithium surface, reducing side reactions and enabling more efficient lithium deposition.
4.	3D ordered porous structures	Using the porous electrodes with ordered porosity	Ordered porosity increases the surface area and increases the nucleation sites resulting in uniform deposition of Lithium.
5.	Charging rates	Use slow charging rates	Using slow charging rates results in the uniform deposition of lithium ion that leads to dendrite suppression.

Out of these, the method that uses the 3D ordered porous structures is the most promising one, as the porous structure provides a large surface area and evenly distributed deposition sites which ensures uniform Li plating and prevents hotspots that cause formation of dendrites [12]. Moreover, 3D structures trap Li within their porous framework, reducing the loss of active Li and increasing utilization efficiency [13].

### 1.1.3 Fabrication of Porous *Cu* Current Collector

Fabricating a porous *Cu* current collector is critical for improving the performance of LMBs[14]. Several methods can be employed, depending on the desired porosity, structure,

and application requirements [15]. The comparison of the methods used for fabricating porous *Cu* current collector are given in Table 1.2. Some of the methods are discussed as below.

**Table 1.2 Comparison of Fabrication Methods**

<b>Method</b>	<b>Advantages</b>	<b>Considerations</b>
Chemical Oxidation & Thermal Reduction	Simple, scalable	Control over pore size may be limited
Space Holder Method	Precise pore control	Requires removal of space holder
Dealloying Techniques	Tunable porosity	Potentially complex processing steps
Liquid Metal-Induced Dealloying	Scalable, uniform structures	Handling of liquid metals required
Hydrogen Bubble Template	Simple setup	Pore uniformity may vary
Template-Assisted Electrodeposition	High precision	Template removal step necessary
Additive Manufacturing	Complex architectures possible	Technology still under development

### **1.1.3.1 Fabrication of Porous *Cu* Electrode using Chemical Oxidation and Thermal Reduction**

This two-step process begins with the chemical oxidation of *Cu* foil to form a *CuO* layer, followed by thermal reduction using hydrogen gas to revert *CuO* back to metallic *Cu*. This results in a three-dimensional porous *Cu* structure composed of micro-sized *Cu* particles. This method is relatively straightforward and scalable, making it suitable for industrial applications.

### 1.1.3.2 Fabrication of Porous *Cu* Electrode using Powder Metallurgy

In this technique, *Cu* powder is mixed with a space-holding material (like salt or polymer beads) [17]. After compacting and sintering the mixture, the space holder is removed, leaving behind a porous *Cu* structure. This method allows precise control over pore size and distribution, which is beneficial for tailoring the collector's properties.

### 1.1.3.3 Fabrication of Porous *Cu* Electrode using Dealloying Techniques

Dealloying involves selectively removing one component from an alloy to create a porous structure [18]:

**Chemical Etching:** An alloy is treated with an acid to dissolve the more reactive metal, resulting in a porous *Cu* network [19].

**Electrochemical Etching:** Utilizing techniques like linear sweep voltammetry, specific metals are electrochemically removed from an alloy, forming a controlled porous structure [20].

**Vapor Dealloying:** This method involves heating an alloy to evaporate one component, leaving behind a porous structure.

**Liquid Metal-Induced Alloying–Dealloying:** A scalable approach where commercial *Cu* foil is alloyed with a liquid metal (like gallium). Subsequent dealloying removes the secondary metal, resulting in a three-dimensional porous *Cu* structure [21]. This method effectively increases surface area and improves Li deposition uniformity.

### 1.1.3.4 Fabrication of Porous *Cu* Electrode using Hydrogen Bubble Template Method

During electrochemical deposition, hydrogen gas bubbles form on the substrate, acting as dynamic templates [22, 23].

Metal accumulates around these bubbles during the deposition process, gradually forming a shell-like structure. Once the bubbles are removed, typically by dissolution or escape, the

spaces they once occupied are left behind, resulting in a porous matrix. This approach provides a straightforward and efficient method for fabricating interconnected porous networks. The resulting structure features a high surface area and interlinked voids, making it highly advantageous for catalysis, sensing, filtration, and energy storage applications. Moreover, the simplicity of this technique allows for easy scalability and adaptability to various metals and processing conditions.

#### **1.1.3.5 Fabrication of Porous *Cu* Electrode using Template-Assisted Electrodeposition**

This method uses templates like anodic aluminium oxide with predefined pore structures. *Cu* is electrodeposited into these templates, and after removing the template, a well-ordered porous *Cu* structure is obtained [23]. This allows precise control over pore size and arrangement.

#### **1.1.3.6 Fabrication of Porous *Cu* electrode using Additive Manufacturing**

Emerging techniques involve using AM to fabricate architected porous *Cu* structures. This allows for complex geometries and precise control over the collector's architecture, potentially leading to enhanced electrochemical performance [24].

Among all of the methods mentioned above, AM is ideal for fabricating porous *Cu* electrodes due to its ability to precisely control microstructures and geometries, which are critical for optimizing electrochemical performance. AM enables the design of electrodes with specific pore sizes and distributions, enhancing mass transport and increasing the electrochemically active surface area. Furthermore, AM allows for the fabrication of complex 3D structures, facilitating the development of electrodes with optimized pathways for electron and ion transport. Porous *Cu* electrodes produced via AM have demonstrated superior catalytic activity, yielding higher production rates of chemicals like acetaldehyde and ethanol compared to conventional *Cu* foils. Additionally, AM is a layer-by-layer

fabrication process, which minimizes material waste, reducing costs and aligning with sustainable manufacturing practices. This approach also allows for quick iteration and customization of electrode designs, enabling rapid testing and optimization for specific applications.

#### **1.1.4 Additive Manufacturing**

AM, commonly known as 3D printing, is a transformative manufacturing process that builds three-dimensional objects layer by layer from a digital model. Unlike traditional subtractive manufacturing, which removes material from a solid block, AM adds material only where needed, minimizing waste and enabling complex geometries that would be difficult or impossible to achieve with conventional methods [25]. AM has revolutionized industries such as aerospace, automotive, healthcare, and consumer goods by offering design flexibility, rapid prototyping, and cost-effective low-volume production.

The various types of AM processes are classified based on the material used and the method of layer deposition. Each technique has unique advantages, limitations, and applications. Below, we explore the most prominent AM processes in detail.

##### **1.1.4.1 Fused Deposition Modelling (FDM)**

FDM is one of the most widely used AM techniques, especially for rapid prototyping and low-volume production. In FDM, a thermoplastic filament is fed into a heated extruder head where it is melted and then deposited layer by layer onto a build platform following a specific path defined by a digital model (CAD file). As the material is extruded, it quickly cools and solidifies, forming the object one cross-sectional layer at a time. The platform moves vertically (along the Z-axis) after each layer is completed, allowing the next layer to be built on top of the previous one. Support structures are often needed for overhanging geometries and are typically made from a different material that can be dissolved or broken

away after printing. FDM uses a variety of thermoplastic materials such as PLA (Polylactic Acid), ABS (Acrylonitrile Butadiene Styrene), PETG, and Nylon, each offering different mechanical and thermal properties. This technology is popular due to its relatively low cost, ease of use, and ability to produce functional prototypes and parts with reasonable strength and durability. However, FDM parts may have visible layer lines and might require post-processing for a smoother finish.

#### **1.1.4.2 Stereolithography (SLA)**

Vat Photopolymerization, commonly referred to as Stereolithography (SLA), is one of the earliest and most precise AM technologies. In this process, a build platform is submerged slightly into a vat containing liquid photopolymer resin. A UV laser or projector selectively cures the resin by tracing the cross-sectional pattern of the object on the resin's surface, causing it to solidify. After each layer is cured, the platform moves incrementally, allowing the next layer of liquid resin to be exposed and hardened in sequence. This layer-by-layer approach continues until the full object is formed. SLA is known for producing parts with extremely high resolution, smooth surface finishes, and fine details, making it ideal for applications like dental models, jewellery, microfluidic devices, and highly detailed prototypes. However, the process typically requires post-curing under UV light to enhance the mechanical properties of the printed part, and the resin itself can be brittle and sensitive to moisture and sunlight. Support structures are necessary for complex geometries and must be removed carefully to preserve the part's surface quality.

#### **1.1.4.3 Powder Bed Fusion (PBF)**

Powder Bed Fusion (PBF) is a highly advanced AM technique that builds parts by using a thermal energy source, such as a laser or electron beam, to selectively fuse regions of a fine powder bed. In the PBF process, a thin layer of powder material which can be metal, plastic, or ceramic is evenly spread across a build platform. The energy source then scans the layer

according to the digital 3D model, melting or sintering the powder particles together to form a solid cross-section. Once a layer is completed, the platform lowers slightly, and a new layer of powder is spread over the surface, repeating the process until the full object is constructed. Common variants of PBF include Selective Laser Sintering (SLS) for polymers, Selective Laser Melting (SLM), and Direct Metal Laser Sintering (DMLS) for metals. PBF can produce highly complex geometries, intricate internal structures, and parts with excellent mechanical properties [26]. However, it often requires support structures (especially for metal parts) and post-processing steps like heat treatment, surface finishing, or stress relief. PBF is widely used in aerospace, medical implants, and high-performance engineering applications where precision and material strength are critical.

#### **1.1.4.4 Binder Jetting (BJ)**

Binder Jetting is an AM process where a liquid binding agent is selectively deposited onto a thin layer of powdered material to bond the particles together and form each cross-sectional layer of a part. The process begins with spreading a fine layer of powder—such as metal, sand, or ceramic—over the build platform. A print head, like that of an inkjet printer, moves across the powder bed, selectively depositing binder according to the digital model. Once a layer is complete, the platform lowers slightly, and a new layer of powder is spread over it, repeating the process layer by layer. After printing, the "green part" (the fragile, bound powder structure) may undergo post-processing steps such as curing, sintering, or infiltration with another material (like bronze) to achieve the final strength and properties. Binder jetting is especially valued for its speed, ability to produce large parts, and capacity to use a wide variety of materials. It is widely used for producing sand casting molds and cores, full-color prototypes, and even metal parts with complex geometries. Unlike some other AM methods, binder jetting does not involve significant heat during

printing, which reduces the risk of warping but does require careful handling during post-processing to prevent damage.

#### **1.1.4.5 Direct Energy Deposition (DED)**

Directed Energy Deposition (DED) is an advanced AM process that uses a focused thermal energy source, such as a laser, electron beam, or plasma arc, to melt and fuse material, typically in the form of metal powder or wire, as it is deposited onto a substrate. Unlike powder bed fusion techniques, DED involves the simultaneous delivery of energy and feedstock material through a nozzle mounted on a multi-axis robotic arm or gantry system, allowing for precise control over material deposition. This process is particularly well-suited for repairing high-value metal components, adding features to existing parts, and building large-scale structures with reduced material waste. DED systems can operate in open environments (such as laser-based systems) or vacuum chambers (electron beam-based systems), depending on material requirements. One of the key advantages of DED is its ability to work with a wide range of metals, including titanium, Inconel, stainless steel, and tool steels, making it valuable in aerospace, defence, and energy sectors. However, parts produced via DED often require post-processing machining to achieve the desired surface finish and dimensional accuracy due to the relatively coarse layer resolution (typically 200–500 microns). Additionally, DED enables hybrid manufacturing by combining additive and subtractive processes in a single machine, allowing for near-net-shape part production followed by precision machining. Despite its higher equipment costs and complexity compared to other AM methods, DED is gaining traction for applications such as turbine blade repair, structural component fabrication, and customized industrial part production, where traditional manufacturing methods would be cost-prohibitive or technically unfeasible.

#### 1.1.4.6 Direct Ink Writing (DIW)

Direct Ink Writing (DIW), also known as Extrusion-based 3D printing, is an AM technique that extrudes a viscous, paste-like ink through a fine nozzle to build 3D structures layer by layer. Unlike fused deposition modeling (FDM), which uses thermoplastic filaments, DIW employs specially formulated functional inks composed of polymers, ceramics, metals, hydrogels, or composites, often loaded with nanoparticles to enhance mechanical, electrical, or biological properties. The ink must exhibit shear-thinning behavior, meaning it flows under pressure during extrusion but solidifies upon deposition, retaining its shape without collapsing. DIW is typically performed at room temperature, though some systems incorporate UV curing, thermal sintering, or solvent evaporation to harden the deposited material. A key advantage of DIW is its ability to produce multimaterial and microscale architectures, including porous scaffolds, flexible electronics, and biomimetic structures, with resolutions ranging from 100 to 500 microns, depending on nozzle size and ink rheology. Support structures are generally unnecessary due to the ink's self-supporting nature, though fugitive or sacrificial materials may be used for overhangs. However, challenges include ink formulation complexity, clogging risks, and post-processing requirements such as sintering or chemical crosslinking. DIW is widely used in soft robotics, tissue engineering, energy storage devices (e.g., batteries and supercapacitors), and customized sensors, where precise material placement and functional properties are critical. Its versatility in processing diverse materials makes DIW a promising technology for next-generation flexible electronics, biomedical implants, and smart materials. In all the above processes of the AM that have been discussed in Table 1.3, DIW is considered the best-suited AM method for fabricating porous *Cu* current collectors due to its unique material handling capabilities and process flexibility [28]. Unlike powder bed fusion or other high-temperature methods, DIW allows the use of *Cu* inks that can be formulated to

include binders, solvents, and fine *Cu* particles, enabling precise control over the material composition and rheology. This control is critical for achieving the desired porosity and structural integrity needed in current collectors, where both high surface area and good electrical conductivity are essential. Furthermore, DIW operates at relatively low temperatures during the printing process, reducing oxidation risks that typically compromise *Cu*'s electrical performance in high-temperature techniques. The layer-by-layer extrusion approach of DIW also allows for the fabrication of complex, interconnected porous architectures that are difficult to achieve with traditional manufacturing methods. This tailored design capability enhances ion transport and mechanical stability in energy storage systems. Additionally, DIW is compatible with post-printing sintering processes that can densify the *Cu* structure without collapsing the designed porosity. Overall, DIW offers a rare combination of material versatility, structural tunability, and processing compatibility that makes it ideal for fabricating advanced porous *Cu* current collectors for applications such as batteries and supercapacitors. Hence, in the present research work HP-*Cu* electrode has been fabricated using the DIW technique.

**Table 1.3 Comparison of various additive manufacturing techniques [27]**

<b>Feature</b>	<b>FDM</b>	<b>SLA</b>	<b>PBF</b>	<b>BJ</b>	<b>DED</b>	<b>DIW</b>
<b>Material</b>	Thermoplastic	Liquid	Powder (metal,	Powder (metal,		
<b>Form</b>	filament	photopolymer resin	polymer, ceramic)	sand, ceramic)	Metal powder or wire	Viscous paste or ink
<b>Energy</b>		UV laser or	Laser or electron	No heat during		
<b>Source</b>	Heated nozzle	projector	beam	printing (uses binder)	Laser, electron beam, or plasma arc	Pneumatic/mechanical extrusion
<b>Layer</b>	Extrusion through	Laser curing of	Powder fusion by	Binder glues	Melting material	Extrusion of
<b>Formation</b>	a nozzle	resin	laser or beam	powder particles	during deposition	viscoelastic material
<b>Support</b>	Required for	Required for	Required (mostly			Depends on material
<b>Structures</b>	overhangs	overhangs	for metals)	Often not needed	Sometimes needed	flow

<b>Surface Finish</b>	Rough (visible layers)	Very smooth, fine details	Medium to good (depends on post-processing)	Rough (requires infiltration or curing)	Rough (requires machining)	Medium to rough (needs post-processing)
<b>Strength of Parts</b>	Moderate (good for prototypes)	Brittle (for functional prototypes, not loads)	High (good for functional parts)	Medium to low (after sintering improves)	Very high (metal parts)	Varies (depends on material)
<b>Print Speed</b>	Medium	Slow to medium	Slow	Fast for large parts	Medium to slow	Medium