



**ADDITIVE MANUFACTURING TECHNOLOGIES FOR LITHIUM-ION  
BATTERY DESIGN**

Lappeenranta–Lahti University of Technology LUT

Bachelor's thesis in Chemical engineering

2023

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Examiner: Associate Professor Ekaterina Laakso

## ABSTRACT

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### **Additive Manufacturing Technologies for Lithium-ion Battery Design**

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The purpose of this thesis is to identify the most potential processes and materials for additive manufacturing (AM) of electrodes and solid electrolytes for lithium-ion batteries (LIBs) as well as detect possible problems with the techniques and materials. This thesis is a literary review, which is based on peer-reviewed articles.

The increase in the percentage of intermittent renewable energy in energy production has increased the need for efficient energy storage devices, such as LIBs. LIBs have high energy density and high voltage, which means that they are lightweight compared to other types of rechargeable batteries of the same voltage. AM is considered for manufacturing LIBs because it could enable fewer production steps, minimise waste production, maximise the use of materials and improve electrochemical performances.

The materials used in AM processes often have low ionic and electric conductivities, which are crucial for the electrochemical performance of LIBs. The conductivities can be increased by adding conductive and porous additives to the printing materials, though active material and additives often affect the rheological and mechanical properties of the printing material and thus printability. Hence, the main challenge of fabricating LIBs via AM is maximizing the content of active and conductive materials in feed material whilst ensuring printability.

All of the AM technologies discussed in this thesis had their advantages and challenges with AM of LIBs and LIB components. Thus, none of the AM technologies was found to be superior to the others. More research is needed on the fabrication of solid electrolytes and high-capacity electrode materials for LIBs via AM technologies.

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Tämän tutkielman tarkoituksena on tunnistaa potentiaalisimmat prosessit ja materiaalit litiumioniakkujen (lithium-ion battery, LIB) elektrodien ja kiinteiden elektrolyyttien materiaalia lisäävään valmistukseen (additive manufacturing, AM), eli 3D-tulostukseen, sekä havaita mahdolliset ongelmat tekniikoissa ja materiaaleissa. Tämä tutkielma on kirjallisuuskatsaus, joka perustuu vertaisarvioituihin artikkeleihin.

Epäsäännöllisen uusiutuvan energian osuuden kasvu energiantuotannossa on lisännyt tarvetta tehokkaille energianvarastointitavoille, kuten LIB:ille. LIB:illä on korkea energiatiheys ja korkea jännite, mikä tarkoittaa, että ne ovat kevyempiä kuin saman jännitteen akkutyypit. AM:ää harkitaan LIB:ien valmistuksessa, koska se voisi mahdollistaa vähemmän tuotantovaiheita, minimoida jätteen syntymistä, maksimoida materiaalien käyttöä ja parantaa akun sähkökemiallista suorituskykyä.

AM-prosesseissa käytetyillä materiaaleilla on usein alhainen ioni- ja sähkönjohtavuus, jotka ovat ratkaisevia ominaisuuksia LIB:ien sähkökemiallisen suorituskyvyn kannalta. Tulostusmateriaalien johtokykyä voidaan lisätä johtavilla ja huokoisilla lisäaineilla. Toisaalta aktiivinen materiaali ja lisäaineet vaikuttavat usein tulostusmateriaalien reologisiin ja mekaanisiin ominaisuuksiin ja siten tulostettavuuteen. Tästä syystä suurin haaste LIB:ien valmistuksessa AM-tekniikoilla on aktiivisen ja johtavien materiaalien pitoisuuksien maksimointi tulostusmateriaaleissa ja samalla tulostettavuuden varmistaminen.

Kaikissa tässä tutkielmassa käsitellyissä AM-tekniikoissa oli etunsa ja haasteensa LIB:ien ja LIB-komponenttien valmistuksessa. Täten minkään AM-tekniikan ei havaittu olevan muita parempi. Lisää tutkimusta tarvitaan LIB:ien kiinteiden elektrolyyttien ja suurikapaseettisten elektrodimateriaalien valmistamisesta AM-tekniikoilla.

## ABBREVIATIONS

3D	Three-Dimensional
AM	Additive Manufacturing
BJT	Binder Jetting
CNT	Carbon Nanotube
DIW	Direct Ink Writing
DLP	Digital Light Processing
FDM	Fusion Deposition Modelling
FFF	Fused Filament Fabrication
LFP	LiFePO <sub>4</sub>
LIB	Lithium-Ion Batteries
LiTFSI	Bis(Trifluoromethane) Sulphonamide
LLZO	Li <sub>7</sub> La <sub>3</sub> Zr <sub>2</sub> O <sub>12</sub>
LTO	Lithium Titanate
ME	Material Extrusion
NASICON	Sodium Super Ionic Conductor
PBF	Powder Bed Fusion
PEDOT	Poly(3,4-ethylenedioxythiophene)
PEO	Poly(Ethylene Oxide)
PLA	Poly(lactic Acid)
PP	Polypropylene
PSS	Poly(Styrene Sulfonate)
SEI	Solid-Electrolyte Interphase

SiNP	Silicon Nanoparticle
SLA	Stereolithography
VPP	Vat Photopolymerization

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# 1 Introduction

Climate change, increasing prices of fossil fuels, and growing energy demand have powered the increase in the percentage of renewable energy in energy production (Akhilash et al., 2021; Ellis and Nazar, 2012). Renewable energy sources, such as wind and solar energy, produce energy intermittently, so the energy needs to be stored until it is needed. With the increase in renewable energy the need for efficient energy storage devices, such as rechargeable batteries, has increased. (Ellis and Nazar, 2012.)

Lithium-ion batteries (LIBs) are the most common type of secondary cells also known as rechargeable batteries (Ellis and Nazar, 2012). The main parts of a LIB are the electrodes, electrolyte, separator, and current collectors (Goodenough and Park, 2013). Electrode material choices can have a significant impact on the performance of the battery (Akhilash et al., 2021). Solid electrolytes can enable the use of new electrode materials, such as lithium metal as an anode, in LIBs (McOwen et al., 2018). In addition, solid electrolytes are considered safer than the most commonly used liquid electrolytes (McOwen et al., 2018; Zheng et al., 2018).

This paper examines the fabrication of electrodes and solid electrolytes for LIBs via additive manufacturing (AM) technology, also known as three-dimensional (3D) printing, with a focus on solid electrolytes because they can be fabricated via AM processes. Studies have shown that batteries fabricated via AM can have better performance than conventionally manufactured batteries (Gulzar et al., 2020; Maurel et al., 2021). AM can enable the fabrication of custom, light-weight batteries, which can be used, for example, in wearable devices (Akhilash et al., 2021; Gulzar et al., 2020; Wei et al., 2018). AM could also enable the fabrication of devices with directly integrated batteries (Wei et al., 2018). However, there are challenges with AM of LIBs, such as ensuring sufficient conductivity and porosity of the feed material. Another challenge is the limited amount of active material, the material participating in the electrochemical reaction, in the feed material.

The purpose of this thesis is to identify the most potential processes and materials for AM of electrodes and solid electrolytes for LIBs. The aim is to also detect possible gaps in existing research on the subject and possible problems with techniques and materials. This

study aims to answer the following questions: what the most potential electrode and electrolyte materials for AM of LIBs are, which AM techniques show the most potential for manufacturing LIBs and what still needs to be researched more to be able to overcome the challenges related to AM of LIBs.

This thesis is a literary review, which is based on peer-reviewed articles from Finnish and international databases. Terminology related to LIB technology and AM was used as search words. After processing the search results, the references of the articles were inspected manually for additional sources. A standard on AM was also used to write this thesis.

The first part of the paper describes the working principles of a LIB as well as electrode and solid electrolyte materials used in LIBs. The second part of the paper introduces different types of AM processes and discusses AM of conductive and porous materials. The third part focuses on different AM techniques for fabricating LIBs and the challenges related to them. The research questions are answered in the third part and the conclusions.

## 2 Lithium-ion batteries

This part of the paper focuses on LIBs and includes information on why LIBs are widely used and an introduction to the working principles of LIBs. This part also includes a brief introduction to the most commonly used and most promising electrode materials as well as the most common types of solid electrolyte materials.

### 2.1 General information on lithium-ion batteries

LIBs are the most common type of rechargeable batteries. Lithium is the lightest metal element and has a low reduction-oxidation (redox) potential. (Ellis and Nazar, 2012.) This enables high energy density and high voltage LIBs, which means that they are lightweight compared to other types of rechargeable batteries of the same voltage (Akhilash et al., 2021). The focus of research has been to develop ever lighter and smaller LIBs by increasing their energy density and capacity. In addition, the research aims to make cheaper and safer LIBs with increased cycle durability. (Li et al., 2018.)

Lithium-ion has a small radius (Ellis and Nazar, 2012). This makes the diffusion of the ions during charging and discharging easier, which enables high power density. In addition, LIBs also have very little self-discharge and a long charge-discharge cycle life. (Akhilash et al., 2021.) All these attributes have made LIBs the most used energy storage device for portable and consumer electronics such as laptop computers, smartphones, and wearable devices (Li et al., 2018; Ponnada et al., 2022). LIBs are also used in transportation devices such as electric bikes and electric vehicles (Reyes et al., 2018; Sanumi et al., 2022). In addition, the long lifespan of LIBs has made them popular in implantable electronics, including pacemakers (Li et al., 2018).

### 2.2 Working principle of lithium-ion batteries

LIBs are electrochemical cells. Their main parts are the two electrodes, electrolyte, separator, and current collectors. Secondary cells, such as LIBs, have two electrodes: an anode and a cathode. (Goodenough and Park, 2013.) The anode is the negative electrode and

the cathode is the positive electrode during the discharging of the battery and will be referred to as such from here on (Qiao and Wei, 2012). The positive electrode of LIBs includes lithium-ions (Ahaliabadeh et al., 2022). The main components of a LIB are shown in Figure 1.

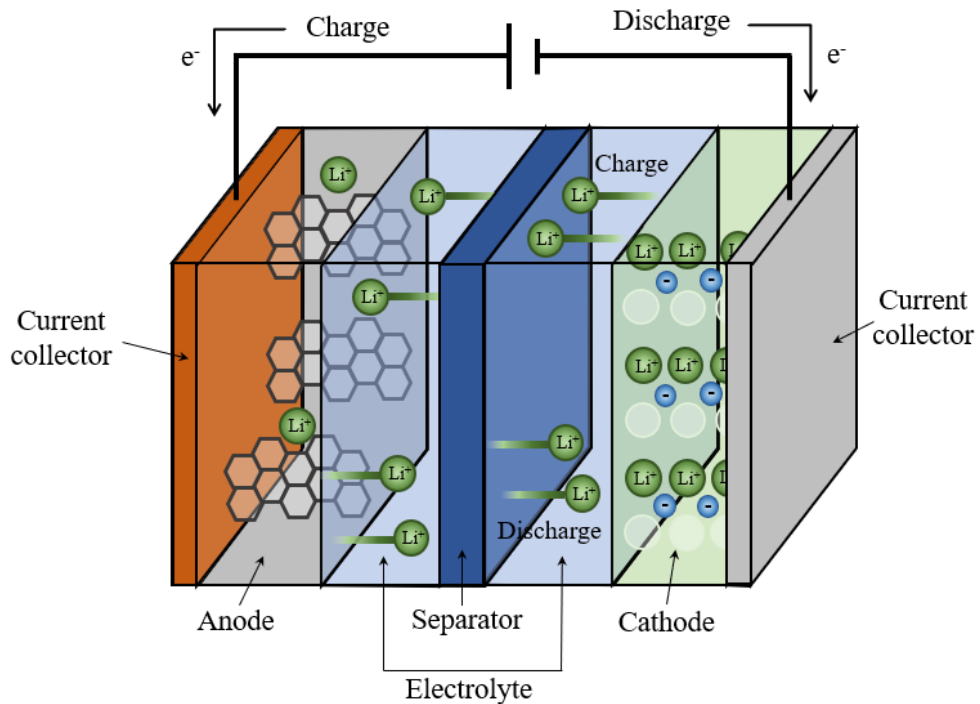


Figure 1. The components of a LIB and flow of electrons and lithium-ions during charging and discharging of the battery.

When the LIB is charged, the positive electrode is oxidised. During oxidation, electrons travel from the positive electrode to the negative electrode through an external circuit. As the electrons leave the positive electrode, it releases positive lithium-ions. The released  $Li^+$  ions travel to the negative electrode through the electrolyte due to diffusion. When the lithium-ions reach the negative electrode, they are inserted into the electrode material. The flow of the electrons and the  $Li^+$ -ions are connected processes, so if one process stops so does the other. (Akhilash et al., 2021)

The oxidation reaction is reversible (Goodenough and Park, 2013). When a LIB is being discharged the positive electrode undergoes a reduction reaction. The negative electrode releases the electrons and the lithium-ions. The electrons travel back to the positive electrode

through the external circuit. The lithium-ions, extracted from the negative electrode material, move back to the positive electrode through the electrolyte. The cell voltage depends on the free energy released from the reversible chemical reaction between the electrode materials and the  $\text{Li}^+$ -ions. (Akhilash et al., 2021)

The electrolyte can be either liquid or solid. This paper focuses on solid electrolytes because solid electrolytes can be fabricated via AM. The electrolyte conducts lithium-ions but not the electrons, which forces the electrons to the external circuit. (Goodenough and Park, 2013.) The separator is usually a membrane that lets the lithium-ions move between the negative and positive electrodes while preventing electron conduction and the battery from short-circuiting (Salini et al., 2020; Zheng et al., 2018). The current collectors are often made of metal, and they deliver electronic current between an electrode and the external circuit (Goodenough and Park, 2013).

### 2.3 Positive electrode materials

The energy density of the battery depends on the electrode materials (Salini et al., 2020). In modern LIBs, the positive electrode materials often have a lower capacity than the negative electrode materials (Akhilash et al., 2021; Ponnada et al., 2022). The most commonly used positive electrode materials in LIBs make the positive electrode the heaviest and most expensive part of the battery. If the energy density of the electrode material is increased, it is possible to make lighter and cheaper LIBs (Akhilash et al., 2021.)

Most commonly used positive electrode materials are lithiated layered oxides ( $\text{LiMO}_2$ , where M is one or more transition metals) because they have relatively high theoretical capacities ( $\geq 259 \text{ mAh g}^{-1}$ ) (Ponnada et al., 2022; Xu et al., 2017). Layered materials are preferred for electrode materials because the layered structure is beneficial for electron conduction and diffusion of Li-ions. First-generation LIBs used layered  $\text{LiCoO}_2$  as positive electrode active material.  $\text{LiCoO}_2$  has a theoretical capacity of  $274 \text{ mAh g}^{-1}$ , but the practical capacity is only about  $140 \text{ mAh g}^{-1}$ . (Akhilash et al., 2021.) With the rising prices of cobalt and lithium, the focus of research has turned to lower-cost nickel-rich positive electrode materials (Ponnada et al., 2022; Xu et al., 2017). In addition, there are environmental and ethical issues with the mining of cobalt (Sovacool, 2021).

Ni-rich layered lithium oxide positive electrode materials ( $\text{LiNi}_x\text{Co}_y\text{Mn}_{1-x-y}\text{O}_2$ ,  $x > 0.8$ ) have higher practical capacities than  $\text{LiCoO}_2$  and fast kinetics of insertion/extraction reaction of Li-ions (Guo et al., 2022; Xu et al., 2017). The nickel content affects the capacity and thermal stability of these materials. In general, a higher nickel content results in higher capacities and lower thermal and structural stabilities of the material. (Liu et al., 2014.) The structural stability can be improved by adding manganese or aluminium to the material (Seong et al., 2020; Xu et al., 2017). Adding aluminium can also improve the thermal stability of the material (Xu et al., 2017). For example,  $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$  has a capacity of about  $200 \text{ mAh g}^{-1}$  (Liu et al., 2014).

Another commonly used positive electrode material in LIBs is  $\text{LiFePO}_4$  (LFP). LFP has a theoretical capacity of  $170 \text{ mAh g}^{-1}$ . (Xie et al., 2006.) It is abundantly available and more environmentally friendly than cobalt. In addition, LFP has a low price compared to cobalt. However, LFP suffers from low electronic and ionic conductivity. The conductivity of the material can be increased with, for example, carbon coating, conductive additives or nanostructuring. (Ha and Lee, 2015)

## 2.4 Negative electrode materials

Graphite is the most commonly used negative electrode material in modern LIBs. Graphite has a maximum capacity of  $372 \text{ mAh g}^{-1}$ , which is higher than the capacities of the lithiated transition metal oxides used as positive electrode materials. Though, graphite can suffer from some lithium dendrite formation during cycling, which can hinder the performance of the battery. (Ponnada et al., 2022.)

Lithium metal has been studied as a potential negative electrode material for LIBs because it has a very high theoretical capacity of  $3860 \text{ mAh g}^{-1}$ . However, the lithium metal negative electrode is not compatible with liquid electrolytes because of Li dendrite formation, which leads to the battery short-circuiting. (McOwen et al., 2018; Ponnada et al., 2022). Although, there has been promising research done on coupling lithium metal negative electrodes with certain types of solid electrolytes (McOwen et al., 2018).

Silicon (Si) and silicon oxides, such as silica ( $\text{SiO}_2$ ), have also been studied as potential negative electrode materials for LIBs (Ponnada et al., 2022). Silicon has a theoretical

capacity of  $4200 \text{ mAh g}^{-1}$ . In addition to the high theoretical capacity, silicon also has a relatively low cost, which makes it an attractive option as a negative electrode material for LIBs. (Lawes et al., 2017.) One of the main challenges with silicon and silicon oxides as an electrode is the large continuous volume change of the material (up to 400 %) with insertion/extraction of Li-ions (Lawes et al., 2017; Ponnada et al., 2022). The volume change causes a loss of electrical contact, which in turn hinders the performance of the battery (Lawes et al., 2017). Other challenges with silicon and silicon oxides are an unstable solid-electrolyte interphase (SEI) and slow diffusion of Li-ions (Tran et al., 2023). Polymer binders and carbon sheath materials have been studied for solving these challenges (Lawes et al., 2017; Tran et al., 2023). Nanostructures can help to solve the above-mentioned challenges by accommodating the volume change and improving diffusion speed by shortening the diffusion lengths (Tran et al., 2023).

Lithium titanate (LTO) is another commonly used negative electrode material in LIBs. LTO is very stable thermally. It also has very little volume expansion during cycling and a long cycling life span. (Reyes et al., 2018.) However, LTO has a theoretical capacity of approximately  $175 \text{ mAh g}^{-1}$ , which is low compared to many other negative electrode materials used in LIBs (Li et al., 2018; Sovizi and Pourali, 2018).

## 2.5 Solid electrolyte materials

Electrolytes for LIBs must have a high conductivity of Li-ions, hardly any electronic conductivity and good electrochemical stability (Zheng et al., 2018). While liquid organic electrolytes have high Li-ion conductivity, they are also highly flammable and have poor compatibility with electrodes (Lu et al., 2019). Solid electrolytes are generally safer than liquid organic electrolytes or polymer electrolytes commonly used in LIBs (McOwen et al., 2018; Zheng et al., 2018). Although, solid electrolytes have lower ionic conductivities than conventional liquid electrolytes used in LIBs (Maurel et al., 2020).

Several types of solid electrolytes can be used for LIBs. For example, sodium super ion conductor (NASICON) -type solid electrolytes can be used for LIBs, if the sodium-ion is replaced with lithium-ion in the NASICON-type electrolyte. This results in a change of the formula from  $\text{NaM}_2(\text{PO}_4)_3$ , where M is a cation or cations, to  $\text{LiM}_2(\text{PO}_4)_3$ . Many NASICON-

type electrolytes, such as  $\text{Li}_{1+x}\text{Al}_x\text{Ge}_{2-x}(\text{PO}_4)_3$ , show high ionic conductivity and good chemical and electrochemical stability but some of the compounds used in the materials can be expensive. Like NASICON-type materials, garnet-type electrolytes have high ionic conductivity. Garnet-type electrolytes are nesosilicate-based oxides with a general formula of  $\text{A}_3\text{B}_2(\text{SiO}_4)_3$ , where A and B are cations. (Murugan and Weppner, 2019). Though some garnet-type materials, such as  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$  (LLZO), are not stable in the ambient atmosphere. (Zheng et al., 2018.)

High ionic conductivities can also be achieved with sulphide- and argyrodite-type electrolyte materials. Sulphide-type electrolytes are lithium compounds that contain sulphur, whereas argyrodite-type electrolytes are compounds with the general formula of  $\text{Li}_6\text{PS}_5\text{X}$ , where X is Cl, Br, or I. However, these types of materials are not stable in the ambient atmosphere, which makes them challenging to use. Similarly, anti-perovskite -type electrolytes also show high ionic conductivities and cannot be operated in the ambient atmosphere. Anti-perovskite -type materials are based on a system of  $\text{A}^-\text{B}^{2-}\text{X}_3^+$ , where A is a halogen atom or atoms, B is oxygen and X is lithium. Anti-perovskite -type materials absorb water and hence they need to be operated in an inert atmosphere. (Zheng et al., 2018.)

Perovskite-type materials are based on a system of  $\text{A}^+\text{B}^{2+}\text{X}_3^-$ , where A is a halogen atom or atoms, B is oxygen and X is lithium. Some perovskite-type electrolyte materials have exhibited lower ionic conductivity compared to other types of electrolyte materials. Similarly, lithium phosphorus oxynitride -type electrolyte materials suffer from lower ionic conductivities. Lithium super ionic conductor -type materials, on the other hand, exhibit good chemical and electrochemical stability, but like lithium phosphorus oxynitride -type and some perovskite-type electrolytes they have lower ionic conductivities compared to other electrolyte materials. In contrast, solid electrolyte materials based on compounds containing lithium and nitrogen suffer from lower voltages, even though they have good ionic conductivities. (Zheng et al., 2018.)

Overall, the most promising electrolyte material types are NASICON, garnet and perovskite, because of their generally good ionic conductivity as well as good chemical and electrochemical stability (Zheng et al., 2018).

### 3 Additive manufacturing

This part of the paper focuses on additive manufacturing and includes the definition, relevancy, and uses of AM as well as briefly explaining the working principles of different types of AM processes and some of their characteristics. The challenges with fabricating conductive and porous material via AM processes are also discussed as they are important for LIB fabrication via AM processes.

#### 3.1 General information on additive manufacturing

In AM or 3D-printing a 3D part or object is made based on 3D-model data from computer-aided design -software (Ponnada et al., 2022; SFS-EN ISO/ASTM 52900:2021). In AM, the material is deposited by a nozzle, print head or other printing technology (SFS-EN ISO/ASTM 52900:2021). The part or object is produced with an additive process by adding material layer-by-layer to build the wanted shape, with a usual layer thickness of 15-500  $\mu\text{m}$  (Gulzar et al., 2020; SFS-EN ISO/ASTM 52900:2021). Depending on the used AM process and materials, the scale of the fabricated product can range from millimetres to over a metre (Ponnada et al., 2022). For example, AM building elements enabled a company in China to make several houses in the space of one day (Gulzar et al., 2020; Wu et al., 2016).

Subtractive processes, like drilling, produce a part by removing material to make the wanted shape (SFS-EN ISO/ASTM 52900:2021). Additive processes compared to conventional formative or subtractive processes can maximize material utilisation and minimize waste production (Gulzar et al., 2020). This makes AM processes cost-effective. In addition, conventional manufacturing processes often need several steps to produce final or near-final parts. (Sanumi et al., 2022.) In comparison, it is possible to produce final or near-final parts in one-step processes with AM, thus minimizing after-processing treatment (Gulzar et al., 2020; Sanumi et al., 2022).

AM can be used to design, prototype and manufacture products fast without the cost of moulds or machining traditional manufacturing processes might need (Gulzar et al., 2020; Reyes et al., 2018). Another advantage of AM is that the design can be changed without

making changes to the manufacturing process (Reyes et al., 2018). This makes manufacturing complex, high-quality, customizable parts attainable (Gulzar et al., 2020; Praveen et al., 2022; Reyes et al., 2018). For example, AM is used in the field of medicine to produce custom-made prosthetics and surgical guides (Gulzar et al., 2020). AM has also been studied for producing electrodes and solid electrolytes for LIBs (Ponnada et al., 2022). A wide array of materials can be used in AM, including polymers, ceramics, and metals (Gulzar et al., 2020).

### 3.2 Types of additive manufacturing processes

There are seven categories of AM processes according to the SFS-EN ISO/ASTM 52900:2021 standard. The categories are (1) powder bed fusion (PBF), (2) binder jetting (BJT), (3) directed energy deposition, (4) material extrusion (ME), (5) material jetting, (6) sheet lamination and (7) vat photopolymerization (VPP). (SFS-EN ISO/ASTM 52900:2021.)

In PBF processes, like selective laser sintering, a bed of feed stock powder is spread on the printing surface and levelled before using focused thermal energy to fuse sections of the powder bed into the wanted shape (Maurel et al., 2021; Ponnada et al., 2022; SFS-EN ISO/ASTM 52900:2021). The working principle of a PBF process is shown in Figure 2 (Wiberg, 2019, p. 11, adapted).

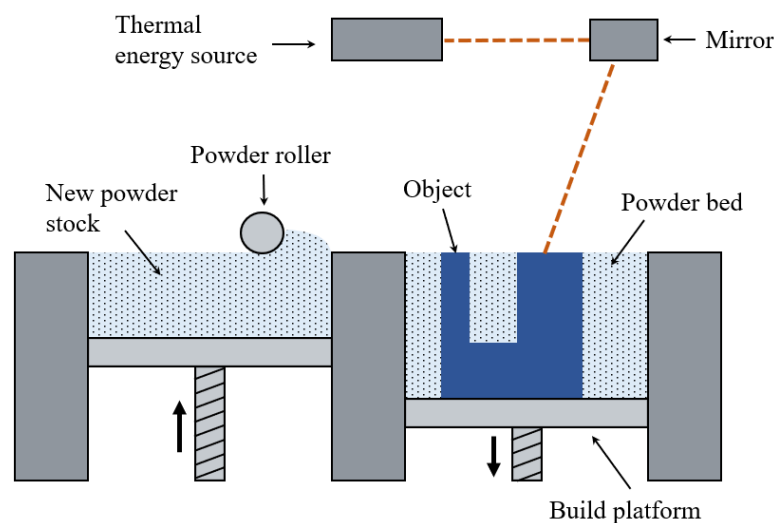


Figure 2. The working principle of a PBF process (Wiberg, 2019, p. 11, adapted).

PBF uses solid material in powder form (Gulzar et al., 2020). These powders are often polymer powders, such as polyamides and polystyrene, but metallic powders can also be used with PBF (Chen et al., 2021; Maurel et al., 2021). As PBF uses a powder bed, only one type of powder can be used in a single print. Another disadvantage of PBF is that the fabricated part may need post-processing to remove any excess powder from its surfaces. (Maurel et al., 2021.)

Another AM technique, that uses solid material is BJT (Gulzar et al., 2020). In BJT a bonding agent, a binder, is deposited on a powder bed to join powder material together into the wanted shape (Gokuldoss et al., 2017; SFS-EN ISO/ASTM 52900:2021). The binder is usually a liquid. Metal, metal alloy, or ceramic powders can be used in BJT processes. The working principle of BJT is very similar to that of PBF, except BTJ uses a liquid binder to join parts of a powder bed together whereas PBF uses focused thermal energy. (Gokuldoss et al., 2017.)

Directed energy deposition is another AM process that uses focused thermal energy (SFS-EN ISO/ASTM 52900:2021). In directed energy deposition the used materials are fused together with focused thermal energy while they are being deposited (SFS-EN ISO/ASTM 52900:2021). Metallic powders and alloys can be used as feed material in directed energy deposition processes (Wolff et al., 2016).

In ME processes, like fusion deposition modelling (FDM) and direct ink writing (DIW), the material is dispensed through a nozzle (Ponnada et al., 2022; SFS-EN ISO/ASTM 52900:2021). It is possible to print multiple different materials simultaneously via ME printers with multiple print heads (Pei et al., 2021). FDM uses highly viscous thermoplastic filaments, such as polyamide, polylactic acid (PLA) and polycarbonate, as feed material (Gulzar et al., 2020; Pei et al., 2021). The working principle of an FDM process is shown in Figure 3.

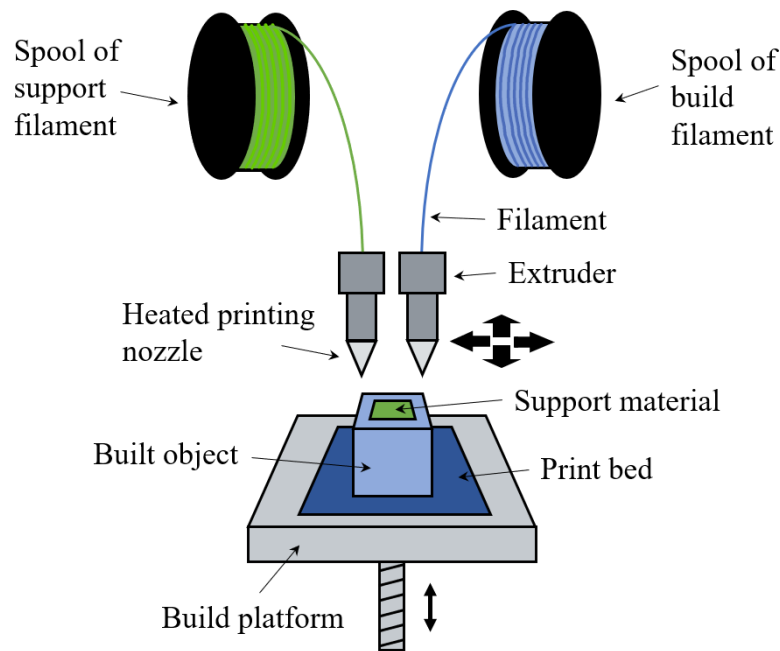


Figure 3. The working principle of an FDM process.

The feed materials used in DIW processes act as a solid with low pressure but begin to flow when the stress increased (Pei et al., 2021). In addition, the materials used in both DIW and FDM processes must solidify rapidly after being deposited (Gulzar et al., 2020; Pei et al., 2021).

In material jetting processes, like inkjet printing, the material is deposited into the design as droplets (Ponnada et al., 2022; SFS-EN ISO/ASTM 52900:2021). Inkjet printing uses low-viscosity inks, which form droplets when deposited (Gulzar et al., 2020; Pei et al., 2021). In inkjet printing, the deposited ink droplets form a layer as the solvent evaporates. Many different materials, such as metals and conductive polymers, can be used for inkjet printing if the ink properties allow printing (Pei et al., 2021).

In sheet lamination processes, such as laminated object manufacturing, a part is formed by laminating sheets of material together (Bhatt et al., 2019; SFS-EN ISO/ASTM 52900:2021). The materials used in sheet lamination processes include metal sheets and foils (Tolochko and Sokol, 2021). In VPP processes, like stereolithography (SLA), liquid photocurable feed stock material, which is usually epoxy or acrylate-based, is cured with light-activated polymerization into the wanted shape (Appuhamillage et al., 2019; Ponnada et al., 2022;

SFS-EN ISO/ASTM 52900:2021). SLA uses photopolymers, such as photosensitive resins (Appuhamillage et al., 2019; Pei et al., 2021).

### 3.3 Conductive material in additive manufacturing

One of the requirements for electrolytes in LIBs is a high ionic conductivity of Li-ions with hardly any electron conductivity (Zheng et al., 2018). Electrodes on the other hand must conduct Li-ions to the electrolyte and electrons to the current collector (Akhilash et al., 2021). Thus, ionic and electric conductivity is important for electrodes. Whereas current collectors need high electron conductivity for delivering electronic current between the electrode and the external circuit (Goodenough and Park, 2013).

The requirements for the used feed materials vary according to the selected AM technique. The feed materials can be for example polymers, plastics, ceramics, composites, or resins (Pei et al., 2021). These materials, such as thermoplastic materials and polymers, often possess inherently low conductivity (Pei et al., 2021; Reyes et al., 2018). Hence, the materials used in AM often need additives to increase the conductivity of the feed materials for high-conductivity applications, such as batteries (Reyes et al., 2018).

By adding conductive additives to the non-conductive printing polymer matrix, a polymer composite with increased conductivity can be created. The additives can be for example particles, fibres, or wires and, they can be mixed into the polymer matrix or added in layers to form composites. (Distler and Boccaccini, 2020; Yin et al., 2019.) Some examples of composite types are shown in Figure 4 (Pastuszak and Muc, 2013, p.122, adapted).

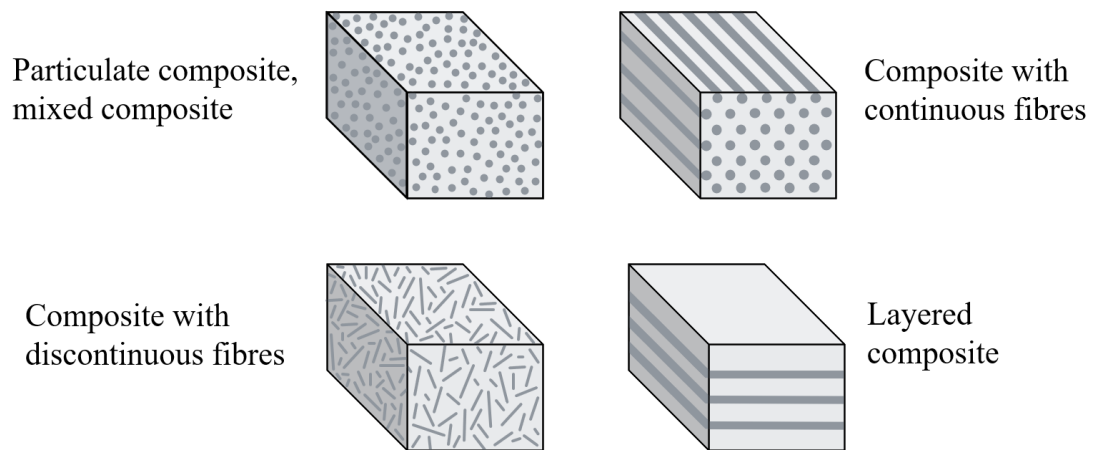


Figure 4. Types of composites (Pastuszak and Muc, 2013, p.122, adapted).

Ionic conductivity can be increased with ionically conductive additives. To make an ionically conductive electrolyte via AM, Rupp et al. (2022) added lithium salts, LiTSFI, to increase the ionic conductivity of a printing polymer. They made a mixed composite filament with a lithium salt and PEG-based polymers for an FDM printer. A conductivity of up to  $10^{-4} \text{ S cm}^{-1}$  at  $80 \text{ }^\circ\text{C}$  was achieved with the formulated lithium salt composite. (Rupp et al., 2022.) This is an increased conductivity compared to the ionic conductivity of pure PEG polymer, which is approximately  $10^{-10} \text{ S cm}^{-1}$  at room temperature (Reddy et al., 2006). Though, the achieved ionic conductivities of the fabricated electrolyte were still well below the conductivity of conventional inorganic liquid electrolytes, which have conductivity values of approximately  $10^{-2} \text{ S cm}^{-1}$  (McOwen et al., 2018). In conclusion, lithium salts can be used to increase ionic conductivity.

To increase the electron conductivity of AM materials, conductive materials, such as carbons and metals, can be added (Distler and Boccaccini, 2020). Some commonly used carbon additives include carbon nanotubes (CNTs) and graphene (Yin et al., 2019). For example, Maurel et al. (2019) made a positive electrode via AM with PLA as a polymer and carbon black, a carbon powder, as a conductive additive. They found that the samples with carbon black had better electric conductivity than a sample without carbon black, which was otherwise identical. (Maurel et al., 2019.)

It is easier to increase the conductivity of the feed material used in some AM processes than others. For example, in PBF processes, which use polymer powders, the conductive material

can be added by simply mixing with the polymer before printing (Maurel et al., 2021). Whereas for AM processes that use inks or filaments, the conductive feed material has to be formulated with suitable rheological properties. The addition of conductive particles to the material can change its rheological properties, such as viscosity, which can affect the printability of the feed material. (Pei et al., 2021; Sanumi et al., 2022.) This can limit the content of conductive additives that can be added to the feed material (Maurel et al., 2021).

It is also important to note that for battery applications the additives should be evenly distributed and there should be enough of them for the conductive additives to form a conductive network through the entire structure fabricated via AM to prevent the conductive particles or fibres from being isolated in the polymer matrix. If the conductive material is isolated in the polymer matrix, the electrochemical performance of the fabricated component suffers. (Maurel et al., 2021.)

### 3.4 Porous material in additive manufacturing

Electron and ion transport kinetics can affect the performance of a battery (Pei et al., 2021). Li-ion diffusivity is especially important for the electrode and the electrolyte materials in LIBs (Akhilash et al., 2021; Goodenough and Park, 2013). Porous 3D-structures can improve the speed of electron and ion transport and hierarchically porous structures can reduce the distance of Li-ion transport (Liu et al., 2022; Ponnada et al., 2022).

Often the feed materials, such as filaments, used for AM processes are not inherently porous. Increasing the porosity of the feed materials can be done by adding porous materials to the feed material. Though, this can affect the rheological properties of the AM material and thus its printability (Sanumi et al., 2022). Another way to produce porous material via AM, which will be discussed next, is to select an AM technique, that enables the printing of a porous structure. Porous additives and AM techniques, that support the formation of porous printed structures, can be used together to optimize porosity.

DIW is one AM technique that produces porous structures. The technique itself produces macropores in the structure. In addition, removing solvent from the printed ink forms micropores in the structure. (Pei et al., 2021.) For example, Liu et al. (2022) used DIW to make porous electrodes with Ketjen black and CNTs as conductive additives. After printing

the solvent was removed by freeze-drying the fabricated structure. The electrodes they made had 71.85 % porosity, which does not include the macropores formed during printing. (Liu et al., 2022.) This shows that DIW is a promising technique for fabricating porous structures. Though, it should be noted that in ME processes, including DIW, the extrusion process of the feed material can result in a denser product (Maurel et al., 2020).

Another AM technique for fabricating porous material is PBF. As stated previously, in a PBF process sections of a powder bed are fused together. This technique can produce highly porous parts if only the surfaces of the powder particles are fused. This can be done by adjusting the printing parameters. For example, Maurel et al. (2021) compared the electronic conductivity of two positive electrodes, with the same composition, made with an ME process and a low-energy PBF process. The low energy settings of the PBF process fused the particles only partially together, thus resulting in a porous structure. They found that the positive electrode made with PBF had approximately 30 times higher conductivity than the electrode made with ME, which did not lead to a micro-porous structure. (Maurel et al., 2021.)

The pore size and pore distribution should be considered when the porosity of feed material is increased. Pore size is important so that the active material ions can move through the pores of solid material during cycling. Thus, the pore size depends on the active material ion diameter. (Liu et al., 2022.) Pore distribution is important for a uniform porous structure that has pathways for active material through the entire fabricated structure (Blake et al., 2017).

Porous additives, such as cellulose and carbon nanofibers, can be added to the feed material before printing to form a composite with enhanced porosity (Ponnada et al., 2022). Some additives, such as CNTs and graphene, can increase both the porosity and the conductivity of the material (Gupta et al., 2021). For example, Maurel et al. (2019) used SiO<sub>2</sub> particles as porous additives to increase the porosity of a PLA filament to fabricate a separator via FDM. They found that the samples with SiO<sub>2</sub> particles had more porosity than the sample without porous additives. (Maurel et al., 2019.)

## 4 Additive manufacturing of lithium-ion batteries

This part of the paper focuses on AM of LIB components and the possibility of fabricating complete LIBs via AM. Different AM techniques and materials for electrodes and solid electrolytes are considered as well as their advantages and disadvantages.

### 4.1 Additive manufacturing of electrodes

AM enables the fabrication of electrodes in a single step and improved control over the structural architecture, geometry, and thickness of electrodes (Pei et al., 2021; Sanumi et al., 2022). This control over the composition of the fabrication process can improve the electrochemical performance of the fabricated electrode (Sanumi et al., 2022). Some examples of different AM techniques for electrode fabrication are presented here as well as the benefits and challenges of certain materials and the techniques themselves.

#### 4.1.1 Fusion deposition modelling and powder bed fusion in electrode fabrication

As mentioned before, Maurel et al. (2021) compared the fabrication of a positive electrode for a LIB via ME and PBF processes. LFP was used as an active material with carbon black and carbon nanofibers as additives. Both techniques used polypropylene (PP) as a printing polymer. The composition for both techniques was 26 wt.% of LFP, 70 wt.% of PP and 4 wt.% of carbon black. The material was used as a powder for PBF and made into a filament for ME. (Maurel et al., 2021.)

The positive electrode fabricated by PBF exhibited approximately 30 times higher electronic conductivity compared to the electrode made via ME. This can be explained by the low energy parameters chosen for the PBF resulting in a more porous structure. In the ME positive electrode, some of the active materials and conductive additives were isolated in the polymer matrix, resulting in lower conductivity. In addition, the ME electrode did not seem to have a microporous structure. As a result, the PBF electrode also displayed higher electrochemical performance. (Maurel et al., 2021.)

This shows that highly porous electrodes can be fabricated via PBF if the printing parameters are selected well. Although, the capacity of the positive electrode made with PBF was 74 mAh g<sup>-1</sup> of LFP, which is still less than half of the theoretical capacity of LFP (Maurel et al., 2021). The importance of porosity in electrodes can be seen in the poor electrochemical performance of the non-microporous ME positive electrode. Though the ME electrode showed nano-porosity, the nano-pores were not accessible to the Li-ions (Maurel et al., 2021). This is why pore size should also be considered in addition to porosity.

It is also worth noting that the low-energy parameters of PBF limit the amount of active material in the printing powder. Whereas the amount of active material in ME can be as high as 50 vol% in the filament when a plasticizer is used. Here paraffinic oil was used as a plasticizer, but it did not result in a porous structure when combined with PP. (Maurel et al., 2021.) Subsequently, the choice of plasticizer is important. In addition, adding active material and conductive additives results in decreased mechanical properties of the electrode (Maurel et al., 2021). Thus, the maximum amount of active material in the electrode, which affects the electrochemical performance, needs to be balanced with the printing parameters and mechanical properties of the electrode.

Plasticizers have been successfully used to increase the active material loading of FDM filaments for LIB electrodes while maintaining printability. Maurel et al. (2019) achieved active material loading of 49 wt.% LFP of total composite for a LIB positive electrode with carbon black as conductive additive by using poly(ethylene glycol) dimethyl ether as a plasticizer. The fabricated electrode displayed capacity values as high as 87 mAh g<sup>-1</sup> of LFP. (Maurel et al., 2019.) Maurel et al. (2018) made a negative electrode for a LIB with active material loading of 49.2 wt.% graphite of total composite with carbon black as conductive additive by adding poly(ethylene glycol) dimethyl ether as a plasticizer. This electrode had capacity values as high as 200 mAh g<sup>-1</sup> of graphite. (Maurel et al., 2018.) In both cases the thermoplastic material was PLA (Maurel et al., 2019, 2018). Without the use of a plasticizer, the maximum amount of active material and conductive additives in the filament would have been approximately 30 vol.% of the total composite to still be printable via FDM (Maurel et al., 2019).

It should also be noted that FDM uses materials that can engage in the electrochemical reactions in LIBs. This can hinder the performance of LIBs fabricated via AM. An example

of these materials is thermoplastics. However, an advantage of FDM is that it rarely needs post-processing. (Ponnada et al., 2022.)

#### 4.1.2 Inkjet printing in electrode fabrication

Inkjet printing has been studied for electrode fabrication as it is versatile in terms of solvents and inks, it has a high resolution and it is cost-efficient (Kolchanov et al., 2020). Silicon has a very high theoretical capacity ( $4200 \text{ mAh g}^{-1}$ ), but it is not widely used due to large volume expansion during cycling, as stated previously. The effects of different polymer binders for accommodating this volume expansion were compared in a study by Lawes et al. (2017). They used inkjet printing to fabricate silicon nanoparticle (SiNP) negative electrodes for LIBs. Carbon black was used as a conductive additive. (Lawes et al., 2017.) All the inks were sonicated to break up agglomerates and guarantee uniform dispersion, which is important for ink printability, as the agglomerates can clog the printing nozzle (Gulzar et al., 2020; Lawes et al., 2017). The inkjet-printed electrode films were dried after fabrication (Lawes et al., 2017).

Poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonate) (PEDOT:PSS) performed best out of the four commercial binders tested. The SiNPs and PEDOT:PSS formed a continuous polymer structure, whereas some of the SiNPs were isolated in the polymer matrix in the inks made with other non-conductive binders. The PEDOT:PSS binder exhibited self-healing properties in the negative electrode, which allowed it to accommodate the volume expansion of silicon during cycling by stretching and shrinking. Thus, ensuring good contact between the electrode and the current collector. In addition, PEDOT:PSS is well suited for inkjet printers, as it is designed for inkjet printing, and thus exhibits stable cycling and good electrical conductivity. (Lawes et al., 2017.)

The SiNPs/PEDOT:PSS negative electrode displayed high initial and reversible capacity. This electrode showed as high capacities as  $2500 \text{ mA h g}^{-1}$  when cycled. The high capacity is partially due to the ionically and electrically conductive nature of PEDOT:PSS. Although, the electrode did also display irreversible capacity loss during the first cycle due to SEI formation. The inkjet-printed SiNPs/PEDOT:PSS negative electrode was also compared to a doctor-bladed electrode with similar composition, and the inkjet-printed electrode

displayed higher capacities and better cycling stability. This ink formulation can produce thin uniform films via inkjet printing. (Lawes et al., 2017.)

Kolchanov et al. (2020) fabricated positive electrodes with a  $\text{Li}_{1.15}\text{K}_{0.05}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$  lithium-rich active material. They used carbon black as a conductive additive, polyvinylidene fluoride as a polymer binder and a surfactant to prevent coagulation. The active material loading of the ink was only 0.03 wt.% as a higher content of active material would clog the nozzle of the inkjet printer. The structures were dried after printing. The inkjet-printed positive electrode had a capacity of  $240 \text{ mAh g}^{-1}$ , whereas an electrode made with conventional casting technology had a capacity of  $250\text{--}260 \text{ mAh g}^{-1}$  depending on the current. The lower capacity was likely due to the degradation of the material and loss of contact between the electrode and current collector during cycling. (Kolchanov et al., 2020).

Inkjet printing has also been used with many other materials. For example, LFP positive electrodes were fabricated for LIBs with water-based solvents and carbon black as a conductive additive (Gu et al., 2015). Other active materials used for fabricating electrodes for LIBs via inkjet printing include graphene and LTO as negative electrode active material and  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  as positive electrode active material (Carey et al., 2022; Gu and Federici, 2018).

In conclusion, self-healing properties can enable the accommodation of volume expansion of some high-capacity negative electrode materials and conductive polymer binders show promise in the fabrication of electrodes for LIBs via inkjet printing. Inkjet printing also has many types of available printing materials and great control over electrode thickness (Kolchanov et al., 2020). Although inkjet printing needs some post-processing, such as drying, it is a promising technique for fabricating thin electrode films. In addition to rheological properties, homogeneity, stability and a porous structure are important for inks used in inkjet printing (Kolchanov et al., 2020). The requirements for rheological properties to ensure printability, lead to a very low active material loading compared to the maximum active material loadings achieved with other types of AM technologies.

### 4.1.3 Direct ink writing in electrode fabrication

DIW has been widely used to fabricate electrodes for LIBs due to the simplicity of the process and the wide range of available materials (Liu et al., 2022; Pei et al., 2021). DIW can also be beneficial in fabricating porous materials (Liu et al., 2022).

Liu et al. (2022) used DIW to make a porous negative electrode for a LIB. They used LTO as active material with Ketjen black and multi-walled CNTs as conductive additives. Carboxymethyl cellulose was used as a binder and water-based 1,4-dioxane as a solvent. The solution was mixed well to ensure homogeneity and filtered to remove XXX. The ink had a 40 wt. % solid content of LTO, Ketjen black and CNTs. After printing the fabricated structure was freeze-dried to remove the solvent. The electrode had 71.85 % porosity and displayed capacity values as high as 150 mAh g<sup>-1</sup>. (Liu et al., 2022.) The achieved capacity is good compared to the theoretical capacity of LTO, which is approximately 175 mAh g<sup>-1</sup> (Li et al., 2018; Sovizi and Pourali, 2018).

DIW has been widely used with metal oxides to fabricate both positive and negative electrodes (Sanumi et al., 2022). For example, Wei et al. fabricated a positive electrode for a LIB with LFP as active material and a negative electrode with LTO as active material. They used Ketjen black as a conductive additive (Wei et al., 2018).

DIW is a promising technique for fabricating porous structures, though it can require post-processing to remove solvent from the fabricated structure. The rheological properties of inks affect printability in DIW processes, similar to inkjet printing. Though, the maximum active material loading in the ink is higher in DWI processes than in inkjet printing processes.

### 4.1.4 Digital light processing in electrode fabrication

Digital light processing (DLP) is a VPP process that uses liquid photocurable feed stock material (SFS-EN ISO/ASTM 52900, 2021; Yee et al., 2021). DLP is a potential AM process for fabricating electrodes as it has a good resolution and it allows the use of a smaller amount of resin than commercial SLA printers (Kadry et al., 2019; Yee et al., 2021). There have been some studies on this technique for fabricating LIB electrodes, though it has not been widely explored.

One example of DLP in electrode fabrication is by Yee et al. (2021). They fabricated positive electrodes for a LIB via DLP. They used  $\text{LiCoO}_2$  as active material, and an aqueous solution of lithium nitrate and cobalt nitrate hexahydrate was used as a metal salt precursor. Polyethylene glycol diacrylate was used as a photoresin with a photoinitiator. The fabricated structure was calcinated after printing. As a result of this, the structure shrank by approximately 44 % and had a mass loss of approximately 92 %. The electrode had a porosity of approximately 56 %. (Yee et al., 2021.) The fabricated positive electrode displayed a capacity of  $121 \text{ mAh g}^{-1}$ , which is much lower than the theoretical capacity ( $274 \text{ mAh g}^{-1}$ ) (Akhilash et al., 2021; Yee et al., 2021). Though, the capacity is comparable to the practical capacity achieved with LIB electrodes made with conventional manufacturing processes, which is approximately  $140 \text{ mAh g}^{-1}$  (Akhilash et al., 2021). It should be noted that Yee et al. (2021) did not use any additives to enhance the conductivity.

Ye et al. (2022) made negative electrodes for LIBs via DLP. They used silicon as active material and, PEDOT:PSS and polyethylene glycol as polymer binders. The fabricated electrode structure was dried after printing. The electrode displayed capacities as high as  $1539 \text{ mAh g}^{-1}$ , though the capacity was well below the theoretical capacity of silicon. The electrode had a hierarchal porous structure. (Ye et al., 2022.)

These examples showcase that DLP can be used to fabricate porous electrodes for LIBs. Though, the structure fabricated via DLP often requires post-processing to remove solvents, which can result in considerable shrinkage. The shrinkage can be difficult to predict as it can change depending on the ratio of metal salt to polymer binder (Ye et al., 2022). This might limit the applications of electrodes fabricated via DLP as it could result in the electrode size determining the size of the battery. DLP is a promising process in terms of the good resolution achievable with the technique and the DLP printer can be operated at room temperature (Kadry et al., 2019).

## 4.2 Additive manufacturing of solid electrolytes

The main challenges with solid electrolytes in LIBs are high cell resistance and poor contact between electrode and electrolyte. Liquid electrolytes can conform to the shape of the electrode, but solid electrolytes must be designed and made to fit the electrodes perfectly.

(McOwen et al., 2018.) Thus, the most difficult part to fabricate via AM for fully printed batteries is the separator/electrolyte layer (Blake et al., 2017; Pei et al., 2021). In batteries that have solid electrolytes, the electrolyte layer usually functions as both separator and electrolyte as the electrolyte layer is not electrically conductive and physically separates the electrodes (Zheng et al., 2018). Uniform pore-size distribution as well as thermal and electrochemical stability are important for this layer. (Blake et al., 2017; Pei et al., 2021.)

#### 4.2.1 Liquid deposition modelling in electrolyte fabrication

Liquid deposition modelling has been widely used in AM of electrolytes, though not many studies have been done on AM of solid electrolytes for LIBs via liquid deposition processes (Maurel et al., 2020). One example of such a study is by McOwen et al. (2018), who made two ink compositions suitable for AM with different binder systems for garnet-type LLZO solid electrolytes. They used a liquid deposition printer to demonstrate the printability of these inks. (McOwen et al., 2018.)

Both inks had LLZO ceramic particles, but different binders and thus distinct rheological properties. The first one of the inks had polyvinyl butyral as a binder with benzyl butyl phthalate as a plasticizer. This ink conforms to the surface it is deposited on, partially wets it, and joins seamlessly due to the ink's rheological properties, in particular low viscosity. Thus, the ink can be used for fabricating thin electrolyte films. Thin electrolyte films have shorter Li-ion diffusion paths than thicker electrolytes, and the thin films can thus help to reduce the high cell resistance. (McOwen et al., 2018) This also demonstrates that liquid deposition modelling is suitable for fabricating solid electrolytes with the right ink composition.

The second ink made by McOwen et al. (2018) had a proprietary texanol-based composition, ESL 441, as a binder. This ink retains its shape and structure directly after printing. This ink had a higher viscosity than the first ink and improved mechanical properties. Both electrolyte structures were sintered after printing. The fabricated electrolytes displayed high ion conductivity associated with LLZO, demonstrated by constant area-specific resistance of  $20 \Omega \text{ cm}^{-2}$  during cycling. (McOwen et al., 2018.) These inks showcase the effect of rheological and mechanical properties of inks on the final fabricated product and its

structure. As binders and solvents can be used for adjusting these properties varying structure types are possible. In addition, McOwen et al. (2018) state that these ink compositions could be tailored for other ceramics and thus other types of solid electrolytes.

#### 4.2.2 Fusion deposition modelling and fused filament fabrication in electrolyte fabrication

Though FDM has been used in fabricating electrodes and gel electrolytes, there are few studies on fabricating solid electrolytes via FDM. Maurel et al. (2020) studied this by making a solid polymer electrolyte filament for an FDM printer. They used poly(ethylene oxide) (PEO) as a printing polymer and lithium bis(trifluoromethane) sulphonamide (LiTFSI) lithium salt powder to increase the ionic conductivity. The filament was made by mixing the PEO and LiTFSI, which were then formed into films, dried, and made into a powder to ensure homogeneity. The powder was made into a filament with an extruder. (Maurel et al., 2020.)

Several molar ratios of PEO to LiTFSI were tested to optimize the composition for ionic conductivity and the molar ratio of 20:1 of PEO:LiTFSI had the best ion conductivity at 90 °C of  $2.18 \cdot 10^{-3} \text{ S cm}^{-1}$ . Solid polymer electrolytes are often operated at temperatures of 70 °C to 90 °C, because of their low ionic conductivity at lower temperatures. The achieved ionic conductivity is good compared to that of liquid electrolytes, which have a conductivity of approximately  $10^{-3} - 10^{-2} \text{ S cm}^{-1}$ , as stated previously. (Maurel et al., 2020.)

However, LiTFSI acts as a plasticizer in the filament and makes it softer and stickier. This effect on mechanical properties made AM of the filament not possible with the FDM printer. Thus, modifications, such as lowering the printing temperature and changing the nozzle, were made to the printer to achieve printability for the formulated filament. (Maurel et al., 2020.) This showcases the significance of mechanical properties for filament formulation and some of the challenges with solid electrolyte fabrication via FDM. Nonetheless, the filament was printed with the modified printer proving its printability, and it showed good ionic conductivity (Maurel et al., 2020). In addition, the fabricated structure did not need post-processing unlike the electrodes fabricated by liquid deposition modelling. Overall, FDM should not be discounted as an AM technique for fabricating solid electrolytes.

FFF is a ME process, that is very similar to FDM (Abel et al., 2022). FFF uses thermoplastic filaments, such as PLA (Reyes et al., 2018). As FFF is a very similar AM process to FDM, it also has similar challenges. There have also been very few studies on fabricating solid electrolytes for LIBs via FFF.

Ragones et al. (2020) fabricated solid polymer electrolytes for LIBs via FFF. They made two solid electrolytes using LiTFSI as lithium salt, PEO and PLA as polymers and ceramic fillers. One of the electrolytes had SiO<sub>2</sub> as ceramic filler and the other had Al<sub>2</sub>O<sub>3</sub>. The composition of the electrolytes was 59 wt.% of PLA, 20 wt.% of PEO, 20 wt.% LiTFSI and 1 wt.% of ceramic filler. They found that printing PLA-PEO-LiTFSI filament was difficult due to the high ductility of the filament. By adding 1 wt.% of SiO<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub> ceramic fillers to the filament, the printability improved significantly. The electrolyte with SiO<sub>2</sub> had a conductivity of  $8 \cdot 10^{-5} \text{ S cm}^{-1}$  at 120 °C. The electrolyte with Al<sub>2</sub>O<sub>3</sub> had a conductivity of  $3 \cdot 10^{-5} \text{ S cm}^{-1}$  at 120 °C. The electrolytes show lower conductivity values than conventional liquid electrolytes. (Ragones et al., 2020.) Though these electrolytes had lower conductivities than the solid electrolyte fabricated via FDM with similar components by Maurel et al. (2020), the printability was greatly improved by the addition of ceramic fillers. This study shows the potential of FFF as an AM process to fabricate solid electrolytes for LIBs as well as the impact of a small amount of ceramic filler on the mechanical properties of filament and thus printability.

#### 4.3 Additive manufacturing of complete lithium-ion batteries

Using AM to manufacture a complete LIB is an appealing idea because AM could enable the production of a complete battery with packaging in a single step without assembly or after-processing (Sanumi et al., 2022). With fewer production steps, the production time could be shorter and with AM waste could be minimized and the use of materials maximized (Gulzar et al., 2020; Sanumi et al., 2022). In addition, AM enables the production of more complex structures, including 3D architectures that have 3D diffusion of Li-ions (Maurel et al., 2021; Sanumi et al., 2022). This in turn could result in LIBs with improved electrochemical performances (Maurel et al., 2021).

The following three examples of complete LIBs fabricated via AM showcase that it is possible to use AM to fabricate functioning LIBs. These examples do not include solid electrolytes as they had either hybrid electrolytes or the structure was infused with liquid electrolytes after printing. It should also be noted that the current collectors were only fabricated via AM in one of these examples whereas the others used substrates the structure was printed on as current collectors.

#### 4.3.1 Fabrication of a lithium-ion battery via fused filament fabrication

Reyes et al. (2018) fabricated a complete LIB in a single step via FFF by changing the filament for each component (Reyes et al., 2018). They fabricated the electrodes, a hybrid electrolyte, and current collectors with different filament compositions. The current collectors were made with a conductive thermoplastic-based commercial filament. (Reyes et al., 2018.)

Reyes et al. (2018) made a PLA hybrid electrolyte by infusing the fabricated PLA structure with  $\text{LiClO}_4$  lithium salt to increase the ion conductivity of PLA. The  $\text{LiClO}_4$  was chosen for its good ionic conductivity and stability. It was dissolved into a propylene carbonate and ethyl methyl carbonate solution. The solvents were chosen for their relatively high ionic conductivity. The ionic conductivity of the fabricated PLA structure was increased from  $8.2 \cdot 10^{-11} \text{ mS cm}^{-1}$  of pure PLA to  $0.085 \text{ mS cm}^{-1}$  of the infused PLA structure. (Reyes et al., 2018.) The increase in ionic conductivity was significant though the values are still below those of liquid electrolytes (Maurel et al., 2020).

Reyes et al. (2018) used (LTO) as negative electrode active material with graphene for increasing the electrical conductivity of PLA. Lithium manganese oxide (LMO) was used as positive electrode active material with multi-walled CNTs as conductive additives. Reyes et al. (2018) found that the optimal ratio of conductive additives to active material was 80:20. The volume percentage of PLA in the electrodes was 70-80 vol%, which resulted in low capacities of the electrodes. The negative electrode had a capacity of only  $3.34 \text{ mAh cm}^{-3}$  compared to the theoretical capacity of LTO, which is  $600 \text{ mAh cm}^{-3}$ . Similarly, the positive electrode had a capacity of only  $6.99 \text{ mAh cm}^{-3}$  compared to the theoretical capacity of LMO, which is  $596 \text{ mAh cm}^{-3}$ . (Reyes et al., 2018.)

The single-print LIB was infused with the  $\text{LiClO}_4$ -salt solution after printing. The performance of the single-print LIB was compared to that of a LIB assembled from corresponding components fabricated via FFF. For the assembled battery the electrodes and separator were infused with the  $\text{LiClO}_4$ -salt solution before assembly. The assembled LTO-LMO LIB had a capacity of  $3.91 \text{ mAh cm}^{-3}$  whereas the single-print LIB had a capacity of  $1.16 \text{ mAh cm}^{-3}$ . Reyes et al. stated that the lower capacity of the single-print LIB could be due to incomplete electrolyte infusion of the electrodes. (Reyes et al., 2018.)

The capacities of these batteries were very low compared to their theoretical capacities. This was due to the high PLA content in the electrode filaments needed for suitable mechanical properties and thus printability. The high PLA content disrupted the electrical contact between the conductive particles and the electrode active materials. In addition, during cycling, the batteries had significant irreversible capacity loss caused by SEI formation. (Reyes et al., 2018.)

This shows that it is possible to use FFF for the fabrication of a complete functional LIB in a single step. The electrochemical performance of the battery suffered from a large amount of printing polymer compared to the content of active materials (Reyes et al., 2018). In addition, the high electrical resistivity of the fabricated batteries compared to that of conventional LIBs likely further hindered the electrochemical performance (Reyes et al., 2018).

#### 4.3.2 Fabrication of a lithium-ion battery via direct ink writing

Wei et al. (2018) used a custom-made DIW printer to fabricate semisolid electrodes, separator/electrolyte layer and packaging of a LIB. The battery was printed on glassy carbon substrates, which functioned as current collectors. (Wei et al., 2018.)

Wei et al. (2018) made thick biphasic semisolid electrodes. They chose LFP as the positive electrode active material and LTO as the negative electrode active material. Ketjen black was used as a conductive additive for the electrode inks. The active material and conductive particles were mixed with LiTFSI and PC solution. A non-ionic dispersant was added to eliminate flocculation. The rheological properties and electrochemical performance of the electrode inks were optimized to ensure printability. (Wei et al., 2018.)

The packaging of the LIB was composed of UV-curable epoxy and fumed SiO<sub>2</sub>. The separator/electrolyte layer was made of ethoxylated trimethylolpropane triacrylate, photoinitiator, liquid electrolyte and Al<sub>2</sub>O<sub>3</sub> particles. The electrolyte was LiTFSI salt in the PC solution. (Wei et al., 2018.)

The packaging was deposited on the glassy carbon substrate/current collector and cured with UV light. The negative electrode was printed on the substrate, followed by the separator/electrolyte layer, which was cured before the printing continued. The positive electrode was printed onto the separator/electrolyte and a glassy carbon substrate was placed on the positive electrode before finishing the printing of the packaging. (Wei et al., 2018.) Printing each component on top of the previous one helps the different component layers adhere to each other (Maurel et al., 2019).

After the second cycle, the fully 3D-printed LIB had an areal capacity of 4.45 mAh cm<sup>-2</sup>, which is equivalent to 17.8 mAh cm<sup>-3</sup>. The LIB showed very little capacity loss. A LIB made from corresponding components without packaging had a higher capacity of 14.5 mAh cm<sup>-2</sup>. (Wei et al., 2018.) This shows that it is possible to use DIW to fabricate a functioning complete LIB. Though, this process required UV-curing as post-processing after the printing of certain components making the printing process less efficient. This was due to the ink composition of the packaging and the separator/electrolyte layer.

#### 4.3.3 Fabrication of a lithium-ion battery via fusion deposition modelling

Maurel et al. (2019) used an FDM printer to fabricate a complete LIB in a single print by changing the filament between layers. They fabricated the negative electrode, separator, and positive electrode layers via AM. After printing, the structure was infused with a liquid electrolyte. (Maurel et al., 2019.)

A graphite-PLA filament was used for the negative electrode and an LFP-PLA filament for the positive electrode (Maurel et al., 2019). Carbon black was used as a conductive additive in the graphite-PLA and LFP-PLA filament. A high amount of active material in the electrode filaments was enabled by adding poly(ethylene glycol) dimethyl ether plasticizer. (Maurel et al., 2019, 2018.) The negative electrode filament had 49.2 wt.% of graphite and the positive electrode filament had 49 wt.% of LFP (Maurel et al., 2019). The plasticizer

made the PLA matrix more ductile and less stiff, thus improving the printability of the filament and allowing higher active material content (Maurel et al., 2018).

The separator was made with SiO<sub>2</sub>-PLA composite filament. The SiO<sub>2</sub> particles were mixed with PLA to increase the porosity of the structure and thus improve the liquid electrolyte uptake. The liquid electrolyte was a LiPF<sub>6</sub> solution. The same plasticizer was used in this filament as in the electrode filaments to optimize the SiO<sub>2</sub> content with printability. (Maurel et al., 2019.)

The single-print battery had a capacity of 30 mAh g<sup>-1</sup> of active material or 6.5 mAh cm<sup>-3</sup> of the total electrode and separator volume. The layers of the single-print LIB were printed on top of each other to promote a continuous interface between the layers. A corresponding assembled cell showed a lower capacity of 15 mAh g<sup>-1</sup> of active material.

The resolution of the first layer thickness of the FDM printer limited the layer thickness of the electrodes and separator to >200 μm, which contributed to the poor electrochemical performance of the batteries. (Maurel et al., 2019) Increased thickness of the electrodes leads to increased Li-ion and electron transport distance (Liu et al., 2022). The single-print battery had a better electrochemical performance as the thickness of the layers could be controlled better (Maurel et al., 2019). This showcases that the low resolution of printers used in AM can also affect the performance of the battery (Gulzar et al., 2020; Maurel et al., 2019). Thus, the printing resolution of the printers should also be considered.

## 5 Conclusions

The purpose of this thesis was to identify the most potential processes and materials for AM of electrodes and solid electrolytes for LIBs. The thesis aimed to detect possible problems with the techniques and materials, and determine what areas still need to be researched more to be able to overcome the challenges related to AM of LIBs. The focus of this study was on solid electrolytes because they can be fabricated via AM processes. This study was done as a literary review.

Ionic and electric conductivities are crucial for the electrochemical performance of LIBs. First, the current collectors need high electron conductivity to deliver electrons between the external circuit and the electrodes (Goodenough and Park, 2013). Second, the electrolyte must have a high ionic conductivity of Li-ions with hardly any electron conductivity to deliver Li-ions between the electrodes (Zheng et al., 2018). Third, electrodes must have a high ionic and electric conductivity for delivering electrons to the current collector and Li-ions to the other electrode through the electrolyte (Reyes et al., 2018).

However, the materials used in AM processes often have low ionic and electric conductivities, which makes AM of LIBs and LIB components challenging. The ionic and electric conductivities can be increased by adding conductive additives to the feed materials to make conductive composite materials (Distler and Boccaccini, 2020). Conductivities can also be increased with porous 3D structures, as they can improve the speed of electron and ion transport by reducing the transport distance (Liu et al., 2022; Ponnada et al., 2022). The fabrication of porous structures can be promoted by adding porous additives to feed material, resulting in porous composite materials.

The amount of active material in feed materials was found to have a large effect on the electrochemical performance of the battery. If the ratio of feed material to active material was too high, the active material particles could be isolated from the conductive material (Reyes et al., 2018). This led to poor contact between the active and conductive materials and thus low capacity (Reyes et al., 2018). Hence, the active material loading should be as high as possible and there should be enough conductive material to form a conductive

network. In addition, a uniform distribution of active and conductive materials is important to form a conductive network throughout the entire structure.

Higher active material and conductive additive content generally lead to better energy yield of the battery (Ponnada et al., 2022). However, adding active material and additives to the materials used in AM processes often affects the rheological and mechanical properties of the printing material and thus printability. (Sanumi et al., 2022.) This leads to the main challenge of fabricating LIBs via AM: maximizing the content of active and conductive materials in feed material whilst ensuring printability. Hence, the printability of the feed material must be balanced with the electrochemical performance of the battery, often resulting in a decreased electrochemical performance.

Because the AM processes have different working principles, they have different requirements for the used materials. The feed material often must be formulated for specific materials and a specific AM technology for optimized performance. The different technologies also have different ways of maximizing the active material loading. The main advantages and drawbacks of the AM technologies discussed in this work are listed in Table 1 with some examples of the applications for fabricating LIB components.

Table 1. The advantages and drawbacks of some AM technologies used to fabricate LIBs.

AM technology	Application for LIBs	Advantages	Drawbacks	Examples
FDM (and FFF)	Electrodes and electrolytes	<ul style="list-style-type: none"> <li>- Multiple materials possible in a single print with several print heads</li> <li>- High maximum active material loading with plasticizers</li> <li>- Simple to use</li> <li>- Often no post-processing is needed</li> </ul>	<ul style="list-style-type: none"> <li>- Printing material limited to thermoplastics</li> <li>- The thermoplastics can engage in electrochemical reactions</li> <li>- Filament formulation, printability vs. electrochemical performance</li> <li>- Poor printing resolution of the first layer</li> <li>- High printing temperatures</li> </ul>	Negative electrode: Maurel et al. (2018) Positive electrode: Maurel et al. (2019) Electrolyte: Maurel et al. (2020)
Inkjet printing	Electrodes and current collectors	<ul style="list-style-type: none"> <li>- Lower printing temperatures</li> <li>- Porous products</li> <li>- Great compatibility with some polymer binders</li> <li>- Many types of available printing materials</li> </ul>	<ul style="list-style-type: none"> <li>- Ink formulation, rheological properties vs. electrochemical performance</li> <li>- Lower active material loading due to low viscosity requirement</li> <li>- Post-processing (e. g. drying) may be necessary</li> </ul>	Negative electrode: Lawes et al. (2017) Current collectors: Gu and Federici (2018)

Table 1. (continues)

AM technology	Application for LIBs	Advantages	Drawbacks	Examples
PBF	Electrodes	<ul style="list-style-type: none"> <li>- High porosity with low energy parameters</li> <li>- No ink or filament formulation is necessary</li> <li>- Addition of active material and additives to printing material simple</li> </ul>	<ul style="list-style-type: none"> <li>- Lower maximum active material loading with low energy parameters</li> <li>- The use of only one material in a single print is possible</li> <li>- Post-processing may be necessary</li> </ul>	Positive electrode: Maurel et al. (2021)
DIW	Electrodes and electrolytes	<ul style="list-style-type: none"> <li>- Multiple materials possible in a single print with several print heads</li> <li>- Promotes fabrication of porous structures</li> <li>- Many types of available printing materials</li> <li>- Lower printing temperatures</li> </ul>	<ul style="list-style-type: none"> <li>- Ink formulation, rheological properties vs. electrochemical performance</li> <li>- Often post-processing needed (e. g. freeze-drying, sintering)</li> </ul>	Electrodes: Wei et al. (2018), Liu et al. (2022) Electrolyte: Blake et al. (2017)
SLA	Electrolytes	<ul style="list-style-type: none"> <li>- Good print resolution</li> <li>- High accuracy</li> <li>- No ink or filament formulation is necessary</li> <li>- Low printing temperatures</li> </ul>	<ul style="list-style-type: none"> <li>- Printing material must be photoactive</li> <li>- High cost</li> <li>- The use of only one material in a single print is possible</li> </ul>	Gel electrolyte: Chen et al. (2017), Rahman et al. (2020)
DLP	Electrodes	<ul style="list-style-type: none"> <li>- Good print resolution</li> <li>- No ink or filament formulation is necessary</li> <li>- Low printing temperatures</li> </ul>	<ul style="list-style-type: none"> <li>- Printing material must be photoactive</li> <li>- The use of only one material in a single print is possible</li> <li>- Post-processing may be necessary</li> </ul>	Positive electrode: Yee et al. (2021)

For FDM and FFF the thermoplastic or mechanical properties of filaments are crucial for printability (Maurel et al., 2021). The main advantages of these AM techniques are that they can achieve high active material loadings when a suitable plasticizer is used, and they usually do not need post-processing. Though, the feed materials are limited to thermoplastics and the lower printing resolution can result in thicker component layers.

Rheological properties are crucial for the printability of inks (Sanumi et al., 2022). Both inkjet printing and DIW use inks and can produce porous structures, but higher active material loadings can be achieved with DIW than with inkjet printing. Though, both techniques often require post-processing to remove solvents from the fabricated structures, making them less efficient. An advantage of these technologies is the wide range of available printing materials. Though, the studies on fabricating electrodes for LIBs via DIW seem to

mostly focus on LFP and LTO as active materials (Sanumi et al., 2022). Other LIB active materials in DIW processes could be explored in future research.

DLP is a promising process in terms of the good resolution of the printer. In addition, DLP does not have as strict requirements for the properties of printing materials as processes that use filaments or inks. Although, DLP can require post-processing to remove solvents.

The main advantages of PBF are the simple addition of active material and additives to the feed material and the ability to make highly porous structures with low-energy parameters. Although, the low-energy parameters of PBF limit the amount of active material in the printing powder. In addition, PBF may need post-processing.

In conclusion, none of the AM technologies discussed here is superior to the others. All of the technologies have their advantages and challenges with AM of LIBs and LIB components. As the components of LIBs have different requirements for electrochemical performance and materials, the most suitable AM technique for each component and material can vary.

Silicon-based negative electrodes fabricated via AM technologies displayed high capacities compared to other types of negative electrode materials, even though the capacities were well below the theoretical capacities of these compounds. Thus, further research into silicon-based electrodes fabricated via AM is warranted. Similarly, the fabrication of high-capacity positive electrodes for LIBs via AM should be researched more. New ways to maximize active material loading in feed material should also be explored.

As this study focused on solid electrolytes, it did not discuss the fabrication of gel electrolytes via AM processes. More research is needed on the fabrication of solid electrolytes for LIBs as there are not many studies on the subject and different AM technologies and materials could still be explored. Solid electrolytes are important for achieving the goal of manufacturing complete LIBs via AM. The AM of current collectors has not been explored in this work, though they are important for fabricating complete LIBs via AM techniques.

It should be noted that this thesis does not discuss every AM technology used for fabricating LIB components and the used search terms could have limited the reach results excluding some technologies and studies. The effect of different architectures on the performance of

LIBs is also an interesting subject and should be considered in AM of LIBs, though it is beyond the scope of this paper. In addition, it should also be noted that the terms AM and 3D-printing are sometimes used for processes that are not strictly AM.

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