CHAPTER 2

LITERATURE REVIEW

2.1 Polymer Electrolyte

The discovery of polymer electrolytes can be attributed to Fenton and his colleagues in 1973. They observed that the combination of polyethylene oxide (PEO) and alkali metal salts through complexation resulted in the development of polymer-salts with ionic conductivity properties (Fenton et al., 1973). This breakthrough discovery laid the foundation for further exploration and development of polymer electrolytes in various applications, including battery technology.

Polyethylene (PE) offers numerous advantages over liquid and inorganic solid electrolytes. These advantages include enhanced resistance to changes in electrode volume during the charge/discharge process, improved safety features, high flexibility, and excellent processability (Long et al., 2016). These qualities make PE a desirable choice for applications where stability, safety, flexibility, and ease of processing are essential considerations, such as in battery technology.

PEs are formed by blending a macromolecule matrix with a low lattice energy salt dissolved in a high dielectric constant and low viscosity organic solvent. This combination results in electrolytes with superior ionic conductivity, high chemical stability, cost-effectiveness, and enhanced safety (Yao et al., 2019). The primary characteristic of polymer electrolytes (PEs) is their ionic conductivity. The conductivity of PEs is influenced by factors such as the degree of crystallinity and viscosity of the polymer matrix. The degree of crystallinity refers to the arrangement of polymer chains and the presence of crystalline regions, while viscosity refers to the resistance of the electrolyte to flow. Many methods have been used to reduce the crystallinity of PEs, including plasticization, the inclusion of nanofillers, and crosslinking with a co-polymer.

The fundamental mechanism of ionic conduction in PEs lies in the formation of covalent bonds between the polymer backbones and the ionizing groups. The electron-donor components of the polymer matrix establish connections with the cationic components of the salt, facilitating the separation of ions. This ionic separation enables an ionic hopping mechanism as shown in **Figure 2.1**, which ultimately leads to the generation of ionic conductivity in PEs.

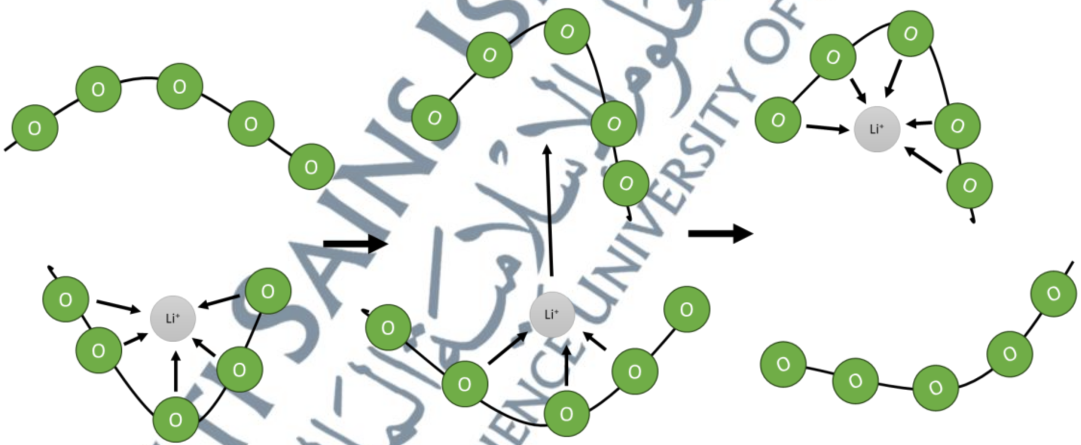


Figure 2.1: Ionic Hopping Mechanism of Ion Conduction

For the formation of an effective polymer-salt complex in polymer electrolytes, it is crucial to have salts with low lattice energy and a host polymer with a high dielectric constant (ϵ). The ionic conduction in polymer electrolytes occurs due to the rapid segmental motion of the polymer matrix combined with a strong Lewis-type acid-based interaction between the cation and a donor atom. This interaction facilitates the movement of ions within the polymer matrix, leading to efficient ionic conduction (Arya & Sharma, 2017).

Generally, PEs are categorized into two main types based on their source and origin: synthetic polymer electrolytes and natural polymer electrolytes as shown in Figure 2.2. Researchers have been investigating natural polymer electrolytes such as chitosan, rice starch, and Gallen gum as alternatives to synthetic counterparts. In addition, PEs can be further classified into three categories based on their physical state and composition: gel polymer electrolyte (GPE), solid polymer electrolyte (SPE), and composite polymer electrolyte (CPE) (Ye & Feng, 2010).

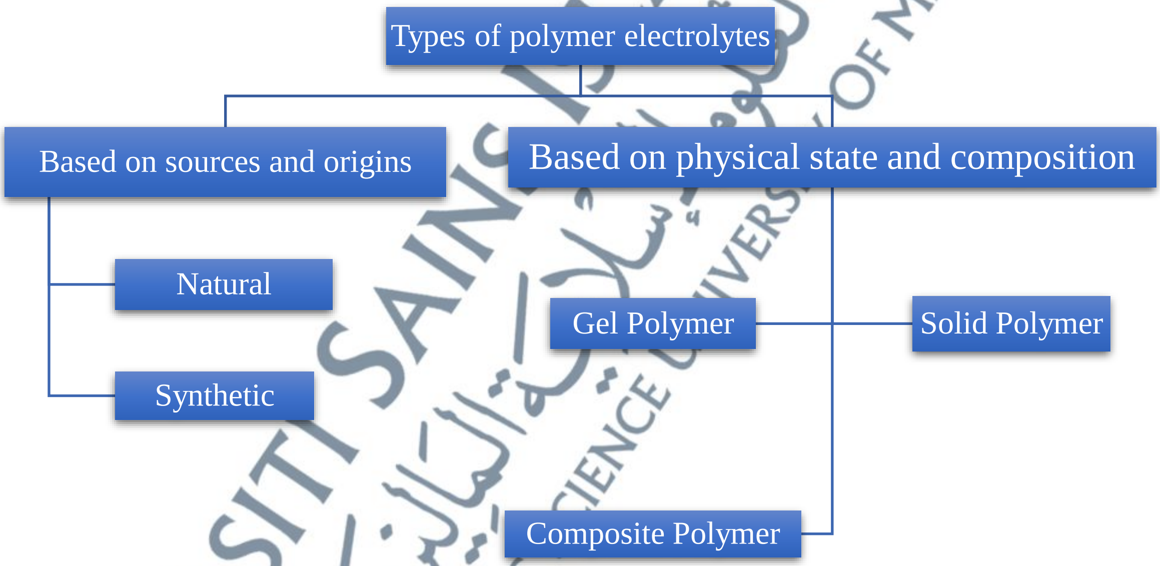


Figure 2.2: Types of Polymer Electrolytes

2.1.1 Gel Polymer Electrolyte

Gel polymer electrolytes (GPEs) are a type of electrolyte used in batteries and fuel cells. GPEs are typically made by adding a small amount of liquid plasticizer and/or solvent to a polymer–salt combination. Feuillade & Perche (1975) were the first one to study the GPEs and they investigated how an aprotic solution containing an alkali metal salt can be used to plasticize a polymer matrix. The polymer matrix's job is to maintain a solid-state matrix that facilitates ion migration in solvents, allowing a conductivity value up to 10^{-3} Scm^{-1} at room temperature to be obtained. The liquid electrolyte can act as a plasticizer, lowering the glass transition temperature and resulting in quicker ionic conduction.

GPEs can be divided into two types based on the technique of preparation: physical and chemical gels (Arya & Sharma, 2017). In physical gel, the liquid electrolytes are trapped inside the polymer matrix without having any bond with polymer and the solvent meanwhile the chemical gel contains a crosslinker that causes formation of chemical bonding between the cross-linker agent with the polymer functional group. The electrochemical properties of GPEs are primarily regulated by the liquid/plasticizer, whereas the polymer matrix influences safety, morphology, and mechanical qualities (Hassoun & Scrosati, 2015).

Gel polymer electrolytes (GPEs) offer several advantages over traditional electrolytes, including liquid electrolytes and solid polymer electrolytes. Firstly, GPEs provide enhanced safety due to their non-flammable nature, eliminating the risk of leakage or combustion associated with liquid electrolytes. This makes GPEs particularly desirable for applications where safety is the main priority.

Additionally, GPEs exhibit excellent flexibility and conformability, allowing them to adapt to various battery designs and accommodate structural changes during operation. This flexibility enables their use in complex and compact battery configurations, maximizing energy storage efficiency. Moreover, GPEs offer improved electrochemical stability, allowing for a wider operating voltage range and enabling the use of high-capacity electrode materials. This results in higher energy density and improves overall battery performance.

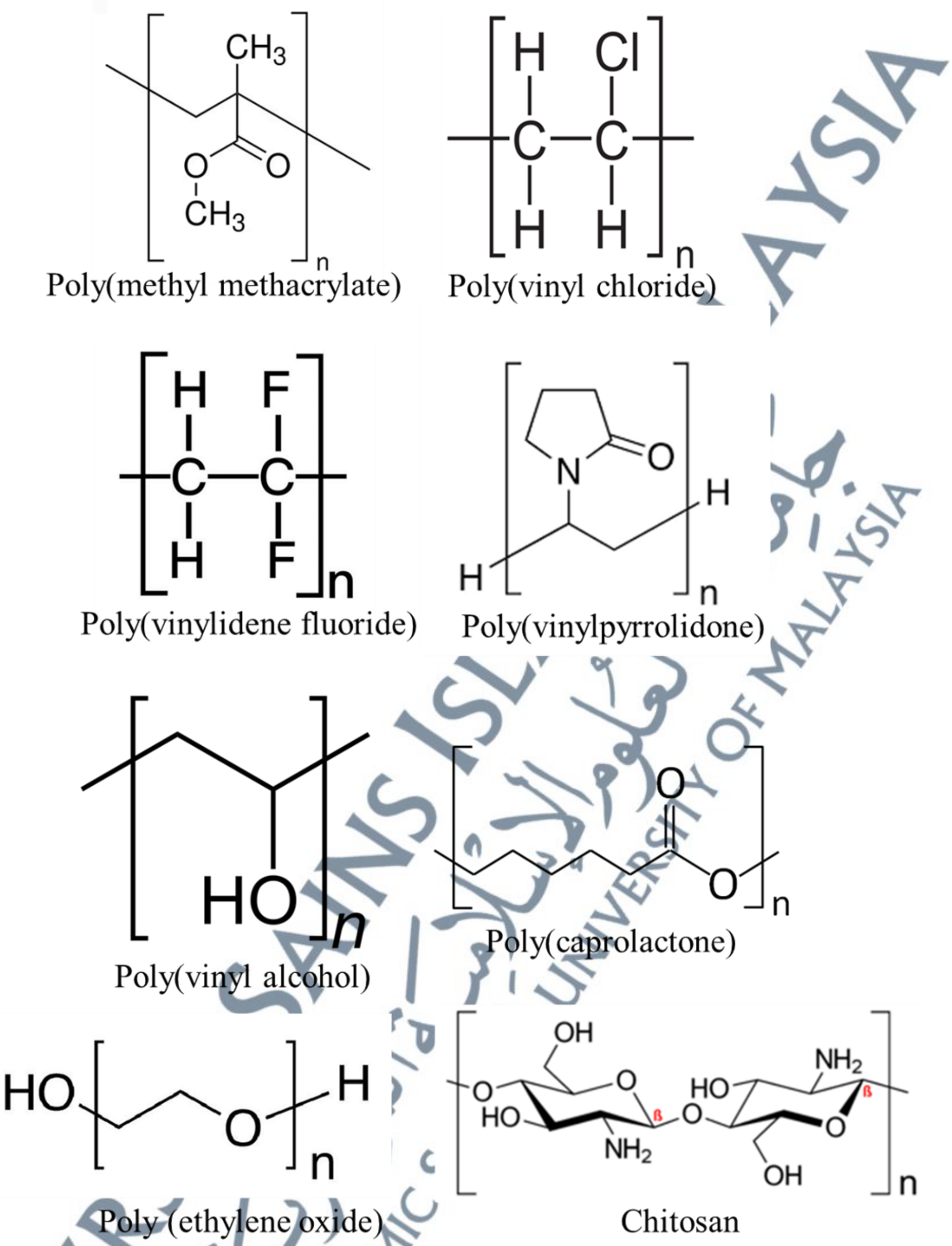
Furthermore, GPEs typically have higher ionic conductivity compared to solid polymer electrolytes, allowing for faster ion transport and improved battery efficiency. This facilitates faster charge and discharge rates, making GPEs well-suited for applications requiring rapid energy transfer, such as electric vehicles. Lastly, GPEs often have better compatibility with different electrode materials, reducing interface resistance and enabling better overall battery performance. They also have a higher temperature stability, which allows them to be used in high-temperature applications. In addition, GPEs can be easily formed into various shapes, making them suitable for use in flexible or unconventional battery designs.

Even though it has poor mechanical properties due to the solvent/plasticizer confinement inside the polymer matrix, it is still far better than SPE in-term of ionic conductivity and better safety than liquid electrolyte. GPE should exhibit good mechanical strength, able to retain a liquid electrolyte, high ionic conductivity, and electrochemical stability toward both electrodes so it can be use in practical application (Long et al., 2016).

GPEs are commonly used in lithium-ion batteries, particularly in portable electronic devices such as smartphones and laptops. They are also being explored for use in other types of batteries, such as redox flow batteries and zinc-carbon batteries, as well as in fuel cells for hydrogen vehicles.

2.2 Polymer Host

As mentioned before, the polymer host is one of the main components in PEs. Therefore, the material selection of PE is crucial to ensure high performance of PEs. Generally, the polymer host selection depends on two factors: first, a low hindrance to bond rotation, and second, the presence of polar (functional) groups with a high power of sufficient electron donor to form coordination with cations (Aziz, 2013). Besides, the polymer host should also have low glass transition temperature, high degradation temperature and high molecular weight (Arya & Sharma, 2017). Poly (ethylene oxide), poly(vinylidene fluoride), poly(vinyl alcohol), poly(methyl methacrylate), poly(vinylpyrrolidone), poly(caprolactone), chitosan, and poly(vinyl chloride) as shown in **Figure 2.3** are the commonly used polar polymer for PE purpose.



Poly(methyl methacrylate) Poly(vinyl chloride)

Poly(vinylidene fluoride) Poly(vinylpyrrolidone)

Poly(vinyl alcohol) Poly(caprolactone)

Poly (ethylene oxide) Chitosan

Figure 2.3: Commonly Used Polymer Host for Polymer Electrolyte

2.2.1 Polyurethane Acrylate (PUA)

Polyurethane acrylate (PUA) is a copolymer that has urethane linkage (-NHCOO-) and acrylate group. It is made by mixing polyol and isocyanate with the addition of an acrylate component (Naiwi et al., 2018). Urethane acrylate oligomer is usually used for UV curable polymer fabrication with addition of reactive diluent and free radical photo initiator via in situ UV polymerization. This UV radiation preparation method can open the way for better energy storage fabrication as high curing speed results in higher productivity, lower energy usage, lower volatile compound emissions, and lower fire danger (Asif et al., 2004).

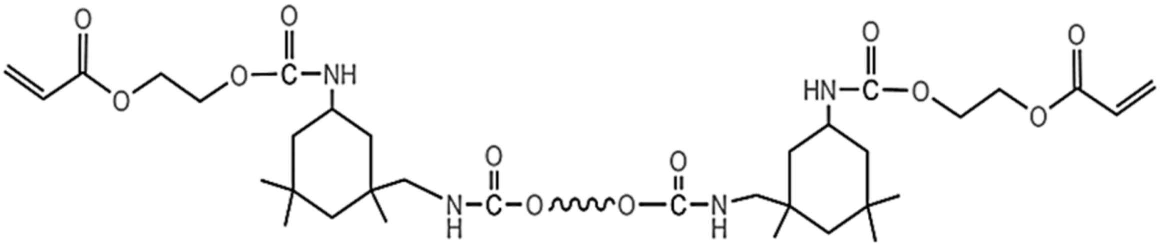


Figure 2.4: Polyurethane Acrylate Molecular Structure

Besides, PUA possesses high ionic conductivity, good mechanical properties, and flexible physical properties (Kim et al., 2020). With these characteristics, it is suitable to be employed as polymer host for energy storage application. There were few studies have been done on PUA based polymer electrolyte. Kai Ling et al. (2019) synthesized PUA from Jatropha oil and doped it with $LiClO_4$ to make GPEs and achieved conductivity achieved at 8.855 x10^{-5} S/cm^{-1} UV irradiation method.

Lv et al. (2017) in their work fabricated PUA and succinonitrile (SN)- based plastic crystal electrolyte with addition of Tetrahydrofuran (THF) as compatibilizer by solution blending and UV curing method. The PE exhibit high ionic conductivity of 0.91 x10^{-3} S/cm^{-1} and improved mechanical strength after the THF addition. Lee et al. (2017) used in situ polymerization to make gel polymer electrolytes based on crosslinked PUA by having various ratios of DMPA–PEG and $LiClO_4$/PC. PC was integrated into an acrylateterminated urethane prepolymer, and the precursor mixture was subsequently combined with $LiClO_4$ and crosslinked (polymerization of terminal divinyl groups).

2.3 Salt for ionic dopant

Lithium salt and organic solvents are the components of the lithium-ion battery. Generally, $LiPF_6$ is the most frequently used salt for commercial Li-ion batteries. However, it has low thermal stability. At temperature above 55 ℃, it will decompose into lithium fluoride (LiF) and phosphorus pentafluoride (PF_5) and the LiF can produce highly toxic products through reaction with the solvent. Besides, LiF is also one of the solid electrolyte interphase (SEI) components (Strmcnik et al., 2018) that can reduce the battery's performance. Furthermore, $LIPF_6$ is extremely sensitive towards moisture and can generate hydrogen fluoride and phosphoryl fluoride (POF_3) through hydrolysis even with a small amount of water or alcohol (Mauger et al., 2018) which can cause the cathodes corrosions (Chen et al., 2019). The reaction $LiPF_6$ with water/humidity is shown in the following equation (Larsson et al., 2017):

(2.1) $LIPF_6 \rightarrow LiF + PF_5$

(2.2) $PF_5 + H_2O \rightarrow POF_3 + 2HF$

(2.3) $LIPF_6 + H_2O \rightarrow LiF + OF_3 + 2HF$

Compare to other lithium salts, $LiClO_4$ is a popular choice for the laboratory test purpose as it offer good solubility, high conductivity, less hygroscopic and relatively stable to ambient moisture (Xu, 2004). Furthermore, it will not form HF which could corrode the electrodes and the usage of $LiClO_4$ as salt can avoid the thermal runaway reaction faced by $LiPF_6$ (Kartha & Mallik, 2020). Figure 2.5 below shows the molecular structure of $LiClO_4$.

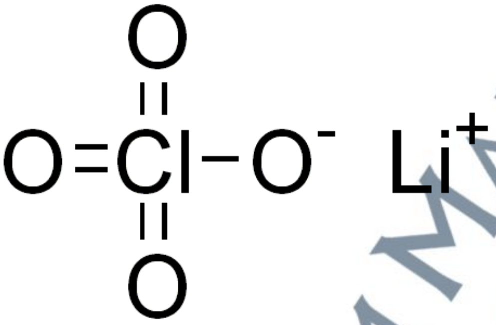


Figure 2.5: Molecular Structure of $LiClO_4$

2.4 3D structured battery

A 3D structured battery is a type of battery that has electrodes with a three-dimensional structure rather than the flat, two-dimensional structure of traditional batteries. The three-dimensional structure of the electrodes allows for a higher energy density, longer life, and improved safety compared to traditional batteries. 3D structured batteries are often used in applications where space is limited, such as in portable electronics or electric vehicles.

This 3D structured battery architecture concept was introduced by J. W. Long et al in 2004 in which this concept increasing the contact area of the battery component within the same footprint areas. This concept was introduced because high energy density and high-power density are hard to come along in a solid-state battery. A high-power density battery usually a tradeoff of lower energy density and vice versa (Lain et al., 2019). The low energy density in battery is usually solved with the electrodes but the energy density will go lower as the ion diffusion path becomes longer. Thus, this concept could optimize the battery performance in both energy density and power density.

There were several ways to construct 3D battery, the first way to achieve this is using an interdigitated structure, which consists of alternating cathode and anode electrode rods surrounded by a solid electrolyte. Another type of 3D battery is the concentric structure, which involves rods of one electrode (such as the anode) coated with an electrolyte, and the remaining volume filled with the other electrode (such as the cathode). A third type of 3D battery is called an aperiodic structure and has a sponge-like appearance, with one electrode coated in electrolyte and filled in with the other electrode. All of these 3D battery structures provide a different approach to creating a three-dimensional battery design.

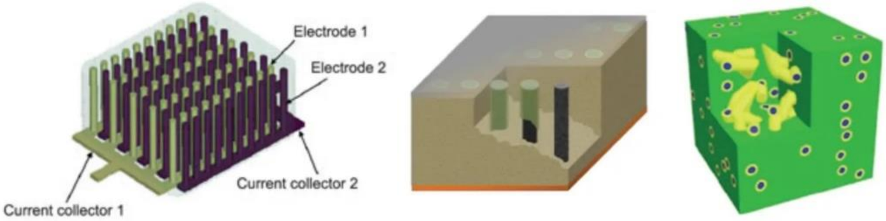


Figure 2.6: Example of 3D Batteries Designs

3D structured batteries offer several advantages over traditional batteries. They have a higher energy density, allowing them to store more energy in a smaller space, resulting in smaller and lighter batteries with the same energy capacity. Additionally, the three-dimensional electrode structure improves the distribution of active materials, reducing the risk of degradation and extending the battery's lifespan. These batteries also exhibit enhanced safety due to their improved stability, reducing the potential for fires and other hazards.

Furthermore, the 3D structure enables faster charging by facilitating more efficient energy transfer. Lastly, 3D structured batteries have higher power density, delivering more power in a shorter amount of time, making them well-suited for high-power applications such as electric vehicles. Overall, 3D structured batteries offer higher energy density, longer life, improved safety, faster charging, and better performance, making them a promising choice for various applications.

There were many ways have been explored to make 3D battery for example semiconductor processing method, photopatterning and porous structured solid state electrolyte for electrodes (He et al., 2020). However, all the methods mentioned are too costly or unable to process the specific 3D structures. One of the ways that extensive explored to create a 3D battery is via additive manufacturing.

2.4.1 3D Solid Electrolyte

One of the methods to fabricate 3D structured battery is using solid-state electrolyte. Kotobuki et al. (2010) in his work fabricated a honeycomb structure ceramic electrolyte as shown in Figure 2.7. Sol-gel method was used to make the electrode particle and infused it into the $Li_{0.35}La_{0.55}TiO_3$ (LLT) honeycomb electrolyte. Zhang et al. (2014) construct high conductivity honeycomb-structure PVDF-based GPE and highly stable toward heat up to $350^{o}C$. However, they did not fully use the 3D GPEs structure since they were still using conventional electrode.

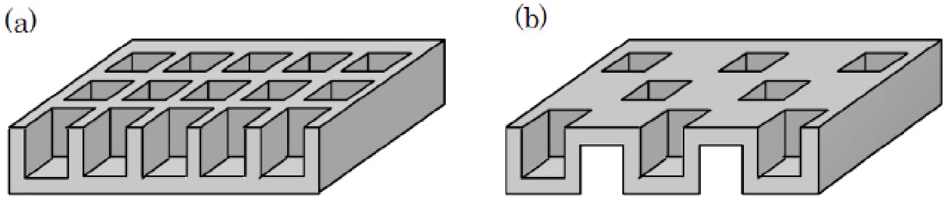


Figure 2.7: LLT Solid Electrolyte in Honeycomb Structure: A) Structure for Half-Cell; B) Structure for Full Cell

2.5 Additive Manufacturing (AM)

AM technology, also known as 3D printing, was first introduced in 1987 for rapid prototyping and building model purposes (Bahnini et al., 2018). The technology can cope with highly complex and detailed structure preparations that are difficult to achieve with conventional methods such as casting and machining simplifying the fabrication process (Gibson et al., 2015). Because of it, AM is being studied extensively especially in science and engineering society. As the precision, repeatability, and material range get better over the years, the application also becomes more versatile and applicable for various fields such as foods, medical, manufacturing, engineering, aerospace, defense etc.

Additive manufacturing or often known as 3D printing is a process that uses 3D modelling software and machine equipment that can read and layer CAD files into a 3D object to make a real 3D object by stacking physical materials one by one based on a digital model (Zhang et al., 2017). In contrast to subtractive manufacturing which develops its final product by cutting away from a block of material, additive manufacturing adds parts layer by layer by laser to form its final product, as seen in Figure 2.8. According to the American Society for Testing and materials, seven 3D printing technique categories are summarized in Table 2.1 (ISO/ASTM, 2013). Each type comes with different printing mechanisms but the same concept producing 3D objects layer by layer.

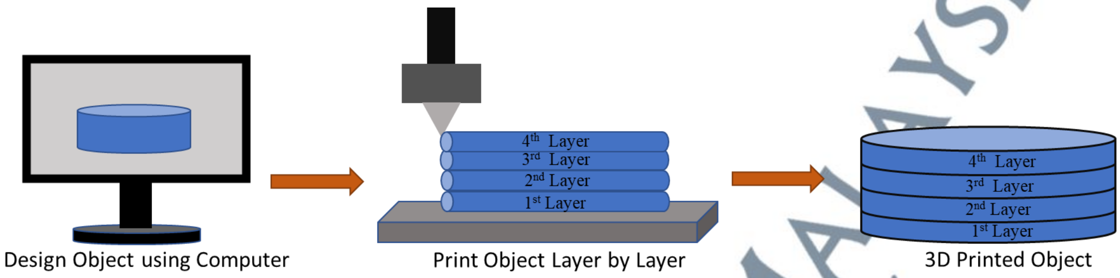


Figure 2.8: General Working Principle of 3D Printing

Table 2.1: ASTM Classification (ISO/ASTM, 2013;Calignano et al., 2017)

Category	Mechanism	Technology	Material
Binder Jetting	A liquid bonding agent is selectively deposited to join powder materials.	• Ink-Jetting	• Metal • Polymer • Ceramic
Directed Energy Deposition	The material is melted by focused thermal energy (e.g., laser or plasma arc) then deposit onto a substrate	• Direct Metal Deposition • Laser deposition • Laser consolidation	• Metal • Powder • Wire
Material Extrusion	Material is selectively dispensed through a nozzle or orifice.	• Fused Deposition Modelling (FDM) • Direct Ink Writing (DIW)	• Polymer

		• Liquid Deposition Modelling (LDM)	
Material Jetting	Build's material droplets are selectively deposited	• Polyject • Ink-Jetting • Thermojet	• Photopolymer • Wax
Powder Bed Fusion	Thermal energy selectively fuses regions of a powder bed.	• Selective laser sintering • Selective Laser Melting • Electron Beam melting	• Metal • Polymer • Ceramic
Sheet Lamination	Sheets of material are bonded to form an object.	• Ultrasound Consolidation4 • Laminated Object Manufacture	• Hybrids • Metallic • Ceramic
Vat Photopolymerization	Liquid photopolymer in a vat is selectively cured by light-activated polymerization	• Stereolithography (SLA) • Digital Light Processing (DLP)	• Photopolymer • Ceramic

Energy storage is one of the disciplines that has profited from AM in order to manufacture better and higher performance energy storage devices, particularly solid-state batteries, by incorporating AM into the production process. It is vital as the fabrication process is the bridge to put energy storage components such as electrodes and electrolytes into devices and contribute to the enhancement of the electrochemical performance of energy storage devices (Chang et al., 2019).

Furthermore, AM doubtlessly open the way for topological enhancement of solid-state battery in the attempt to decrease dead-volume and dead-weight of the battery. (Ragones et al., 2018). Besides, battery components such as electrodes, solid electrolytes, separator, and current collector can be modified into any desired design, allowing the battery and electronics assembly all at once, which could decrease the final device assembly and packaging step. Although it is still in research and development, it shows great potential for the advancement of energy storage devices.

2.5.1 Additive Manufacturing Electrolyte

In the past few years, abundant research has been done on PEs based on additive manufacturing technique. So far, three AM techniques have been used in PEs which are FDM, DIW, and SLA. Each of these methods specifics printing material requirements for example, viscosity and ink rheology for DIW, thermoplastic filaments for FDM, and photosensitive resins for SLA. So far, most of the studies focused on the LDM process in which ink is deposited from an extruder while moving across a platform (Lewis, 2006). The ink extruded is in a liquid state but maintains its shape instantly.

In Blake et al. (2017) studies, they combined PVDF in a dual solvent solution of N-methyl-2 pyrrolidone and glycerol to induce significant porosity within the polymer host due to phase separation during the drying step. Aluminum oxide (Al_2O_3) as nanofiller was added to the mixture to obtain sub-micrometer pore formation within the final membrane.

The membrane showed better performance in terms of wettability and thermal stability compared to commercial polyolefin separator. Finally, the electrolyte was printed over electrode using DIW method.

Cheng et al. (2018) printed a hybrid solid-state electrolyte consist of PVDF-HFP co-polymer matrix and TiO_2 nanofillers immersed in an ionic liquid electrolyte. The solid-state electrolyte was printed in a complex 3D Hilbert structure and showed high ionic conductivity (0.78 × 10^{-3} S cm^{-1}). McOwen et al. (2018) printed 3D pattern solid electrolyte microstructure that consists of texanol- $\mathrm{Li}_7\mathrm{L}a_3Zr_2O_{12}$(LLZO) and polyvinyl butyral-benzyl butyl phthalate-LLZO inks on both sides of a LLZ substrate. Then, the 3D pattern solid electrolyte structure was placed in a furnace for binder burnout and sintered. Finally, it is ready for complete battery assembly. Meanwhile, LDM is widely explored because of its substantial advantages of pulling off high mass loading within the electrodes, the main disadvantage of the LDM is it needs post-process such as freeze-drying and sintering before obtaining the final product.

Hence, FDM may offer a good alternative as it does not need a complicated post-process. Maurel et al. (2020) developed SPEs filament made from poly(ethylene oxide) incorporated with lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) and printed through a modified 3D printer. The printed SPE conductivity was 2.18 ×10^{-3} S cm^{-1} at 90 °C. Their study also showed different conductivity values for different EIS sample holders (sandwich, lateral and interdigitated comb) within the same sample. For the moment, this is the only study that utilizes FDM to fabricate SPE. It may be caused by the complicated process of producing printable filament to feed the FDM 3D printer.

Consequently, SLA seems the best choice among the AM technique to be used for electrolyte fabrication in the processing process compared to FDM and SLA as it does not possess the problems FDM and LDM have. Pan, (2018) used Micro-SLA to create a ziz-zag structure of poly (ethylene glycol) diacrylate (PEGDA) based GPE, which is then assembled into a micro-battery. The study showed impressive results with high ionic conductivity membrane at room temperature and the assembled micro-battery measured capacity was 1.4 μAh cm^2 for 2 cycles under potentiostatic charging condition.

Rahman et al. (2020) fabricated gel polymer electrolyte (GPE) with different polyvinylidene difluoride (PVDF) wt% with the best conductivity (3.7×10^{-4} S cm^{-1}) at room temperature for 5wt% PVDF. Besides, they also studied the effect changing several printer parameters (amount of UV light, scanning time and scanning velocity) on the mechanical properties. Their study showed the higher the PVDF content the higher the mechanical strength it lowers the conductivity of the GPE. He et al. (2020) utilized SLA to print SPE with a 3D-Archimedean spiral structure that demonstrated good conductivity and has proven to reduce interfacial resistance as well as having a greater specific capacity than the standard structure. The printed SPE exhibited a high ionic conductivity of 3.7×10^{-4} S cm^{-1} at 25°C.