CHAPTER 1

INTRODUCTION

1.1 Research Background

Along with the advancement of technology, the usage of battery has been deployed in a wide range of electrical devices especially for portable devices such as laptops, smartphones, vacuum, implantable medical, etc. Due to the high demand for battery applications, many studies have been started and conducted to improve the performance of the battery so it can cope with the power and energy needed from the electronic device. Generally, battery technology is a highly sought-after form of energy storage due to its high energy density, long lifespan, and portability.

The effectiveness of batteries relies on various factors, including the inherent characteristics of the electrodes and electrolyte, as well as the overall structure of the device. These elements play critical roles in determining the performance of batteries. The electrodes are typically made of materials with high energy storage capacity which facilitate the transfer of electrons during charging and discharging processes. On the other hand, the electrolyte acts as a medium for ion transport between the electrodes, enabling the flow of charge and sustaining the electrochemical reactions.

Additionally, the overall design and configuration of the battery device and parameters such as energy density, power output, and cycle life could affect the battery's performance. Therefore, a comprehensive understanding and optimization of the intrinsic properties of the electrodes and electrolytes coupled with the appropriate device architecture are essential for enhancing the performance of batteries.

Over the past few years, there has been a notable rise in the exploration and advancement of energy storage technology by researchers and industry professionals. Their primary objective has been to enhance the properties of materials used in batteries, aiming to achieve superior performance. However, comparatively less attention has been placed on the fabrication process which is responsible for transforming these materials into functional devices or products.

One of the reasons is because conventional approaches for the electrodes and solid-state electrolytes fabrication face limitations in accurately controlling the shape and structure of battery components. These traditional methods often involve complex manufacturing processes, such as sintering, coating, and assembly, which may result in variations in the final product. Achieving precise control over the morphology and architecture of battery components is crucial for optimizing their electrochemical performance and overall device functionality (Chang et al., 2019).

Furthermore, traditional 2D battery designs require a larger footprint to achieve higher capacity (Cai et al., 2018). With the increasing demand for smaller and more portable electronic devices, there is a strong need for energy storage devices that can provide higher capacity while maintaining a smaller footprint. This demand arises from the desire for longer battery life, improved performance, and enhanced functionality in a wide range of applications such as smartphones, wearables, and IoT devices.

3D structural electrolytes offer several advantages over conventional 2D electrolytes in terms of their available surface area and ion diffusion pathways (Pang et al., 2020). 3D structured electrolytes play a crucial role in the production of 3D batteries. The concept of 3D batteries involves integrating electrode, electrolyte, and current collector materials into a three-dimensional architecture, enabling higher energy density and improved performance compared to conventional planar batteries.

The concept of 3D batteries can significantly optimize space in electronic devices, making it easier for manufacturers to design and integrate batteries into various products such as smartphones, laptops, smartwatches, and other portable devices. Hence, additive manufacturing (AM) or 3D printing is indeed a promising technique for producing flexible structural designs including electrolytes in the field of energy storage.

Additive manufacturing, also known as 3D printing, is a highly flexible and efficient method of creating complex 3D structures. It enables the production of objects with intricate geometries and customized designs, utilizing materials that are of equal or better quality than those produced through traditional manufacturing methods (Calignano et al., 2017) thus offers numerous scopes in applied sectors. The various benefits offered by 3D printing have sparked interest among researchers to integrate this technology into energy storage fabrication, particularly in battery fabrication. The flexibility of 3D printing technology allows for the customization of battery form factors to fit specific product designs. This capability opens up new possibilities for integrating batteries as structural components, which can have a positive impact on energy and power density.

Stereolithography (SLA) is a one of 3D printing method that has potential to be integrated into energy storage fabrication. This method constructs a three-dimensional object by layering and solidifying each layer of photo-polymer resin through photopolymerization. Unlike Direct Ink Writing, SLA does not necessitate intricate material preparation for printable inks or complex post-treatment of printed objects, it is a more straightforward and efficient process, which can produce high-quality 3D printed objects with high resolution and precision.

When compared to other 3D printing techniques, SLA offers several advantages, including the ability to create true 3D structures with high efficiency, low cost, and high-resolution printing capabilities (Chang et al., 2019). Consequently, SLA has the potential to decrease interfacial impedance while simultaneously increasing the mass loading of active materials (He et al., 2020). This could enhance the performance and overall efficiency of the printed batteries. Despite the potential advantages, researchers have not focused much on utilizing SLA for printing electrolytes in energy storage applications. While SLA holds significant promise, it is not extensively adopted in the field and necessitates additional research and development to realize its full potential.

Basically, the process of creating 3D printed structures using SLA or other additive manufacturing methods comprises three key components: materials, a 3D printer, and computer-aided design (CAD). Any modifications made to these components can impact the characteristics or performance of the final 3D printed products. Presently, SLA is constrained to using photopolymers as materials, which solidify upon exposure to light. Among the widely utilized photopolymers is poly(urethane acrylate) or PUA. PUA has gained significant popularity as a photopolymer for the SLA process, and it has also been explored as a polymer matrix for creating polymer electrolytes in some research studies (M. L. Digar et al., 2002; Lee et al., 2017; Ren et al., 2003).

In addition to its suitability as a photopolymer, PUA also has several properties that make it a suitable material for fabricating polymer electrolytes. It has a high ionic conductivity, which is essential for efficient energy storage. PUA also exhibits excellent mechanical strength, which is important for the long-term stability and durability of the battery. The material also has the ability to be physically tuned, which means that its properties can be adjusted to suit the specific application (Kim et al., 2020). These characteristics of PUA make it an attractive option for use in energy storage devices, particularly in the fabrication of polymer electrolytes for batteries.

In this study, the SLA technique was employed to produce 3D printed gel polymer electrolytes by utilizing PUA as the polymer host. The PUA resin (commercially available) used in the research was blended with lithium perchlorate ($LiClO_4$) dissolved in dimethylformamide (DMF) to form the electrolyte solution, which was subsequently printed to create GPEs samples. The study focused on investigating the impact of different salt concentrations on the conductivity, dielectric properties, structural properties, and thermal stability of the 3D printed gel polymer electrolytes (GPEs). Various salt concentrations were examined to analyze their effects on these key properties.

1.2 Problem Statement

The field of rechargeable battery technology has witnessed remarkable progress; however, the advancement through fabrication of 3D polymer electrolytes remains a significant challenge. One of the challenges is the conventional methods for polymer electrolyte fabrication cannot fulfill the special requirement and customization in producing 3D electrolyte (Lyu et al., 2021)(F. Zhang et al., 2017). Addressing these challenges is essential for unlocking the full potential of 3D-structured polymer electrolytes which could enhance the overall efficiency and durability of batteries. Therefore, this research aims to pioneer a solution by employing 3D printing, specifically stereolithography to fabricate 3D polymer electrolytes with superior precision, mechanical stability, and enhanced precursor printability. By doing so, this study seeks to contribute to the advancement of battery technology, enabling the development of more efficient and reliable energy storage systems for diverse applications.

1.3 Objectives

1. To produce 3D printed film PUA based gel polymer electrolyte with different $LiClO_4$ concentration (0-25 wt.%).
2. To determine the effect of $LiClO_4$ concentrations on the ionic conductivity, electrical, and physical properties.
3. To develop 3D structures PUA based gel polymer electrolyte using the best formulation into three different structural designs.

1.4 Boundaries of Research

The work was focused on integrating SLA into GPEs fabrication and characterization of GPEs that fabricated by using SLA material. The 3D printed GPEs were characterized in terms of their ionic conductivity, dielectric properties, structural properties, and thermal behavior 3D printed GPEs. PUA photosensitive resin was deployed as polymer host, $LiClO_4$ as the ionic donor and dimethylformamide (DMF) as the solvent and plasticizer. The samples were prepared using the SLA technique. The characterization was done by using electrical impedance spectroscopy (EIS), transference number (TNM), the Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and scanning electron microscope (SEM), thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC). The characterization of 3D printed GPEs and 3D structure GPEs in terms of battery performance was not studied in this research.

1.5 Thesis Layout

Chapter 1 gives a brief introduction to gel polymer electrolytes (GPEs), 3D structures electrolyte and additive manufacturing. This chapter also states the problems with current electrolytes which open the space to utilize the new flexible solid electrolyte fabrication method, the objectives, research boundaries, and the research's layout.

In Chapter 2 gives the background study on polymer electrolytes, gel polymer electrolytes, additive manufacturing, and previous studies about electrolytes fabrication through additive manufacturing.

Chapter 3 explains the methodology of the research which is divided into four phases. The first phase was sample preparation, the second phase was sample characterization, followed by the third phase was results compilations and data analysis and final phase was printing 3D structure electrolyte. The sample was prepared via stereolithography technique and characterized by using Fourier transform infrared spectroscopy (FTIR), electrical impedance spectroscopy (EIS), transference number (TNM), X-ray diffraction (XRD) and scanning electron microscope (SEM), thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC).

Chapter 4 provides the discussion of the result and the analysis obtained from the sample characterization according to the research objectives.

Chapter 5 shows the conclusion for this study based on the objectives. Besides, the recommendations improvement for future work are also stated in this chapter.