CHAPTER 3

METHODOLOGY

The methodology of this work was divided into four phases; (1): Preparation of polyurethane (PUA) based gel polymer electrolytes (GPEs) film; (2): sample characterizations; (3): results compilation and data analysis and (4): Printability validation of the best GPEs formulation. The 3D printed electrolytes were characterized using electrochemical impedance spectroscopy (EIS), transference number measurement (TNM), Fourier transform infrared (FTIR), X-ray diffraction (XRD), scanning electron microscope (SEM), thermogravimetric analysis (TGA) and scanning calorimetry (DSC). The overall activities of the research can be seen in as shown in Figure 3.1.

3.1 Materials

The materials used in this research are summarized in Table 3.1

Table 3.1: List of Material with Corresponding Grade, Purity, and Brand

Materials	Grade/ Purity	Brand
PUA based Resin	-	Anycubic
Lithium Perchlorate ($LiClO_4$)	ACS reagent / 95.0%	Sigma Aldrich
Dimethylformamide (DMF)	ACS reagent / 99.8%	Sigma Aldrich
Anhydrous ethanol	ACS reagent	Sigma Aldrich

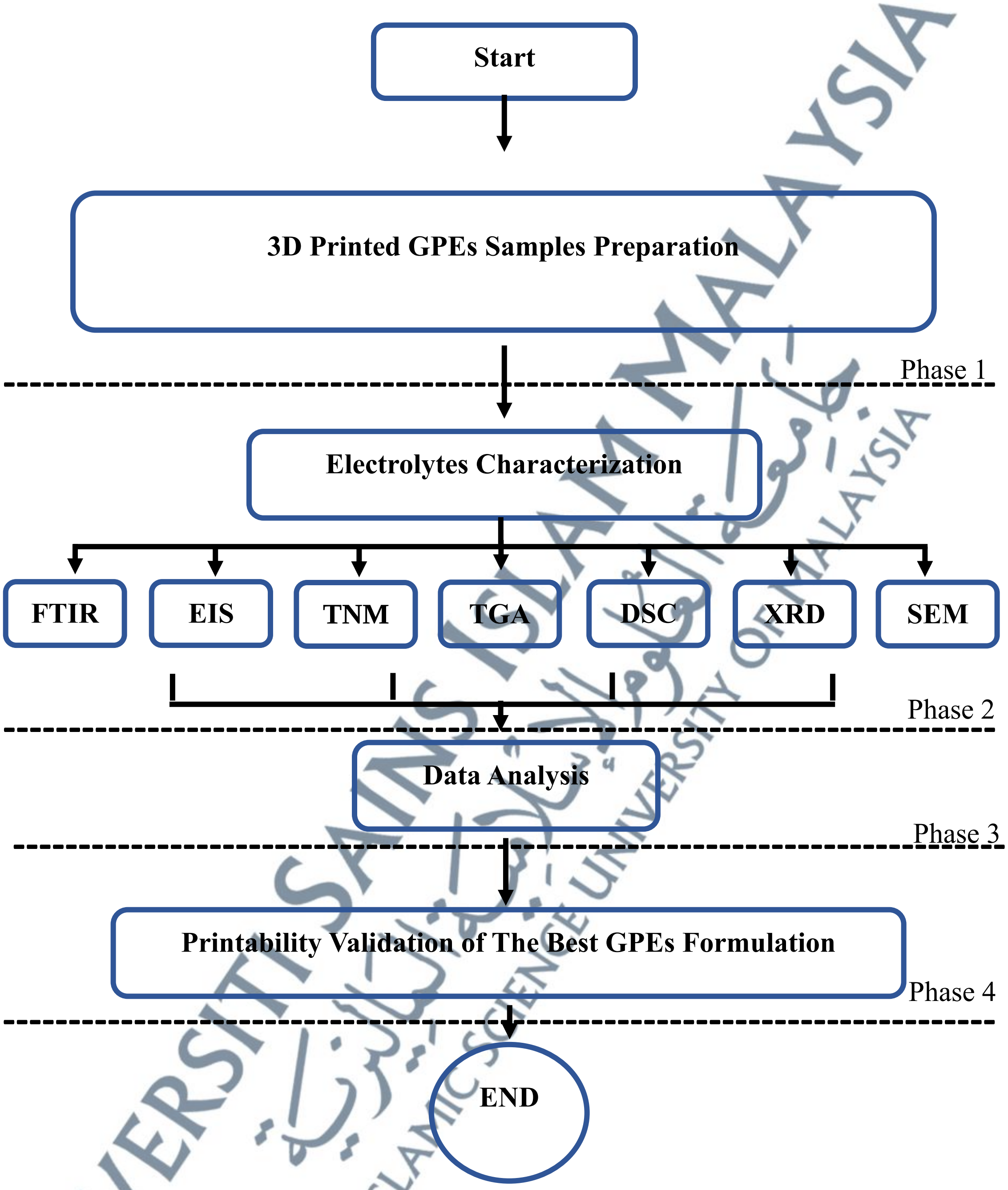

Figure 3.1: Flow Chart of Research Activities

3.2 Phase 1: Preparation of 3D Printed PUA Based Gel Polymer Electrolyte Films

At room temperature, lithium perchlorate ($LiClO_4$) was dissolved in 1.5 g of dimethylformamide (DMF) and stirred at 700 round per minute (rpm) at 60°C in amber vial for 30 minutes. The concentration of the $LiClO_4$ was varied by weight percentage as shown in Table 3.2 in the range of 0 to 25 wt.% based on the sample weight. Then, 2.0 g PUA based resin was added to the solution and stirred again at 400 rpm until homogenous mixture obtained. Then, the mixture was poured into the 3D SLA printer resin vat and ready to be printed.

Table 3.2: 3D Printed PUA GPEs Sample Compositions

$LiClO_4$ Concentration (wt.%)	Resin (g)	$LiClO_4$ (g)	Solvent(g)
0	1	0.00	0.75
5	1	0.09	0.75
10	1	0.19	0.75
15	1	0.31	0.75
20	1	0.44	0.75
25	1	0.58	0.75

Once the 3D SLA printer as shown in Figure 3.2 setting parameters have been set up according to Table 3.3. The mixture was printed into thin film and designated 3D structures. The uncured polymer electrolyte solution from the printed sample was rinsed using anhydrous ethanol. The prepared 3D printed GPEs were dried in a desiccator overnight to ensure proper drying before proceeding with further characterizations. An overview of the procedure for preparing the 3D printed GPEs is shown in Figure 3.3.

Figure 3.2: ANYCUBIC Photon S 3D Printer

Table 3.3: 3D Printer Setting Parameter

Parameter	
Layer (mm)	0.02
Exposure (s)	10
Off time (s)	4

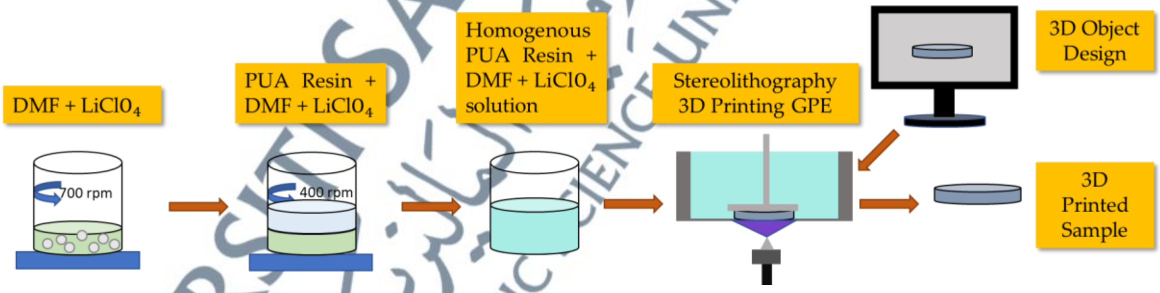

Figure 3.3: 3D Printed PUA GPEs Sample Preparation Flow

3.3 Phase 2: Characterization of 3D Printed PUA Based Gel Polymer Electrolytes

The 3D printed PUA GPE were characterized by EIS and TNM for electrical characterization, FTIR, XRD and SEM for physical characterization, TGA and DSC for thermal behavior of the PUA 3D printed GPEs.

3.3.1 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR was carried out by using Thermoscientific Nicolet iS 50. The samples were examined using Attenuated Total Reflectance (ATR). The sample was placed on the top of the FTIR accessory with a germanium crystal allowed infrared pass through the GPEs. FTIR was recorded with the wavelength range from 4000 to 500 cm^{-1} and resolution of 4 cm^{-1} at room temperature. The FTIR was used to determine the effect of lithium salts toward the functional group of the PUA polymer matrix. Besides, FTIR also used to study the lithium-ion dissociation properties within the PUA 3D printed GPEs by using deconvolution method on selected FTIR peaks. The deconvoluted peak was in the range of 600-650 cm^{-1} because of the ClO_4^- presents within the range. The analysis of FTIR deconvolution was conducted using Origin software. The area under the graph corresponding to the free ion and ion pair peaks was calculated using the following equations:

(3.1) $$f_{ions}(\%) = \frac{A_f}{A_f+A_P} = 100\%$$

(3.2) $$P_{ions}(\%) = \frac{A_p}{A_f+A_P} = 100\%$$

3.3.2 Electrical Impedance Spectroscopy (EIS)

The ionic conductivity (σ) of 3DP PUA based GPEs was determined by using HIOKI 3532-50 HiTester from 50 Hz to 5 MHz. In this research, the test sample was printed into 1.89 cm diameter and 0.5 mm thickness film. The sample then sandwiched between two stainless steel (SS) electrodes under spring pressure as shown in Figure 3.4. The data obtained from the test was used to determine the conductivity of the sample by sketching the Cole-Cole plot to determine the bulk resistance,R_b, of the sample. The conductivity of the electrolyte was calculated using the equation below:

(3.3) $$\sigma = \frac{t}{R_b A}$$

Where it is the thickness of the sample, R_b is the bulk resistance and A is the area of the sample. The thickness of the sample was measured by using a digital micrometer gauge to get accurate thickness.

Figure 3.4: Schematic Cross-section of SS/3D Printed GPEs Film/SS During EIS Characterization

3.3.3 Dielectric Studies

The number density (n), mobility (μ) and diffusion coefficient (D) were determined using equations 3.4, 3.5 and 3.6 accordingly.

(3.4) $$n = \left(\frac{m_{LiClO_4}}{M_W} \text{ x } N_A\right)\frac{1}{V_T} \text{ x } \% f_{ions} \text{ x } 2$$

(3.5) $$\mu = \frac{\sigma}{ne}$$

(3.6) $$D = \frac{\mu K_b T}{e}$$

Where m_{LiClO_4}= mass of $LiClO_4$, M_W= molecular weight, V_T=total volume, e= electron charges, K_b= Boltzmann constant, and T= temperature (Kelvin). Besides, the dielectric constant (ε_r), dielectric loss (ε_i), real electrical modulus (M_r), imaginary electrical modulus (M_i) and tan σ were calculated using these following equations:

(3.7) $$\varepsilon_r = \frac{Z_r}{\omega C_o(Z_r^2+Z_i^2)}$$

(3.8) $$\varepsilon_i = \frac{Z_i}{\omega C_o(Z_r^2+Z_i^2)}$$

(3.9) $$M_r = \frac{\varepsilon_r}{\varepsilon_r^2+\varepsilon_i^2}$$

(3.10) $$M_i = \frac{\varepsilon_i}{\varepsilon_r^2+\varepsilon_i^2}$$

(3.11) $$\tan\sigma = \frac{Z_r}{Z_i}$$

3.3.4 Transference Number Measurement (TNM)

The TNM of the sample was determined using the DC polarization technique. A constant DC potential of 1.5V was applied across the SS/electrolyte/SS cell, and the DC current was measured as a function of time. The data was recorded using a UT803 multimeter connected to the UT803 interface software on a computer. The electronic and ionic transference numbers were calculated using the following equations:

(3.12) $$t_e = \sigma_e/\sigma_t = i_e/i_t$$

(3.13) $$t_i = 1- i_e/ i_t = 1- t_e$$

where t_e and t_i are the electronic and ionic transference numbers, respectively. i_e and i_t are the electronic and total currents, respectively, while σ_e and σ_t refer to the electronic and total conductivities, respectively.

These calculations allowed for the determination of the electronic and ionic contributions to the total current in the SS/electrolyte/SS cell. Figure 3.5 below illustrates the setup of the TNM experiment, with the stainless steel (SS) electrode serving as an ion-blocking electrode.

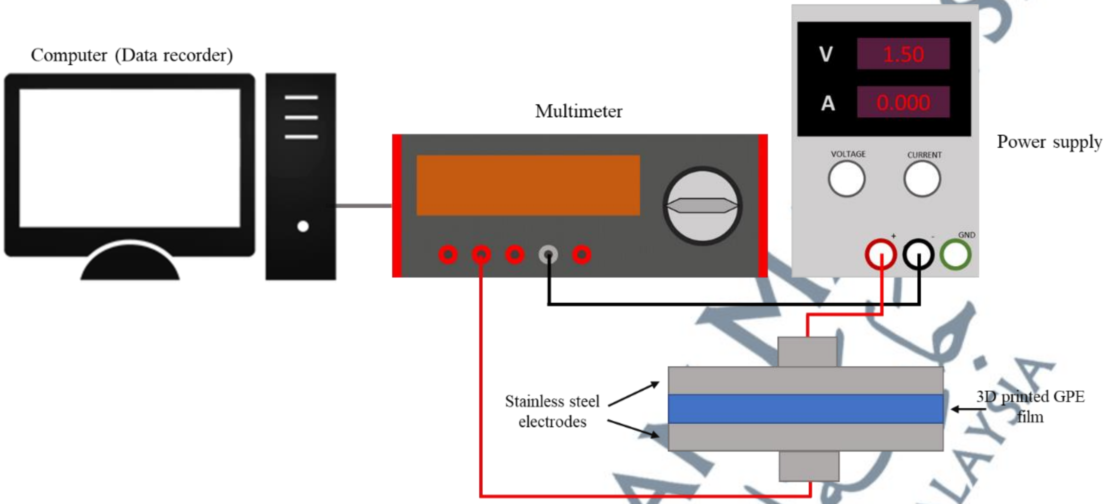

Figure 3.5: Schematic TNM Setup

3.3.5 Thermogravimetric Analysis (TGA)

TGA was conducted on a TA Instruments-TGA 550 and carried out through a dynamic nitrogen atmosphere with a flow rate of 20 mL/min. The temperature range for the analysis was from 50 °C to 600 °C, with a heating rate of 10 °C/min. The raw TGA data obtained from the experiment was analyzed using TRIOS software.

3.3.6 Differential Scanning Calorimetry (DSC)

DSC was conducted using TA instruments-DSC 250. The study was conducted between -20°C to 150 °C, at 10 °C/ min scanning rate under nitrogen atmosphere at 10 mL/min flow rate. The changes of DSC curves towards the $LiClO_4$ addition and the glass transition (T_g) and melting point temperature (T_m) of the GPEs were observed. The T_g was determined as the midpoint temperature of the heat capacity changes and T_m was the onset temperature of endothermic peak. The raw data from the DSC was analyzed using TRIOS software from TA instruments to get the T_g and T_m value.

3.3.7 X-ray Powder Diffraction (XRD)

XRD was conducted using. Rigaku Mini Flex 600 diffractometer with scanning angle 2θ in range of 10° to 60° at 0.004°/S and X-ray radiation wavelength of 1.5406 Å. in ambient temperature condition. The formation or changes of peak or hump from the XRD results and the full width at half maximum (FWHM) of the XRD hump from the data obtained were determined using Origin software. The data was used to study the effect of $LiClO_4$ towards the sample amorphous fraction.

3.3.8 Scanning Electron Microscopy (SEM)

SEM was conducted using JEOL JSM-7600F at 100000 times magnification. The changes on the samples surface with addition of $LiClO_4$ into 3D printed GPEs sample surface was observed.

3.4 Phase 3: Printability Validation of The Best GPEs Formulation

Based on EIS results, the best sample formulation that resulted the best ionic conductivity was chosen to be printed in different structure design by using SLA technique to validate its printability towards complex structures. The PUA based GPEs was printed into honeycomb pattern, interdigitated and scaffold structure as shown in Figure 3.6, Figure 3.7, and Figure 3.8 accordingly. The printing parameters were set the same as 3D printed film sample preparation that can be refer at Table 3.3.

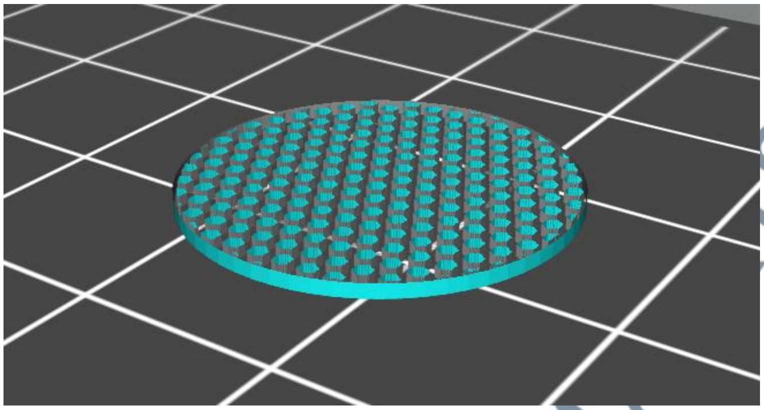

Figure 3.6: Honeycomb Pattern

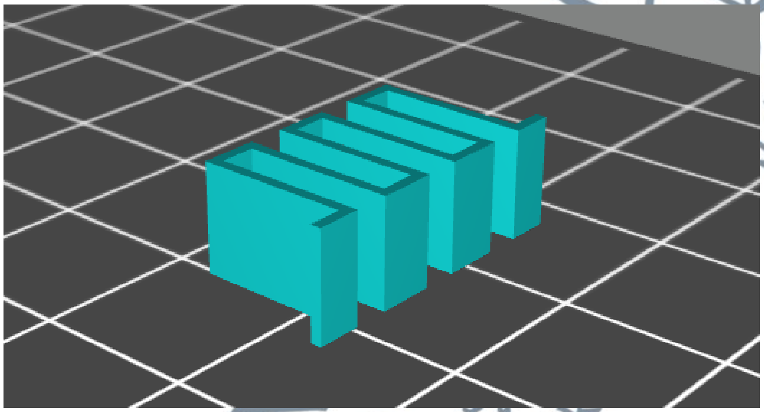

Figure 3.7: Interdigitated Structure

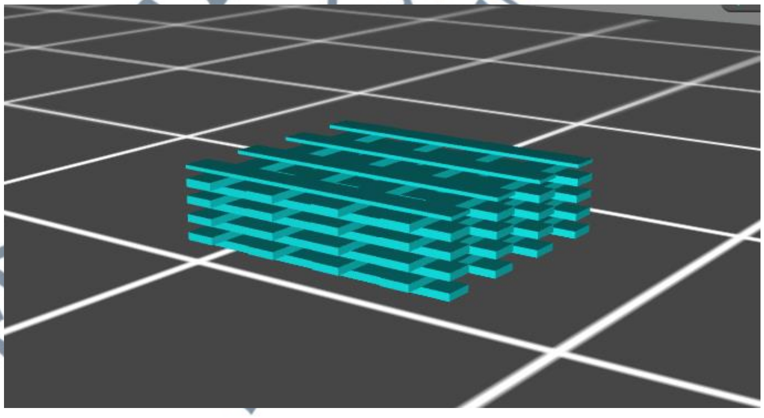

Figure 3.8: Scaffold Structure