INVESTIGATION ON THE PERFORMANCE OF TETRAGLYME-BASED SOLID COPOLYMER ELECTROLYTES FOR SOLID-STATE ELECTRICAL DOUBLE LAYER CAPACITORS (EDLCs)

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FACULTY OF SCIENCE
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Name of Candidate: SHARMILAH SINASAMY

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Field of Study: Material Science

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INVESTIGATION ON THE PERFORMANCE OF TETRAGLYME-BASED SOLID COPOLYMER ELECTROLYTES FOR SOLID-STATE ELECTRICAL DOUBLE LAYER CAPACITORS (EDLCs)

ABSTRACT

Solid polymer electrolytes (SPEs) have been the focus of intensive research due to their large demand in applications such as electrochemical capacitors, fuel cells, solar cells and batteries. They have shown many advantages such as wider electrochemical potential window, good thermal stability, low volatility and easy handling. Due to these advantages, SPEs have great potential in energy storage applications. Usually, SPEs suffer from poor conductivity, which hinders its performance for energy storage applications. In order to enhance the conductivity of the SPEs, the host polymer incorporated with salt to provide ions for conductivity, ionic liquid to enhance the conductivity and fillers to increase the thermal and electrical stability. Herein, Poly (vinylidene fluoride-hexafluropropene) PVDF-HFP used as a host polymer with $LiCIO_4$ salt to provide ions and tetraglyme as an additive. SPEs prepared by facile solution casting technique and its performances were evaluated for electric double layer supercapacitor (EDLC). The effects of tetraglyme (Diethylene glycol dimethyl ether) on the enhancement of ionic conductivity and on the performance of EDLC was investigated. Conductivity studies revealed that, tetraglyme significantly improvised the ionic conductivity of the SPEs by assisting ion mobility in the host polymer and has shown high ionic conductivity at room temperature. The highest ionic conductivity value of 1.34 x 10^{-3} Scm^{-1} is achieved upon addition of 20 wt. % tetraglyme (STG20). Temperature-dependant ionic conductivity studies confirmed that SPE system follows Arrhenius thermal activation model. The crystallinity and complexation of the SPEs were characterized using X-ray diffraction (XRD) and Fourier transform infrared (FTIR) spectroscopy, respectively. XRD results confirmed the complexation of $LiCIO_4$ salts with the host polymer. FTIR spectra presented that tetraglyme and $LiCIO_4$ salt successfully incorporated with the host polymer. The electrochemical performance of prepared SPEs evaluated by cyclic voltammetry, galvanostatic charge discharge and electrochemical impedance spectroscopy. It was found that SPE incorporated with tetraglyme displayed excellent performance for EDLC compared to the SPE without tetraglyme. From the electrochemical studies, STG 20 achieved the maximum specific capacitance of 14.06 F/g, which is larger than STG 30 (sample with 30 wt. % tetraglyme) (4.87 F/g) and ST30 (0.11 F/g) at 100 mA/g.

Keywords: Solid polymer electrolytes, tetraglyme, supercapacitors, ionic conductivity

PENYELIDIKAN PRESTASI ELEKTROLIT PEPEJAL BERASASKAN TETRAGLYME UNTUK SUPERKAPASITOR LAPISAN DUA GANDA (EDLC)

ABSTRAK

Penyelidikan berasakan Elektrolit polimer pepejal (SPE) telah menjadi tumpuan intensif berikutan permintaan yang tinggi dalam aplikasi seperti kapasitor elektrokimia, sel bahan bakar, sel suria dan bateri. Ia telah menunjukkan banyak kelebihan seperti potensi elektrokimia yang lebih luas, kestabilan tenaga terma yang baik, volatiliti yang rendah dan pengendalian yang mudah. Oleh kerana kelebihan ini, SPE mempunyai potensi besar dalam aplikasi penyimpanan tenaga. Biasanya, SPE mengalami kekonduksian yang lemah yang menghalang pencapaiannya untuk aplikasi storan tenaga. Untuk meningkatkan kekonduksian SPE, polimer digabungkan dengan garam untuk menyediakan ion untuk kekonduksian, cecair ionik untuk meningkatkan kekonduksian dan pengisi untuk meningkatkan kestabilan terma dan elektrik. Dalam penyelidikan ini, Poli (vinilidena fluorida-hexafluropropene) PVDF-HFP digunakan sebagai polimer bersama dengan garam $LiCIO_4$ untuk menyalurkan ion dan tetraglyme sebagai bahan tambahan(aditif) kekonduksian. SPE telah disediakan melalui teknik solution casting dan prestasinya dinilai dalam superkapasitor lapisan ganda elektrik (EDLC). Keberkesanan tetraglyme (Diethylene glycol dimethyl ether) terhadap penambahan kekonduksian ionik dan prestasi EDLC dikaji. Kajian konduktiviti menunjukkan bahawa, Tetraglyme secara signifikan telah mengubah keadaan kekonduksian ion SPEs dengan membantu pergerakan ion dalam polimer dan telah menunjukkan kekonduksian ionik yang tinggi pada suhu bilik. Nilai kekonduksian ionik tertinggi 1.34 x 10^{-3} Scm^{-1} dicapai selepas penambahan 20 wt. % Tetraglyme (STG20). Kajian konduktiviti ionik yang bergantung kepada suhu mengesahkan bahawa sistem SPE mengikuti model pengaktifan haba Arrhenius. Kajian kristal dan komposisi SPE dibuat dengan menggunakan X-ray difraksi (XRD) dan Fourier transform spektroskopi inframerah (FTIR). Keputusan XRD mengesahkan penguraian garam $LiClO_4$ dengan polimer hos. Spektrum FTIR membuktikan bahawa tetraglyme dan garam $LiClO_4$ berjaya digabungkan dengan polimer hos. Prestasi elektrokimia SPE dinilai melalui kajian voltametry siklik, Cas discas galvanostatik dan spektroskopi impedans elektrokimia. Berikutan ini, telah disimpulkan bahawa SPE yang digabungkan dengan tetraglyme menunjukkan prestasi lebih baik dalam aplikasi EDLC berbanding dengan SPE tanpa tetraglyme. Merujuk kepada penyelidikan elektokimia, sampel STG 20 telah mencapai kapasitansi specifik maximum sebanyak 14.06 F/g, iaitu, melebihi kapasitansi specifik maximum STG 30 (penambahan 20 wt. % Tetraglyme) (4.87 F/g) dan ST30 (0.11 F/g) pada 100 mA/g.

Kata kunci: Elektrolit polimer pepejal, tetraglyme, superkapasitor, kekonduksian

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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF SYMBOLS AND ABBREVIATIONS

PEMA	:	Poly (ethyl methacrylate)
PMMA	:	Poly (methyl methacrylate)
PEO	:	Poly (oxyethylene)
PVAc	:	Poly (vinyl acetate)
PVA	:	Poly (vinyl alcohol)
PVC	:	Poly (vinyl chloride)
PVP	:	Polyvinylpyrrolidone
PSA	:	Poly (styrene sulphonic acid)
TPU	:	Thermoplastic polyurethane
macPSSNa	:	Macromonomer Poly (sodium styrenesulfonate)

CHAPTER 1: INTRODUCTION

1.1 Research background

Solid polymer electrolytes (SPEs) are emerging as versatile materials to replace liquid electrolytes due to their many advantageous properties. Solid polymer electrolytes possess properties such as low vapour pressure, high thermal and electrochemical stability, wider electrochemical potential window, easy handling and low flammability which are among attractive features when developing safe electrolytes. SPEs are in demand for the applications not only in lithium ion batteries but also other electrochemical storage devices like supercapacitors, fuel cells and solar cells. These advantages of SPEs have great potential in energy storage applications to substitute liquid electrolyte. Liquid electrolytes have shown many disadvantageous such as the release of harmful gases that causes the decomposition of a protective layer at the carbon electrode layer, the growth of lithium dendrite which has causes poor long-term stability due to the evaporation of the liquid electrolyte and they are also temperature sensitive. Studies have also shown that liquid electrolytes freeze at low temperature and expand at high temperature. Liquid electrolytes also have high volatility which causes evaporation and degradation of platinum counter electrodes (Tan, Farhana, Saidi, Ramesh, & Ramesh, 2018). There are also other safety measures need to be solved in liquid electrolyte as some solvents in liquid electrolytes are organic solvents which are flammable and this can cause faulty in the electrochemical appliances used such as internal short circuit and blasting of device (Ramesh & Wong, 2009). In conjunction with this, replacing liquid electrolyte with solid polymer electrolyte has definitely a promising strategies to eliminate safety concerns encountered with liquid electrolytes due to their intrinsic solid character.

Solid polymer electrolytes are an active area of study in material science research. Solid polymer electrolytes are solvent-free electrolytes based on polymer. Solid electrolytes are prepared by complexing polymers with alkali metal salts to allow the movement of ions in the absence of liquid or soft membrane separating the electrodes. Lightweight and flexible characteristics of SPE encourage incorporation of SPE in many solid-state electrochemical devices (Aziz & Abidin, 2013). Wide range of polymers have been extensively studied in recent years showed improved conduction mechanism. SPE has a basic preparation method using polymer of choice with inorganic alkali metal ions dissolved. SPEs suffer from poor conductivity, which hinders their performance for energy storage applications. In order to enhance the conductivity of the SPEs, the host polymer was incorporated with salt to provide ions for conductivity, ionic liquid to enhance the conductivity and fillers to increase the thermal and electrical stability. Several other studies have come forward to improve the understanding of the motion of ions in a polymer host and how the addition of new substances can be introduced to enhance the conductivity.

EDLC, electric double layer capacitor is a significant choice as an electrochemical device. EDLCs appears as new type of electrochemical devices to supplant lithium ion batteries and other conventional electrolytic capacitors. EDLC is an electrochemical energy storage device that able to provide high power density and fast charge-discharge cycle. EDLC stores energy fast, reversible in a simple formation of double layer electrode interface. Therefore, EDLC is a preferred electrochemical energy storage device when high power density and fast charge-discharge cycles are required. EDLC also has capability in rapid energy storage as well as reversible by a simple formation of the double layer in electrode/electrolyte interface. Conventional supercapacitor mostly uses carbon as electrodes in combination with liquid electrolytes which consist of aqueous, organic or ionic liquids. EDLC incorporated with liquid electrolytes requires separators to prevent the contact between electrodes and strong encapsulation is required to avoid leakage of electrolyte. These makes the EDLC inevitable and unsuitable to be applied in textiles, microelectronics and lightweight energy storage systems. (Palma, Anderson, Tiruye, Mu,

& Marcilla, 2016). Therefore, replacement of SPE in EDLCs is the main effort to improve the above drawbacks mainly to avoid strict sealing and housing for the supercapacitors. In addition to this, SPEs are also inert toward metallic Li and also act as a separator, helping resist to dendrite growth.

However, the concern in using SPE as electrolyte is their low electrochemical stability window which limits the operating voltage. The attainable cell voltage depends mainly on the electrolyte breakdown voltage. Hence, choice of suitable electrolyte plays a dominant role in enhancing the efficiency of the supercapacitor. Various polymer matrixes such as poly(methyl methacrylate) (PMMA), polyacrylonitrile (PAN), poly(vinyl chloride) (PVC), poly(vinyl pyyrolidone)(PVP), poly(ethylene oxide) (PEO) and poly(vinylidene fluoride)(PVDF) or poly(vinylidene fluoride-co-hexafluropropylene)(PVDF-HFP) have been reported in the literature. Keeping this in mind the prime aim of the this is study is investigate the role of tetraglyme addition into polymer poly(vinylidene fluoride-hexafluoropropylene)(PVDF-HFP) matrix to enhance the ionic conductivity and produce good performance in EDLC .

1.2 Scope of Research

The motivation behind this research work is to investigate on the performance of tetraglyme, on solid polymer electrolytes (SPE), made of PVDF- HFP and $LiCIO_4$ salt. Tetraglyme is an additive that has the ability to enhance the electrical performances of the polymer electrolytes. The performances of SPEs were evaluated for electric double layer supercapacitor (EDLC).

1.3 Objective of Research

1. To prepare and optimise SPEs based on PVDF/HFP polymer and $LiClO_4$ salt by enhancing the ionic conductivity of SPEs by incorporation of tetraglyme into the optimized SPE system.

2. To evaluate and analyse the molecular and structural component of the SPEs using X-ray diffraction (XRD) and Fourier-transform infrared (FTIR) studies.
3. To investigate the electrochemical performance of fabricated EDLC using SPEs

1.4 Outline of thesis

Chapter 1 begins with the introduction of solid polymer electrolyte and Electrical double layer Capacitor. Then, the motivation and research objectives were discussed.

Chapter 2 provides the literature review on polymer electrolytes and Ionic conduction mechanism and EDLCs. The latter part discusses the reasons for choosing the materials and the applications of the polymer in electrochemical device.

Chapter 3 presents the methodology of the sample preparation, sample characterization including Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), dielectric studies, cyclic voltammetry and electrochemical device fabrication.

Chapter 4 discusses the results obtained from all the characterizations, compares and explains the results obtained from the system.

Chapter 5 is the conclusion of this research and the future study.

CHAPTER 2: LITERATURE REVIEW

This chapter explains the literature on polymer electrolytes. The review begins from the discussion of different types of polymer electrolytes to parameters governing the ionic conduction in the polymer electrolytes and reviews the methods to enhance the ionic conductivity of polymer electrolytes. This chapter also discusses the significance of choosing PVDF-HPF polymer and tetraglyme in this research. The last section explains the applications of the SPE in the electrochemical devices and the advantages of EDLCs compared other electrochemical devices.

2.1 Types of polymer electrolytes

Polymer electrolyte is known as an ion conducting membrane and as a separator with range of ionic conductivity at ambient temperature. The four types polymer electrolytes are the Solid Polymer Electrolytes (SPEs), Gel Polymer Electrolytes (GPEs), Composite Polymer Electrolytes (CPEs) and Liquid Crystals Polymer Electrolytes (LCPEs).

2.1.1 Solid Polymer Electrolytes

SPEs have been introduced to replace the liquid electrolytes. SPEs have captured interest among the researchers over last three to four decades due to the intrinsic phenomenon of a solid material exhibiting liquid-like conductivity without motion of the solvent. Polymer electrolyte captures interest among researchers as it can be easily manufactured into shapes, which is impossible with liquid electrolytes and it provides more fascinating features compared to liquid electrolytes. The advantages of solid electrolytes include easy preparation techniques, dimensionality, flexibility, good electrochemical stability, safety, and durability. SPEs are proven to perform with a wide range of advantages compared to the conventional liquid electrolytes. SPEs, which is made of solvent free electrolyte, possess more safety features as it eliminates corrosive solvent and harmful gas formation. SPEs have high elastic relaxation properties under stress, have low volatility and easy handling (Ramesh, Liew, & Arof, 2011). SPE reduces dendritic growth rate on lithium electrode without affecting the high capacity of the lithium metal (Farah et al., 2019).

SPE is formed by using the concept of dissolving inorganic salts in functional (polar) polymer. Thus, interactions of metal ions with polar groups of polymer occurs due to electrostatic forces and formation of coordinating bonds are formed. There are several factors that affects the interactions of metal ions and polar group of the polymer such as, the nature of functional groups attached to the polymer backbone, compositions and distance between functional groups, molecular weight, degree of branching, nature and charge of metal cation and counter ions. The cations from the inorganic salts are able to move from one coordinated site to another site in an electrical field (Aziz, Woo, Kadir, & Ahmed, 2018).

SPEs were first introduced by Wright and his group in 1975. He invented SPEs by introducing crystalline poly (ethylene oxide) (PEO)-based polymer electrolytes. Their study explained the effect of ammonium, sodium and potassium salts which incorporated in PEO. The PEO showed good solvating properties, however, the ionic conductivity was relativity low (~ 10^{-8} to 10^{-7} Scm^{-1}). This was mainly due to the high crystallinity in the polymer and high recrystallize (Wright, 1975).

The first generation of polymer electrolytes was also initiated by Armand et al. in 1978 who investigated on high molecular weight poly (ethylene oxide) and lithium salts. The second generation were based on modified PEO and new polymer based electrolytes. The third generation focused on room temperature dependence and dimensional stability of the polymer electrolyte. In order to increase the ambient temperature conductivity, many other polymers were attempted, such as the PVC, PAN, PMMA, PVDF etc (Ulaganathan & Rajendran, 2010) .

Further studies have been carried out to improve the conductivity in the polymer electrolytes; this includes the polymer modifications, polymer blending, and the addition of ionic liquid, additives, plasticizers and inorganic fillers.

Apart from the advantages, there are also many technical problems to be solved in SPEs. Low electrical conductivity is one of the particular problem to be solved. Low ionic conductivity eventually delays the electrochemical devices. The viscosity of a polymer electrolytes is relatively higher than that of liquid electrolyte which effects the charge mobility of lithium ions. Therefore, the commercialization is limited and more focussed in considering enhancement of ionic conductivity is being studied (Das & Ghosh, 2017).

2.2 Ion Conduction Mechanism

2.2.1 Illustration of Ion Conduction Mechanism

The presence of electric field causes the mobile charge carrier undergoes diffusion from one place to another place. The movement of ions will obey Brownian motion principle in the absence of electric field. Hence, the charge carriers will move along the direction of electric field from positive to negative terminals. This phenomena takes place when a voltage is applied across the electrolyte. In the presence of an electrical field, the ion conduction will experience a resistance such as the potential barrier in the lattice sites of crystalline phase of the polymer. The movement of ions consists of ion conduction, ion migration, ion hopping or ion diffusion. However, the ions need to overcome the potential barrier to move to adjacent lattice sites. There are two ion mechanisms that explains the ion diffusion in solid polymer electrolytes, which are vacancy mechanism, and interstitial mechanism.

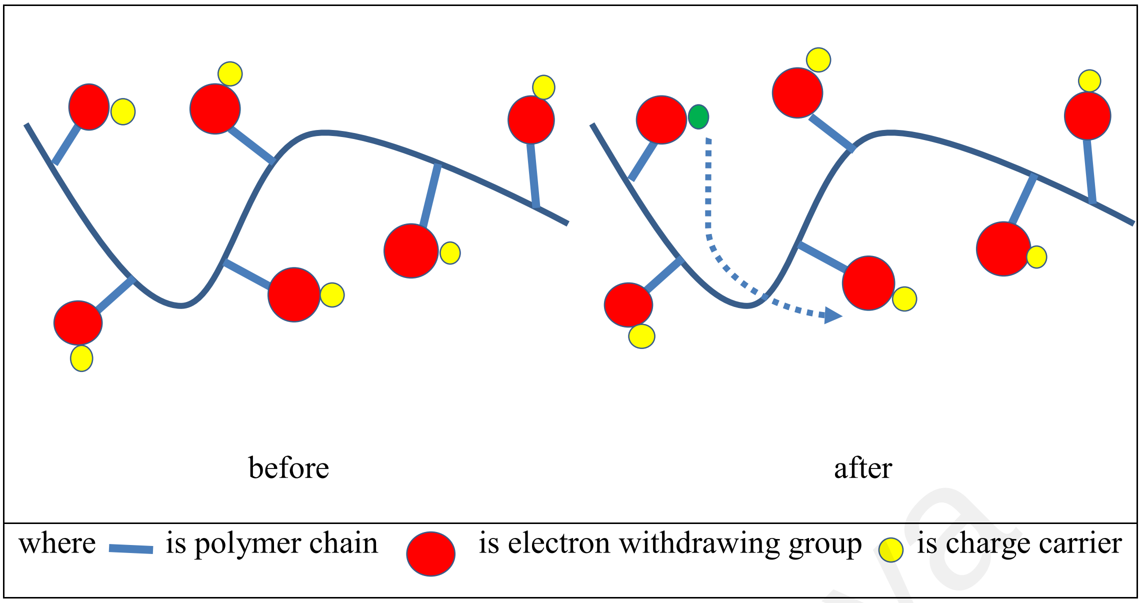


Figure 2.1: Schematic illustration of ion diffusion before and after a vacancy mechanism (Souquet, Nascimento, & Rodrigues, 2010).

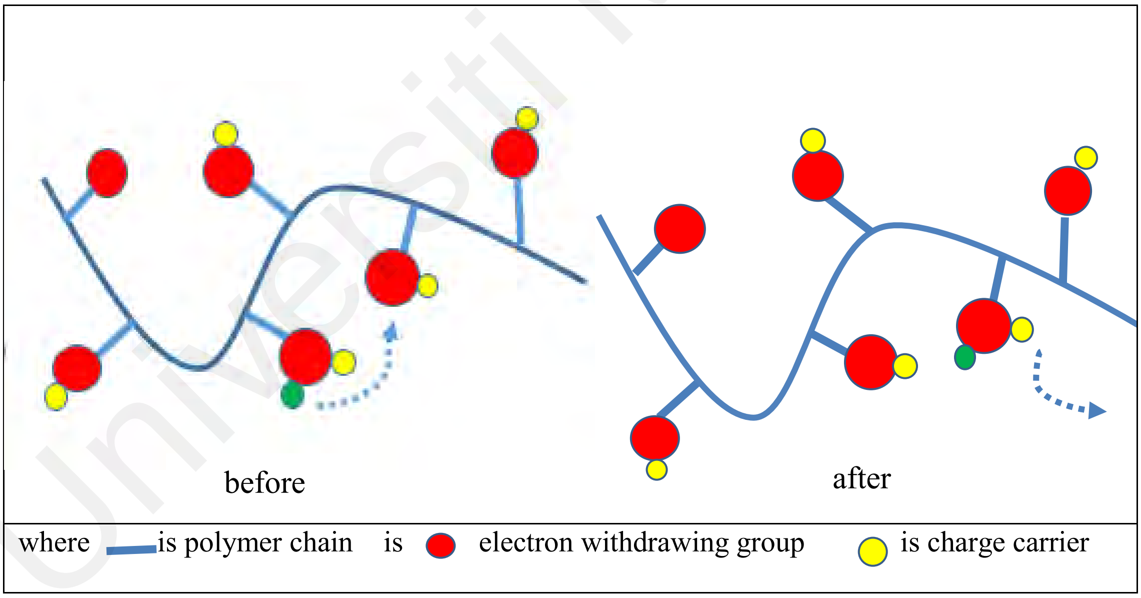


Figure 2.2: Schematic illustration of ion diffusion before and after an interstitial mechanism (Souquet et al., 2010).

The vacancy mechanism involves the hopping of an ion from its original position to an empty adjacent site. The shifting of the ions requires sufficient thermal energy to overcome the coordination bonds and hop from one site to the adjacent empty site.

The interstitial mechanism happens when a mobile charge carrier migrates from one interstitial position to the next position. Interstitial diffusion occurs faster than the vacancy diffusion due to the weak bonding of the interstitials with surrounding ions and more available empty adjacent interstitials site for ion hopping.

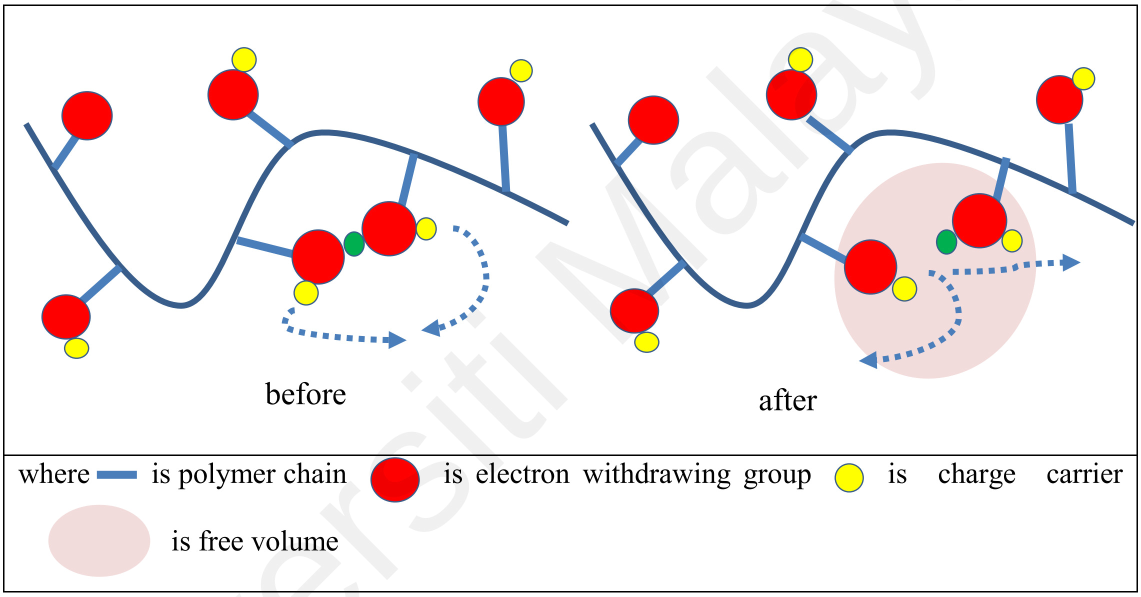


Figure 2.3: Schematic illustration of ion diffusion before and after a free volume mechanism coupled with the chain movement (Souquet et al., 2010).

Another possible interesting ion migration which is the cooperative mechanism where the ions migrate from one site to the nearest neighbour's site. This mechanism called free volume mechanism. This phenomenon occurs when there is a chain movement of polymer, which produces the free volume in the polymer matrix. The random density fluctuation occurs and produces an adjoining cage to allow the ion transport to take place (Souquet et al., 2010).

2.2.2 Basic factors to Generate the Ionic Conductivity

The Ion conduction mechanism in the polymer electrolytes consists of following five basic requirements:

(a) The quantity of mobile ions for migration

(b) The availability of vacant sites

(c) The activation energy (Activation barrier) of the vacant sites and available sites should be equal and low potential energy to facilitate the ion hoping.

(d) The structure of the polymer should be in three-dimensional framework to ease the mobile transport

2.2.3 Parameters that Govern the Ionic Mechanism

The ionic conductivity of a solid polymer electrolyte is calculated using Equation 2.1:

$$\sigma(T) = \sum_i n_i \, q_i \mu_i \tag{2.1}$$

Where n_i represents the number of charge carriers of type i per unit volume, q_i represents the charge of type *I*, μ_i represents the mobility of type *I*, which is the measurement of the average velocity in a constant electric field. Therefore, conductivity of the solid polymer electrolytes must have required the following criteria:

1. Increases in number of charge carriers that can be freed from coordination bond
2. Increase in movement of charge carriers in the solid polymer electrolytes

Below are the factors that favor the increase ion conductivity in the solid polymer electrolytes;

a) decrease in degree of crystallinity (or increase in degree of amorphousness)

b) increase in flexibility of polymer chains

c) increase of dielectric constant of solid polymer electrolytes

d) low T_g

e) increase in ion mobility

f) increase in concentration of mobile ions

Polymers often described as crystalline and amorphous. Normally polymers are not 100% crystalline; otherwise, they would not be able to melt due to their highly organized structure. Most polymers are about 80% crystalline. Crystalline polymers are highly organized and tightly packed molecules. Amorphous materials have no pattern order between the molecules, like a bowl of spaghetti; they normally have the presence of polar groups.

The movement of ions are restricted in crystalline polymer electrolytes as the coordinative bonds among the molecules are highly organized and tightly packed but in the amorphous region the charge carriers migrate in higher rate (Aziz et al., 2018).

2.3 Methods to Enhance Ion Conduction Mechanism

Current studies have introduced many different modifications on the polymer electrolytes to produce a well-enhanced conductivity. Among all the modifications that have been made are; gamma ray irradiation, mixed salt system and addition of additives, such as plasticizers, ionic liquids and fillers.

2.3.1 Polymer Modifications

Most polymers known to have high crystallinity, which reduces the conductivity in the electrolytes. Hence, many studies have been carried out to reduce the crystallinity and increase the amorphousness. This is to produce more space for ion mobility. Efforts to improve conductivity includes comb copolymer, graft copolymers and network polymers (Aziz et al., 2018).

Researches show that flexibility in polymer chain is required to increase ionic conductivity. Therefore, more flexible polymer-salt chains with low glass transitions have been studied to aid polymer segmental mobility. Studies have shown that polymer complexes of poly(methylsiloxane)s and oligo(polyethylene) with $LiClO_4$ as a salt have exhibited high ionic conductivity of 7 x 10^5 S cm^{-1} at room temperature and conductivity achieved above 10^{-4} S cm^{-1} at room temperature.(Das & Ghosh, 2017)

The synthesis and electrochemical characterization of copolymer poly (lauryl methacrylate)-b-poly[oligo (oxyethelene) methacrylate] electrolyte reported by Soo showed improved ionic conductivity. Solid polymer electrolyte also exhibited improved stability with a wide potential window up to 5V compared to those glassy block copolymer systems. The fabrication of this copolymer has shown high reversible capacity and good capacity retention (Soo et al., 1999). Guilherme introduced block copolymer electrolytes compromised of polyethelene-b-poly (ethylene oxide) (PE-b-PEO) and $LiClO_4$ salt. This study has showed the highest conductivity of 3 x 10^{-5} Scm^{-1} at ambient temperature with the addition of 15% of $LiClO_4$ salt. The ionic conductivity reached ~10^{-3} Scm^{-1} at 100 °C (Guilherme et al., 2007). Block copolymerization is known to reduce the degree of crystallinity of polymer electrolytes (Didier Devaux, 2015).

In addition to this, Lyons introduced the comb-shaped polymer which was used as a host polymer in the preparation of polymer electrolytes. The polysilane comb polymers $[(CH_3CH_2OCH_2CH_2O(CH_2)_4)Si(CH_3)]_n$ with ethhoxybutane in the side chain of the polymer and lithium triflate salt achieved 1.2 x 10^{-7} Scm^{-1} at [Li]/[O] = 0.25. The comb-branch copolymers were also synthesized by Lyons. The polymer electrolytes based on this comb polymer host and lithium trfilate achieved ionic conductivity of 1.2 x 10^{-7} Scm^{-1} at [Li]/[O] = 0.25 at room temperature (Zhang et al., 2004) (Farah et al., 2019). Another Comb-branch copolymers are synthesied using copolymer poly(ethylene oxide methoxy) acrylate with lithium 1.1.2-trifluorobutane sulfonate acrylate salt. This new flurorinated, single ion, copolymer posseses high ionic conductivity and low T_gs (Cowie & Spence, 1999). Comb-shaped polyethers are synthesised by poly(4-hydroxystyrene)(PHSt) as a multifunctional initiator through graft polymerisation of the ethlyne oxide (EO) or a mixture of EO and propylene oxide(PO). The host polymer of polyethers and lithium triflate ($LiCF_3SO_3$) achieved ionic conductiivity of almost 10^{-5} S cm^{-1} at room temperature. The grafting reaction reduced the crystallinity of these polymer electrolytes having comb-shaped polymers (Jannasch, 2000).

A novel series of graft copolymers containing graft chains of macromonomer poly(sodium streresulfonate) (macPSSNa) and the polystyrene (PS) backbone were synthesized using a combination of stable free radical polymerization (SFRP) and emulsion polymerization by Ding (Ding, Chuy, & Holdcroft, 2002). Although the graft polymer electrolytes showed lower water uptake, they gave remarkably good proton conductivity compared to the membranes prepared from random copolymer styrenesulfonic acid and styrene (PS-r-PSSA) (Ye, Rick, & Hwang, 2012).

2.3.2 Polymer Blending

Another approach in the effort of increasing ionic conductivity is polymer blending. Polymer blending consists of two or more different polymers or copolymers mixed physically and no bonding is involved here. This produces a material with improved properties, such as one material with active transporting species in the electrolyte, whereas the second material improves mechanical support for electrolyte. Polymer blending also facilitates sample preparation and controls the physical properties of polymer membrane within the definite parameter change. In such, polymer blending reduces cost in preparations compared to polymer modification, as it does not require polymerization process. The properties of polymer produced in polymer blending depends on the physical and chemical properties of the participating polymers and phase state, homogenous or heterogeneous. The homogenous polymer blend is produced when the different polymers are able to dissolve in a common solvent. This due to fast thermodynamic equilibrium achieved with same solvent used for dissolving (Braun, Cherdron, Rehahn, Ritter, & Voit, 2012).

The effect of blending on the properties of SPE has been studied systematically to find the best composition leading to a maximum conductivity at room temperature. The polymers are analyzed accordance to their structure–property correlation.

Table 2.1 shows collection of binary polymer electrolytes have been prepared and investigated over the years. The following Binary polymer electrolytes have been studied over the years; PMMA-PVC, PVA-PMMA, PMMA-PVdF, (PVAc)-PMMA, PVAc-PVdF, PEO-PVdF, PVC-PEMA, PVA-PSA, PHEMO-(PVdF-HFP), PEO-PVP, TPU-PEO to name a few.

2.3.3 Gamma Irradiation

Gamma irradiation can affect the microstructure of the polymer chains. Gamma irradiation can alter the chemical, physical structural, optical, mechanical and electrical properties of polymer complexes. γ rays produces free radicals in polymer chain through intermolecular cross-linking and/or main chain scission. γ rays can suppress the crystalline region, change the molecular weight distribution, increase the ionic conductivity and improve the mechanical strength of polymer electrolytes. Therefore, exposing γ rays is certainly a feasible way to improve the ionic conductivity (Rahaman et al., 2014).

PEO was initially cross-linked with $LiClO_4$ via γ rays and further prepared by blending PVDF and cross-linked PEO. The polymer blend subjected to γ radiation to produce a simultaneous interpenetrating network (SIN). This study has shown that γ ray induced SIN polymer electrolytes provided a high mechanical modulus of 10^{-4} Pa and produced high room temperature ionic conductivity of more than 10^{-4} Scm^{-1} (Song, Wu, Jing, Sun, & Chen, 1997).

Another study on the electrolytes based on γ radiated PEO-ammonium perchlorate (NH_4ClO_4) showed that the ionic conductivity increases greatly. γ rays has attributed to the decrease in crystallinity of polymer electrolyte and further increases the mobility of the ions. (Braun et al., 2012). Studies have also shown that the PVDF-lithium bis(oxalate)borate (LiBOB) solid polymer electrolyte reached its highest conductivity of 3.05 x 10^{-4} Scm^{-1} which is 15% higher than polymer electrolyte without the γ radiation. However, high dosage of γ radiation can cause the degradation of the polymer electrolyte (Braun et al., 2012). Gamma radiation is a potential way to improve the ionic conductivity. However, the only drawback is that electrolytes may get degraded at high gamma radiation (Akiyama et al., 2010).

2.3.4 Mixed Salt System

In years of studies of polymer electrolyte, PEO is still the most studied and researched host polymer. The presence of oxyethylene ($CH_2 - CH_2 - O$) repeating units in PEO polymer, provides strong solvating properties for vast variety of salts. This takes place due to the interaction of ether oxygen(s) with cations. Studies have also shown the efficiency of PEO on coordinating metal ions. PEO able to coordinate metal ions due to orientation and optimal distance of the ether oxygen atoms in polymer chains.

A novel dual-salt based polymer electrolyte has been reported by Si Li using LiTFSI, lithium bis(oxalate)borate (LiBOB), glutaronitrile (GN) plastic crystal, and poly (ethylene glycol) diacrylate (PEGDA) prepolymer hosts. PEGDA with low molecular weight allowed complete mixing with salt and plastic crystals. The corporation of this crosslinking reaction, a freestanding SPE achieved. By using ternary phase diagram analysis, a dual-salt SPE (DS-SPE) with superionic conductivity (1.0 $mScm^{-1}$) at 30°C was achieved. The Electrochemical performance evaluation of LIBs of Li/SPE/$LiFePO_4$ demonstrated that the novel polymer electrolyte exhibited excellent electrochemical stability during a long of cycle testing. Ionic conductivity over 1.0 $mScm^{-1}$ at 30°C was achieved for the SPE in the isotropic phase (Li et al., 2018).

2.3.5 Additives

2.3.5.1 Plasticizer

Plasticization is one of the efforts to improve ionic conductivity as it focused on decreasing the degree of crystallinity of polymer electrolyte. Due to the fact that polymer electrolytes contain both crystalline and amorphous region and ion transport is preferred in amorphous region, and the plasticizer added to improve ambient ionic conductivity. Plasticizers, increases the amorphous region as well as ion aggregation dissociation in PE. Studies have shown that the ionic conductivity in plasticized PE can be increased at the expense of decreased mechanical strength (Aziz et al., 2018).

Plasticized polymer electrolytes are prepared by incorporating polymer host with low molecular weight compounds; ethylene carbonate, propylene carbonate and poly ethylene glycol (PEG) as this decreases the glass transition temperature of the PE system. Plasticizers have shown reduction in the number of active centers as it weakens the intermolecular and intramolecular forces between the polymer chains. Hence, this results in easing the rigidity of the 3D structure formed upon drying as well as modifying the mechanical and thermos-mechanical properties of the prepared films. Plasticized polymer works on reducing crystallinity and increases amorphous fractions, which increases salt dissociation, which increases mobility of the charge carrier (Aziz et al., 2018).

It has been reported by Sameer, that crystallinity decreases when PEG200 is used as plasticizer in polyethylene oxide (PEO) and increases the amorphous fractions of the materials. Plasticized polymer electrolytes has also shown some drawbacks. Such as inadequate mechanical properties at high level of plasticization, reactivity of the polar solvents with lithium electrode and solvent volatility.

2.3.5.2 Ionic Liquids

The approach in using ionic liquid has certainly shown improvement in ionic conductivity of electrolytes. Ionic liquid helps to achieve relatively high ionic conductivity with good thermal and chemical stabilities as well as provides high safety performance, high electrochemical potential window, non-volatility, non-flammability, low viscosity and has ability to dissolve the co-polymer.

Ionic liquids are salts in molten state (do not solidify at low temperature) in room temperature used in small quantities. Ionic liquid has shown good ability to enhance the ionic conductivity of the polymer electrolyte as it has good electrical performances. Ionic liquid plays a major role in SPE to provide free moving ions to allow ion conductivity within the polymer of SPEs. Besides, ionic liquid is also low in combustibility and has excellent chemical and thermal stability which is one of the criteria of improvement to look at in SPE. The ionic liquid that have been studied so far are as below; 1,3-dialkylimidazolium, 1,3-dialkylimidazolium, 1,3-dialkylpyridinium, Tetraalkyl ammonium, Trialkylsulphonium, Tetraalkylphosphonium, N-methyl-N-alkyl prrrolidium, N,N-diakylpyrrolidium, N-alkylthiazolium, N, N-dialkyltriazolium, N, N-dialkyloxazolium, Guanidinium to name a few. Inorganic ionic liquids are also as follows; Acetate (CH_3COO^-), Nitrate, (NO_3^-), Triflate (Tf^-), Tetrafluroborate (BF_4^-), Bis(trifluromethylsufonyl imide ($TFSI^-$), Bis (perfluoroethyl sulfonyl) imide [$N(C_2F_5SO_2)^{2-}$], Hexaflurophosphate (PF_6^-), Halides (Cl^-, Br^-, and I^-).

2.3.5.3 Fillers and Nano-fillers

In the effort to increase conductivity and enhance the electrochemical stability window, PEs must also exhibit good thermal and mechanical properties. These properties can be achieved by incorporating nanosized fillers into PE. Weston and Steele, has added Al_2O_3 particles, nanocomposite SPEs to improve ionic conductivity and mechanical stability of PE (Aziz et al., 2018).

2.3.5.4 Liquid Crystals

Liquid crystal (LC)-embedded polymer electrolytes are another way of electrochemical enhancement in solid polymer of the Li-ion batteries, Liquid crystals have the ability to turn polymer electrolytes into ordered manner and provide ion-conductive nanoscale domains. Studies reported that liquid crystals are preferred on soft ordered materials consisting of self-organized molecules. The assembling of liquid crystals can be built by molecular interactions, which consists of hydrogen bonds, ionic bonds, and charge-transfer interactions.

Sakuda et al have prepared the composite materials of lipotropic liquid crystal electrolytes. Electrolyte blending was done with ionic liquid with non-polymerized amphiphilic liquid crystal molecules to generate ordered, non-phase-separated assemblies. Another study done by Yoshio *et al.* using lipotropic liquid crystal was also based electrolyte materials. The electrolytes were the Li-salt-doped organic liquid electrolyte solutions used to increase the ion conductivity and to make the non-polymerized lipotropic liquid crystal blends more responsive. Ionic liquid (IL), which is based on organic salts, has a melting point below room temperature and exhibit new properties, such as low vapor pressure, flame retardancy, and high ionic conductivity. Polymerized ionic liquid (PIL) are polymers which are covalently bonded with IL monomers. This can be an ideal polymer electrolyte for LIBs due to the specific film forming ability, secure handling, excellent electrochemical performance and chemical compatibility toward IL. Chen and team has synthesized the poly **(**1-(hexyl methacrylate)-3-buty imidazole tetra fluoroborate**)** (PMOBIm-BF_4) copolymers cross-linked with poly(ethylene glycol) diacrylate (PEGDA) in the presence of liquid crystal of 1-hexadecyl-3-methylimidazolium tetrafluoroborate ([C_{16}mim]BF_4) and lithium salt ($LiBF_4$), and obtained the poly(ionic liquid)-based SPE. The ionic liquid crystal was added as inducer to form composite electrolytes in LIBs. This effort produced conductivity value of 7.14×10^{-5} S cm^{-1} at 25 °C, and the cell showed a stable discharge capacity of 136.7 mAh g^{-1} under a current rate of 0.1 C, (Chen et al., 2020).

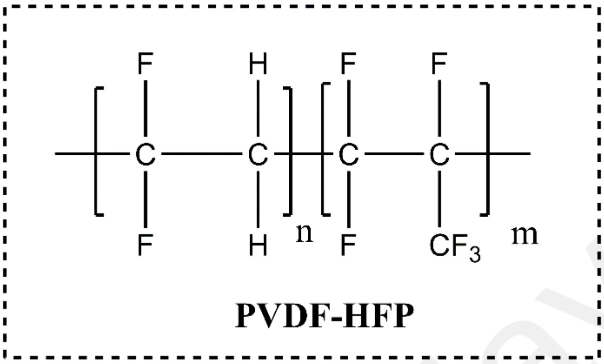
This polymer is also preferred in DSSC application as well, due to LC alignment in the polymer electrolytes, which enhances photovoltaic performance in DSSCs. The presence of LC, which increases the ordering strength in the polymer electrolyte, provides superior charge carrier pathway in PE. Among the ionic liquids, Imidazolium iodide based ionic liquids are widely used for dye-sensitized solar cell (DSSC) applications because of better performance (Khanmirzaei, Ramesh, & Ramesh, 2015).

2.4 Reasons of Choosing the Materials

2.4.1 PVDF-HFP

PVDF - poly(vinylidenefluoride), HFP- hexafluoropropylene (PVDF-HFP), is a copolymer that consists of crystalline vinylidene fluoride and amorphous HFP structures and is used as the polymer host. The mechanical stability is provided by vinylidene fluoride polymer and plasticity properties is provided by HFP polymer. The amorphous property of HFP facilitates higher ionic conduction (Stephan, Nahm, Kulandainathan, Ravi, & Wilson, 2006). PVDF-HFP has higher conductivity in compared to other polymers, which is between 10^{-8} to 10^{-10} Scm^{-1}. PVDF-HFP has shown high dielectric constant value of $\varepsilon = 8.4$. This explains that PVDF-HFP is able to increase the salt solubility which eventually increases the ionic conductivity of the polymer electrolyte (Noor, Careem, Majid, & Arof, 2011).

Figure 2.4: Structure of PVDF- poly(vinylidenefluoride), HFP- hexafluoropropylene (PVDF-HFP)



2.4.2 LiClO$_4$

Choosing a salt plays a very important path in determining the conductivity in SPE. A salt that determines the conductivity in crystalline complex formation, intra-molecular cross-linking of the polymer chains and the degree of salt dissociation (the number of charge carriers) (Ramesh & Wong, 2009)

Lithium perchlorate is an ionic compound that completely ionizes to form Li^+(aq) and ClO_4^-(aq) ions. This white or colourless crystalline salt is noteworthy for its high solubility in many solvents. It exists both in anhydrous form and as a trihydrate. LiClO$_4$ is highly soluble in both inorganic and organic solvents.

2.4.2 Tetraglyme

Tetraglyme is used to solvate Li^+ cations. This is due to the ability of the flexible glyme polyether chains to adopt numerous conformations, permitting multidentate cation, coordination through the ether oxygen electron lone pairs, meaning it involves a ligand that can form bonds at more than one point.

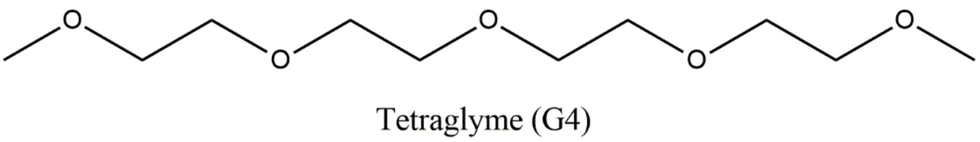


Figure 2.5: Structure of tetraglyme (G4)

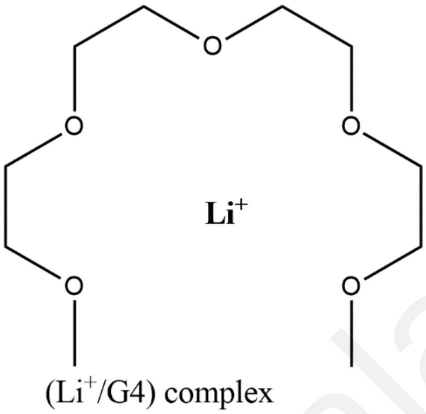


Figure 2.6: Structure of Li^+/tetraglyme complex

Glyme and Lithium salts able to form a crystalline structure, which has low energy, idealized models of solvates. They enable one to gain insight into the preferential coordination behavior between the cations and EO (Ether oxygen) chain, which exist in amorphous solid polymer electrolytes. No crystal structure of tetraglyme-Li^+ cation complexes have yet been reported in the scientific literature and Cambridge crystallographic,(Henderson, Brooks, & Young, 2003).

Glyme is well known for complexing with metal-ions through their multiple ether-like oxygen atoms. When Li salts dissolve in glyme-based solvents, they show promising ionic conductivity and Li^+ ion transport properties. Tetraglyme also possesses methylene groups that can undergo hydrogen abstraction and following inter-radical reactions to form oligomers, or bond to the adjacent polymer chains.(Porcarelli, Gerbaldi, Bella, & Nair, 2016)

Tetraglyme is used as an ionic conductivity booster. Studies have shown that the addition of tetraglyme significantly increases ionic conductivity. Tetraglyme is proven to have a number of advantageous properties such as wide electrochemical potential window, wide decomposition temperature (>200 °C), negligible vapor pressure (< 0.5 mmHg at 20 °C) and less toxicity. The multiple ether oxygen atoms in tetraglyme act as the electron donating groups and is used as polymer-salt complexes as they able to dissociate salt molecules effectively through the formation of glyme-alkali metal salt complex, (abbreviated as $[M\ (glyme)x]^+$, where M = metal salt, x = counter ion). Bidin et al. described how the addition of tetraglyme has increased the ionic conductivity of PVBVA-LiTFSI from 6.22 to 21.9 µS cm^{-1} and Wang reported that the ionic conductivity of PEO-LiTFSI has increased significantly from 5.64 to 68.3 µScm^{-1} at room temperature (Guan et al., 2020). Hence, in this work, it is predicted that the complexation between PVDF-HFP with $LiClO_4$ and tetragyme can minimize ion pair formation and boost the ionic conductivity of SPE.

2.5 Supercapacitors

Supercapacitor is a type of power source. Supercapacitors, is also called ultracapacitors, or electrochemical capacitor. Supercapacitor is an electrochemical energy storage device, which gives preference to high power density and fast charge-discharge cycles. Supercapacitor consists of a pair of electrode and electrolyte. The electrode can be made of carbon, metal oxide, conducting polymers and so on. Supercapacitors are divided to three main categories which are pseudocapacitors, electrical double layer capacitors (EDLCs) and hybrid capacitors (Liew, Ramesh, & Arof, 2016)

2.5.1 Pseudocapacitors

Pseudocapacitor is fast, reversible and works as redox capacitors. Pseudocapacitors store charge via surface redox reaction. Redox reaction takes place during charge and discharge process. Faradaic redox reactions take place at the surface of the electrode. The pseudocapacitor is known to achieve higher energy densities than the EDLC devices, with expense power densities and cycle life. This application uses electroactive materials, which is known to improve the capacity behavior of supercapacitors. Transition metal oxides are commonly studied as electrodes in pseudocapacitor. Transition metals electrodes are known to contribute high capacitance due to their change in oxidation states (Boota & Gogotsi, 2019).

However, they exhibit some limitations such as a shorter cycle life, limited electrochemical stability and it involves a higher cost compared to carbon based electrodes. (Liew et al., 2016b). Pseudocapacitors can only store charge in the first few nanometers from the surface, this limits these materials being thin films and small particles (Lee et al., 2018).

A process called fast faradaic process takes place in surface of electrodes in a pseudocapacitor. In this Faradaic process, intercalation, under-potential deposition and redox reaction may occur using electroactive conducting polymers. Pseudocapacitors normally use electroactive conducting polymers or/and metal oxide-based electrodes (Liew, Ramesh, & Arof, 2016a).

2.5.2 Electric Double Layer Capacitors (EDLCs)

Electrical double layer capacitors (EDLCs) are the energy storage devices, which have been capturing the interest of many researchers. This is due to the performance of EDLC which produces high powered density and long cycle life (Ionic liquid-based polymer gel electrolyte)(Liew et al., 2016b). EDLC is extensively used in consumable electronics, hybrid electric vehicles, and medical devices etc. EDLC is capable to rapidly store energy which is suitable to be integrated with the intermittent power plants. EDLC which consists of carbon based electrodes (e.g. activated carbon, graphene, and carbon nanotubes) and electrolyte. EDLC able to offer quicker charging rate and longer lifespan than batteries. EDLC does not use any Faradaic reaction, meaning that the charge storage kinetics are fast and reversible, which facilitate fast energy uptake and delivery, and hence allow good power performance. EDLC involves electrolyte ion adsorption and desorption mechanism at the electrode/electrolyte interfaces, which make the energy storage process faster than batteries. Therefore, the contact area between electrode and electrolyte plays a vital role in determining the efficiency of EDLC. Apart from large surface area of carbon-based electrodes, high ionic conductivity of electrolyte is also crucial to obtain good performance of EDLC (Guan et al., 2020).

The energy storage of EDLC arises from ion accumulation at the interface of electrode-electrolyte of active materials. This is a rapid and reversible adsorption of charge carriers. EDLC electrodes are generally very stable. This is due to the storage mechanism, which is purely electrostatic. However, this may cause limitations in energy densities. (Lee et al., 2018)

Initially, EDLC uses liquid electrolytes as electrolytes to allow high number of ion movement during charging and discharging processes and improves the capability of the device. The major issue in liquid electrolytes are due to leakage problem, heavy and bulky especially when EDLC needed into manufacture of modules to support high power application [5]. Hence, solid polymer electrolytes (SPEs) has been focused to overcome these issues due to their physical form, light weight, and flexibility.

A new electric double-layer capacitor (EDLC) which works based on the charge being stored in between the interface of high surface area carbon electrode and an organic electrolyte solution has been in developed and been extensively used as maintenance free power source for IC memories and microcomputers. The requirement of a high performance capacitor requires:

(i) an electrode fabricated with high surface area activated carbon of suitable surface properties and pore geometry;

(ii) an high range electrolyte with good conductivities and electrochemical stabilities over wide range of temperature to allow the capacitor to be operated at high voltages and

(iii) cell construction materials that do not produce electrochemical corrosion during anodic polarization. The performance of a capacitors depends not only due to the materials however it also the construction of the cell. (Morimoto, 1999).

They store electrical energy by simple formation of the double layer in electrode/ electrolyte interface. Most SC use carbon electrodes with liquid electrolytes, however, a separator is needed to prevent the electrical contacts between electrodes is needed to prevent the liquid leakages (Tiruye, Muñoz-Torrero, Palma, Anderson, & Marcilla, 2016).

In this research, flexible and lightweight SCs is designed to replace liquid electrolytes. Extensive study has been carried out to improve the charge storage between electrode and electrolyte interface. Investigation on different types of carbon used as electrodes was carried out to improve the shortcomings such as low mesoporosity and poor accessibility of dissolved ions in the electrolytes. Other studies have also been carried out to increase surface area, porosity and conductivity of the carbon electrode (Liew et al., 2016b). The electrolytes used in the EDLC can be liquid electrolyte, solid polymer electrolytes, gel electrolyte or composite polymer electrolyte; the main concern is it must be conductive with high ionic mobility. The ion accessibility within the electrode and electrolyte is the parameter to control the capacitance of supercapacitors.

Poly (vinylpyrrolidone) (PVP), poly (vinylidenefluoride) (PVDF), poly (ethylene oxide) (PEO) and poly (vinyl alcohol) (PVA) were reported as good host polymers in EDLC as these SPEs due to their transparency, good formation of thin film, flexible, environmentally friendly, and non-toxic (Guan et al., 2020).

2.5.3 Hybrid Capacitors

Hybrid capacitors are generally new. Hybrid capacitors consist of combination of pseudocapacitors and EDLCs. Hybrid capacitors uses asymmetrical electrodes (Liew et al., 2016)

Asymmetric hybrid capacitors comprise of two different electrodes (e.g. activated carbon and battery electrodes separated by the electrolyte/ separator). Li-ion hybrid capacitors (LICs) has introduced advanced asymmetric hybrid supercapacitors by combining EDLCs with high fast charging rate and high energy and power density Li-ions batteries. Hybrid battery-capacitor (BatCap) system is another type of hybrid supercapacitors, BatCap consists of a capacitor electrode for high power density and a battery electrode to ensure the high specific energy (Singh & Hashmi, 2017).

2.6 Summary

This chapter focused on the literature review. The general information about SPEs and Superconductor, together with their working principle and their advantages were discussed. The literature about ionic conduction and the reason for chosen materials in this research as well was discussed in this chapter.

CHAPTER 3: METHODOLOGY

3.1 Introduction

This chapter focuses on the materials used in this research. The second section describes the methodologies of sample preparation and characterization. The preparation of the electrode is elaborated in the following section and followed by the last section that explains about the EDLC fabrication and characterization.

3.2 Materials

PVDF-HFP (Poly(vinyl fluoride-co-hexafluoropropylene) (Sigma-Aldrich, USA with molecular weight 400000 g mol^{-1}) and Lithium perchlorate, $LiClO_4$ (Sigma-Aldrich, USA, 99% with metallic impurities < 100 ppm and molecular weight 106.39 gmol^{-1}) were used as the polymer host and salt, respectively: Tetra-ethylene glycol dimethyl ether (Tetraglyme) (Sigma-Aldrich, USA with molecular weight of 222.28 g mol^{-1}) has been employed as additive.

3.3 Preparation of solid polymer electrolyte (SPE)

The preparation of PVDF-HFP based SPEs involves the solution casting method. An appropriate weight of PVDF-HFP and $LiClO_4$ were dissolved in acetone. Both materials were dissolved in 25ml of acetone. The mixture is stirred continuously at room temperature until the mixture took a homogeneous viscous liquid appearance. The mixture was then poured onto a petri dish and the solvent was allowed to evaporate at room temperature and pressure. This procedure provided a mechanically stable, free standing and flexible thin films with thickness in the range of 20 – 80 µm. The dried free-standing thin film was peeled off, and the ionic conductivities of polymer electrolytes were evaluated by Electrochemical Impedance Spectroscopy (EIS). This procedure was repeated with different weight ratio of PVDF-HFP and $LiClO_4$ as shown in Table 3.1 for optimization purpose.

Table 3.1: The weight ratio of PVDF-HFP, $LiClO_4$ with their designations.

Designations of polymer electrolytes	Weight percentage of materials (wt.%)	
	PVDF-HFP	**$LiClO_4$**
ST 10	90	10
ST 20	80	20
ST 30	70	30
ST 40	60	40

3.3.1 Preparation of SPEs incorporated with tetraglyme

The highest conducting SPE based PVDF-HFP and $LiClO_4$ salt system was selected to incorporate with tetraglyme additve. The same method as described above was used with different weights of tetraglyme to produce the PVDF-HFP-$LiClO_4$-Tetraglyme based SPE. The different weights of tetraglyme were varied according to Table 3.2, in order to obtain the best SPE. This procedure also provided mechanically stable, free standing and flexible thin films of thickness in the range of 20 – 80 µm. The free-standing thin film was obtained and the ionic conductivities of the polymer electrolytes were evaluated by EIS.

Table 3.2: The weight ratio of PVDF-HFP, $LiCLO_4$ and Tetraglyme with their designations.

Designations of polymer electrolytes	Weight percentage of materials (wt.%)		
	PVDF-HFP	**$LiClO_4$**	**Tetraglyme**
ST 30 (STG 0)	70	30	0
STG 10	63	27	10
STG 20	56	24	20
STG 30	49	21	30
STG 40	42	18	40

3.4 Characterization of PVDF-HFP based polymer electrolytes

Several required characterizations have been conducted to study the electrical characteristics, structural and electrochemical properties of the prepared polymer electrolytes. The electrical characterization was carried out using the EIS study. The FTIR and XRD were used to study the structural properties of the polymer electrolytes.

3.4.1 Electrochemical Impedance Spectroscopy (EIS)

The analysis of electrical conductivity of a range of polymer electrolytes was carried out using the EIS technique. The HIOKI 3532-50 LCR Hitester impedance analyzer was used to study the conductivity studies through EIS at room temperature. Measurements of electrical conductivity were performed in the frequency range of 50 Hz – 5 MHz to obtain bulk resistance. The samples of SPE were prepared freshly to carry out the EIS study. The SPE sample was cut and placed between two stainless steel electrodes. The temperature dependent ionic conductivity studies of SPEs were carried out in a temperature range of 30 -70°C at intervals of 10 °C. At each temperature, the samples were allowed to stabilize for about 30 mins before the measurements were taken. The ionic conductivity (σ) of each sample was calculated using bulk resistance measurements obtained from complex impedance plots. The following Equation 3.1 below was used to evaluate ionic conductivity of each polymer electrolytes:

$$\sigma = \frac{l}{R_b \times A} \tag{3.1}$$

Where, σ is the ionic conductivity of SPE (S cm^{-1}), A is the surface area of the electrode (cm^2). l is the thickness of SPE measured by the micrometer screw gauge, R_b is the bulk resistance (Ω) obtained from the Nyquist plot produced by EIS.

The Cole-Cole plots were generated for each SPE to determine the bulk resistance value (R_b). The ionic conductivity values of each SPE were calculated using the R_b as mentioned above.

3.4.2 Ambient Temperature-Ionic Conductivity Study

The temperature-dependent ionic conductivity is a measurement of the ionic conductivity at different temperatures. The temperature dependence study helps to investigate the thermal behavior of the SPEs. There are two generic thermal activated models, which, are the Arrhenius model, and Vogel-Tammann-Filcher (VTF) model and these were used to study the activation energies for each SPE.

The Arrhenius model explains the thermal behavior of SPEs. Based on their respective ionic conductivity values, Activation energy is calculated based on the below Equation 3.2 below.

$$\sigma = \sigma_o exp \left[\frac{-E_a}{kT}\right] \tag{3.2}$$

where σ_o is the pre-exponential factor, E_a is activation energy (eV) and k is Boltzmann constant (eV/K)

Activation energy values for each SPE was calculated using log σ versus 1000/T plot and Equation 3.2.

3.4.3 Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR spectroscopy is an important analysis to study the molecular structure in SPE system. FTIR is used to investigate the interaction and complex formation in the polymer electrolyte films based on the fundamental vibration of the polymer electrolytes. Investigating interactions in the SPEs helps to explain identity of materials and the quality of SPE performance for application in EDLCs. The Thermo Scientific Nicolet iSIO Smart ITR machine was used in the region between 4000 and 400 cm^{-1} at a resolution of 1 cm^{-1}. The FTIR spectrum is generated when a beam of infrared light passed through the sample. The transmitted light will produce the amount of energy absorbed at every wavenumber. FTIR spectrometer is able to measure all the wavenumber in the range of 4000 and 400 cm^{-1}. The transmittance and absorbance of infrared light produces the fingerprint called FTIR spectrum. The details of the molecular structures of a sample can be analysed using the transmittance and absorbance obtained. Screening of FTIR spectrum helps the understanding of the chemical bonds the molecules for further investigation of the structural properties. Figure 3.1 shows the FTIR instrumentation and how a FTIR spectrum works.

The primary optical principle of FTIR spectrometer can be explained base from intereference of various frequencies of light that produces a spectrum. FTIR instrument comes with a source, sample, two mirrors, a laser reference and a detector. The assembly of components include a beamsplitter which comes with two strategic mirrors. The mirrors functions as an interferometer. When source energy strikes the beamsplitter, it produces two beams roughly of the same intensity; one beam at the fixed mirror and another at moving mirror. Both the beams returns to the beamspliiter and they recombine and passes through the sample. The difference in their path length forms constructive and destructive interference form an interferogram. The sample then absorbs all wavelength characteristics of the spectrum and substracts specific wavelegths from the interferogram. The detector then reports variation in energy against time for all wavelengths. A laser beam is superimposed to provide a reference for the working operation of the instruments. The Fourier transform mathematical function is used to convert the intensity over time spectrum to an intensity over frequency spectrum.

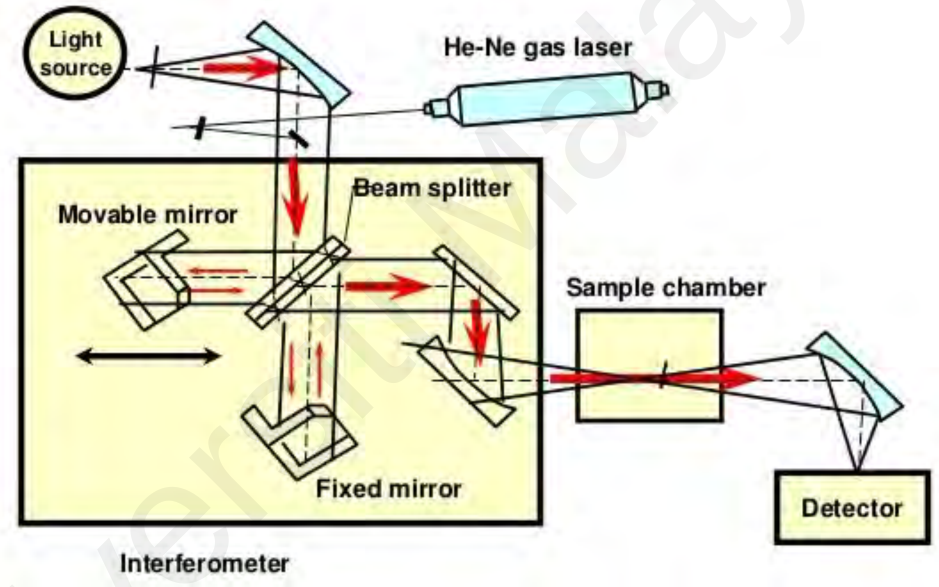


Figure 3.1: Fourier transform infrared spectroscopy (FTIR) instrumentation (Vedantam, 2014)

3.4.4 X-ray Diffraction Spectroscopy (XRD)

XRD characterization determines the structural properties of polymer electrolytes. XRD analysis shows the crystalline and amorphous region in the polymer. CTX benchtop x-ray diffractor with Cu-Kα radiation (λ=1.54060 Å) was used to produce the x-ray patterns of the samples, over the range of 2θ, at 5 to 50° at ambient temperature. X-ray radiations consist of high energy electromagnetic radiations with short wavelength. X-ray radiation has ability to easily penetrate into solid objects. X-ray diffractometer consists of sample holder, X-ray tube and X-ray detector. X-ray tube produces X-ray radiation by engaging a voltage for acceleration of electrons generated by heating a filament. Filters were applied to produce monochromatic radiation from X-rays. The resultant radiation then collimated and concentrated on the sample. The constructive interference of the radiation on the sample produces diffracted rays as follows Bragg's law ($n\lambda = 2d\ sin\ \theta$). X-ray detector detects the diffracted rays for counting. The X-ray radiation able to penetrate into the sample. The X-ray radiation removes electrons from the inner shell of the atom to ionize the atom. This produces different type of intensities (K_α and K_β) in the X-ray spectra of the sample. Figure 3.2 shows the structure of an X-ray diffractometer.

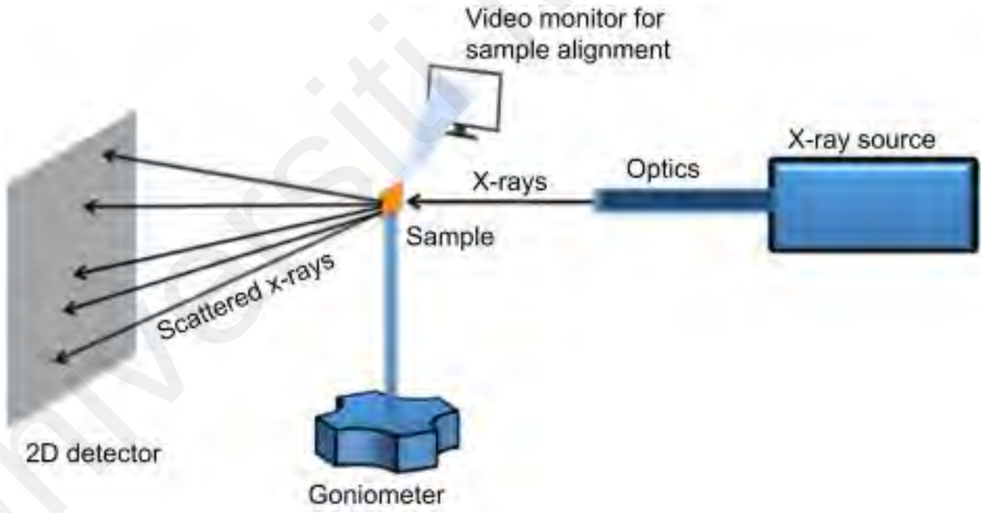


Figure 3.2: X-ray diffractometer sourced from ScienceDirect.com

3.5 Electrode Preparation

The activated carbon-based EDLC electrodes were prepared by coating techniques. The EDLC cell was constructed in the configuration of electrode/polymer electrolyte/electrode. The electrodes were fabricated by coating the carbon-based slurry onto aluminium foil and dried the coated foil in the oven at 70 °C for few hours. The slurry was prepared with the mixture ratio of 80 % activated carbon. 10 % acetylene black and 10 % poly (vinylidene fluoride) was added into the NMP (1-methyl-2-pyrrolidone) solvent and the mixture was stirred at 80 °C for few hours until a homogenous slurry was obtained. The viscous slurry was later drop-casted on an aluminium foil (area of 1 cm^2).

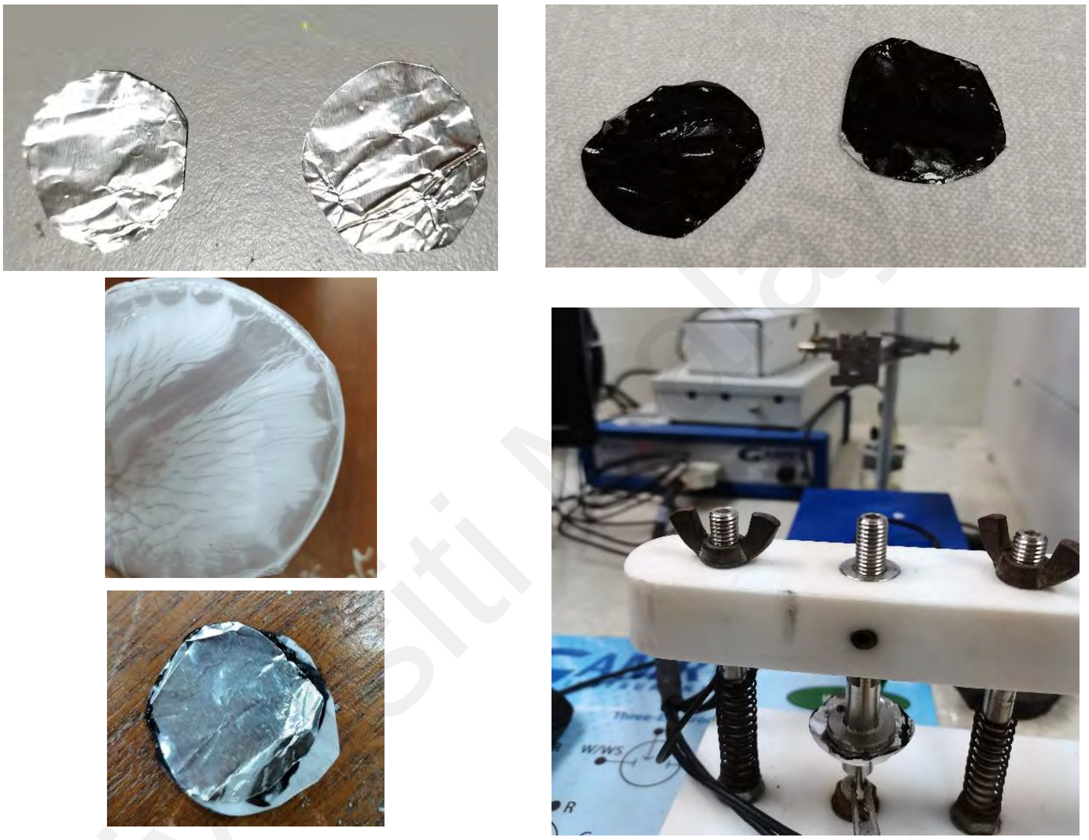


Figure 3.3 Electrode preparation schematic diagram

3.6 EDLC Fabrication

The EDLC was fabricated by sandwiching the prepared SPE between the two AC electrodes following AC electrode/SPE/AC electrode configuration. The devices for STG 20 and STG 30 were prepared as AC/STG20/AC and AC/STG30/AC. The electrochemical performance of the EDLC was analyzed by Cyclic Voltammetry (CV) in a potential window ranging from 0 to 1 V at different scan rates (3,5,10,20,30,40 and 50 mV/s) and galvanic charge discharge (GDC) (with potential range of 0 - 1 V at different current densities (10, 50, 100, 200 and 600 mA/g). The EIS studies were carried out in a frequency range from 0.01 to 100 kHz. The specific capacitance (C_{sp}) of cells was calculated using CV and GCD measurements. The following equations is used to calculate specific capacitance.

$$C_{sp(CV)} = 2\frac{\int Idv}{v\Delta Vm} \tag{4.6}$$

$$C_{sp(GCD)} = \frac{I\Delta t}{\Delta Vm}\ x\ 2 \tag{4.7}$$

where $\int I\,dv$ is area of CV loop, ΔV is the potential window, v is the scan rate in V/s, m is the mass of active material on both electrodes, I is the discharge current, and Δt is the discharge time. (Wang et al., 2018).

The study of CV for EDLC was probed out using Gamry Interface 1000 electrochemical analyzer. The cell was left to rest for 2 seconds before commencing with the measurement. The EDLC cell was then evaluated at 10 mVs^{-1} scan rates in the potential range between 0 and 1 V. The capacity of electrochemical devices can be detected using three different techniques via cyclic voltammetry, EIS and galvanostatic charge-discharge performance (Lewandowski, 2003).

3.7 Summary

In this chapter, the materials and chemicals that were used in this research and their properties were discussed. The experimental methods for preparation of SPEs and electrodes and the characterization for both SPEs and fabricated EDLCs were discussed.

CHAPTER 4: RESULTS AND DISCUSSION

In this chapter, we discuss the effect of tetraglyme into the polymer electrolytes and EDLC. The first section explains the ionic conductivity of additive-free polymer system. The second section reports the results obtained from all the characterization of polymer electrolytes. The electrochemical performances are then further elaborated in final section of this chapter.

4.1 Fourier-transform infrared (FTIR)

Fundamentally, Fourier-transform infrared spectroscopy (FTIR) is used to gauge the structural insights of organic-based compound, which are Solid Polymer Electrolyte (SPE) samples in our context. In this study, FTIR characterization is carried out to characterise the molecular and structural changes in the tetraglyme-based PVDF-HFP/$LiClO_4$ SPEs. The Fourier-transform infrared spectra (FTIR) of PVDF-HFP/$LiClO_4$ samples are shown in Figure 4.1. ST0 (pure PVDF-HFP) exhibits fundamental vibrational modes at several wavenumbers, aligning with the reported FTIR characteristics in the state-of-the-art (Yang, Lian, Lin, Shih, & Chen, 2014). ST0 spectrum showed peaks at 3026 and 2985 cm^{-1}, which explains the presence of symmetric and antisymmetric stretching vibration of CH_2. Peak at 1407 cm^{-1} is assigned to CF stretching vibrations PVDF-HFP and 1298-1039 cm^{-1} are attributed to CF and CF_2 stretching vibrations. Meanwhile, peak at 873 cm^{-1} is assigned to vinylidene group of polymers. The presence of $LiClO_4$ is observed at 1630, 1089 and 616 cm^{-1} which is assigned to anion ClO_4^-. Upon addition of $LiClO_4$ in polymer host (PVDF-HFP) in sample ST30, the peak at 758 cm^{-1} blue shifted to 748 cm^{-1}. This attributed to wagging band of CH_2Cl. Stretching vibration of C–Cl shown in frequencies 840–560 cm^{-1}.

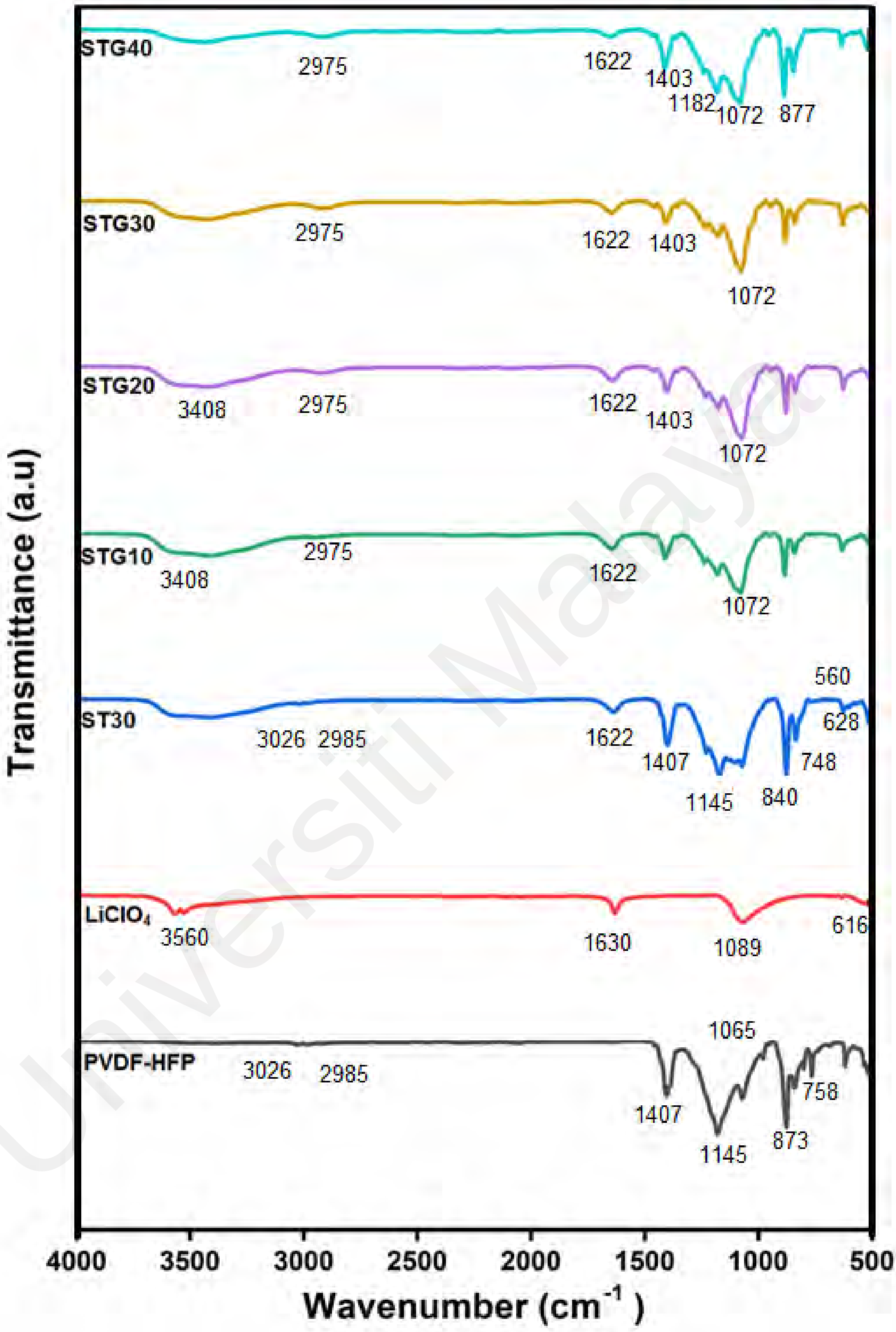


Figure 4.1: FTIR spectra of PVDF-HFP, $LiClO_4$ and SPE samples

The characteristic absorption vibrations of $LiClO_4$ at 1630 and 1089 cm^{-1}, attributes to symmetrical vibration of ionic pairs between Li^+ and $ClO_4{}^-$. Stretching vibration of $ClO_4{}^-$ is at frequency of 616 cm^{-1}. There are also the sharp peaks 3560 and 1630 cm^{-1} which indicating stretching and bending vibrations of OH bonds of the absorbed water. ST 30 shows absorption peaks at 2985 and 3026 cm^{-1}, which are assigned to the symmetrical and non-symmetrical stretching vibration of CH_2 groups, appears upon addition of $LiClO_4$ to polymer host as it shows the interaction between lithium ions and F atoms (Angulakshmi N. T., 2011). Comparing spectra ST 0 and ST 30 the peak at the 628 cm^{-1} region been broadened with lower intensity for ST 30 sample, Suggesting the presence of 628 cm^{-1} peak that indicates stretching vibration of ClO_4. The shifting, reducing in intensity of the peaks indicate that the complexation between polymer PVDF-HFP and $LiClO_4$ (Prabakaran, Mohanty, & Nayak, 2014).

The addition of tetraglyme in STG samples (STG10, STG20, STG 30 and STG 40) has also shown some peaks similar to sample ST 30, however the peaks intensity reduces. Figure 4.1 also shows that the deformed vibration of CH_2 group moves to 1403 cm^{-1} with decreases in intensity after addition of tetraglyme into polymer matrix from 1407 cm^{-1}.

Meanwhile another phenomenon can be observed in Figure 4.1 where all STG samples exhibit more intensified 1072 cm^{-1} as compared to ST30. However, moving from STG10 to STG40, the FTIR spectrum possess similar characteristics, with exception of STG40 where 1182 cm^{-1} exhibits high amplitude, possibly due to high Li^+ ion content (Isa et al., 2014). The obtained FTIR outcomes contribute a preliminary understanding on the effect of tetraglyme and Li^+ ion addition towards the FTIR characteristics of PVDF-HFP (Ulaganathan & Rajendran, 2010). Presence of tetraglyme in the SPE complexes contributes the formation of complex ion which increases the ion mobility to enhance ionic conductivity. The detection of formation of complex ion can be observed through the band region of ether group which present in tetraglyme. Lithium ion forms bidentate coordinate bond with ether oxygen, therefore the ether oxygen vibrational modes will be shifted to a lower wavenumber. Peak 1072 explains presence C-O-C stretching mode. STG samples clearly have shown peaks at 1072, which are broader and less intense. This further verifies the formation of tetraglyme-salt complex. (Su, 2019).

4.2 X-ray diffraction (XRD)

X-Ray Diffraction (XRD) is a nondestructive technique that provides detailed information about the crystallographic structure, chemical composition, and physical properties of materials. In this study, XRD characterization determines the structural properties of SPE, which provide preliminary insights on their crystallinity properties.

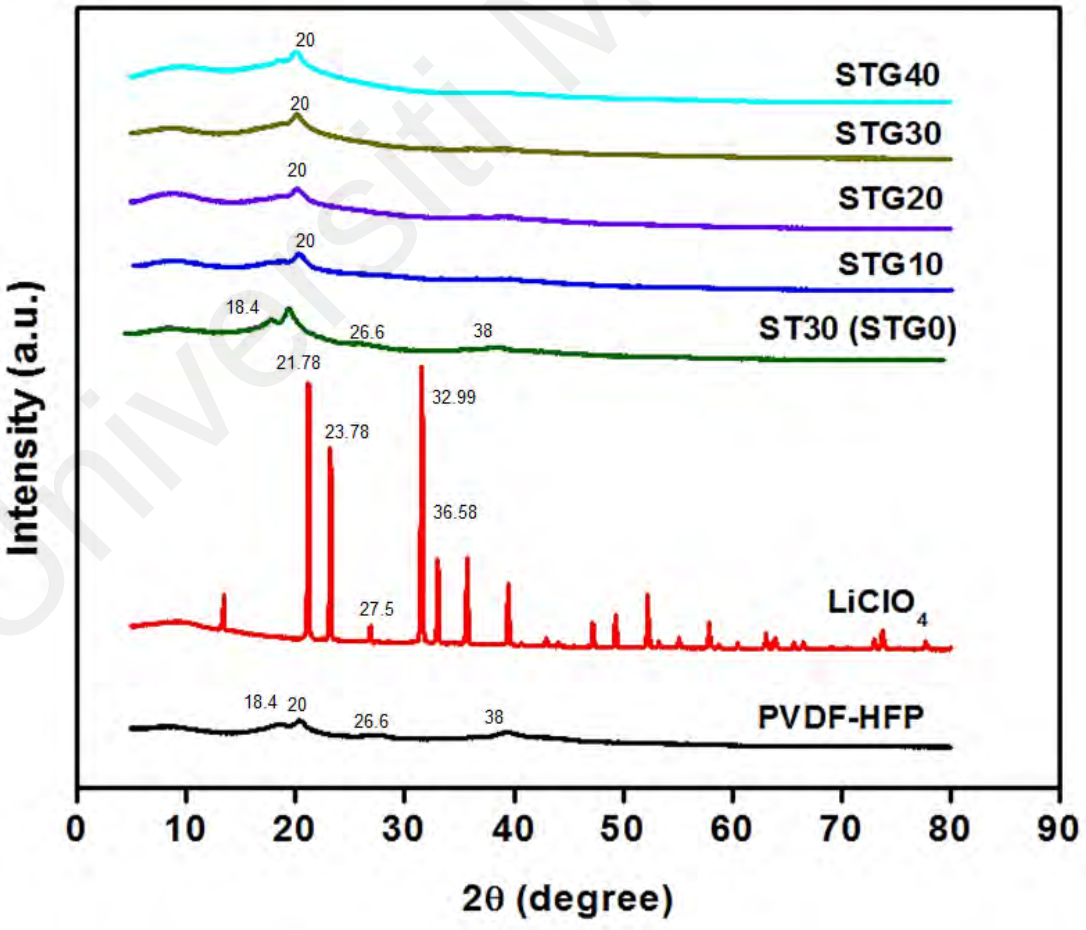


Figure 4.2: XRD diffractogram of PVDF-HFP, $LiClO_4$ and SPE samples

The XRD diffractogram of PVDF-HFP, $LiClO_4$, ST30 (STG0), STG 10, STG 20, STG 30 and STG 40 samples are shown in Figure 4.2. The diffraction peaks at 2θ = 18.4°, 20°, 26.6° and 38° correspond to (1 0 0), (0 2 0), (1 1 0) and (0 2 1) atomic plane reflections of crystalline PVDF-HFP (Wilson, Ravi, & Kulandainathan, 2006). The appearance of the above mentioned diffraction peaks suggests partial crystallization of the PVDF structure to yield a semi-crystalline structural morphology for PVDF-HFP (Angulakshmi et al., 2011). $LiClO_4$ shows intense peaks at angles 2θ = 21.78, 23,78, 27.5, 32.99 and 36.58 and they describe the crystalline nature of the ionic salt [JCPDS:30-0751] (Baskaran et al., 2007). Since $LiClO_4$ is complexed in the polymer matrix, peaks corresponding to $LiClO_4$ are not observed in ST 30 and STG 20, which also indicate that the lithium salt is completely dissolved in the polymer matrix. It can be noted that ST 30 sample exhibits more visible 2θ = 18.4° as compared to its PVDF-HFP counterpart. This observation infers that the lithium ion interactions in the blend are strong, resulting in the damage of crystals in (1 0 0) plane. Apart from that, the diffraction peak at 2θ = 26.6° in PVDF-HFP disappeared upon impregnation of Li^+ ion (ST 30), which suggests the disruption of diffractive signals from (1 1 0) atomic plane by strong Li^+ ion (Sengwa & Dhatarwal, 2020). Both peaks of PVDF-HFP 26.6° and 38° are reduced in intensity and become broaden as the addition of $LiClO_4$ salt. This reveals the reduction in the degree of crystallinity of PVDF-HFP.

From Figure 4.2, it can be approximately seen that both 2θ = 18.4° and 38° became less visible from STG 10 to STG 40. This further affirms the postulation on the destruction of (1 0 0) and (0 2 1) crystal plane in PVDF-HFP by strong Li^+ ions. Similar to the reported state-of-the-art (Amici et al., 2016; Gohel & Kanchan, (2018); Jagadeesan et al., 2019; Mauger et al., 2019)), the increase in Li^+ does not induce a significant difference in 2θ = 20° peak, which can be attributed to the saturation in the degree of crystal plane destruction by Li^+. There is also reduction in PVDF-HFP peak intensity, which forms a broaden peak after addition of tetraglyme. From Figure 4.2, STG 20 has shown the lowest degree of crystallinity which also signifies highest amorphous nature among the other STG samples, which supports its highest ionic conductivity. Nevertheless, the XRD outcomes preliminary infers that Li^+ ions and tetraglyme additive homogeneously dissolved in PVDF-HFP, which gives a positive impact on its ionic conductivity.

4.3 Ambient Temperature-Ionic Conductivity Study of Ionic Liquid Free Polymer Electrolyte

Ambient temperature-ionic conductivity study carried out using Electrochemical Impedance Spectroscopy (EIS). Figure 4.3 shows the Cole-Cole impedance plot of all SPE samples at room temperature. From the graphs, two different domains were observed. The two domains are observed which are linear domain and semicircular domain. Linear domain are seen at low frequency and semicircle domain at high frequency. The appearance of the two different domains was due to the effect of ion blocking effect in electrolytes and conduction of ions in the polymer bulk. The semicircular domain is not seen at the highest frequency domain. This is due to main current carriers in the samples are free moving ions. However, R_B, namely as bulk resistance is measured by extrapolation the semicircular region to the highest frequency, which also can be interpreted as the intercept between semi-circle and linear domain. The obtained bulk resistance is then substituted in Equation 3.1 to calculate ambient temperature-ionic conductivity values for respectively SPE samples. The results are shown in Figure 4.4 and 4.5.

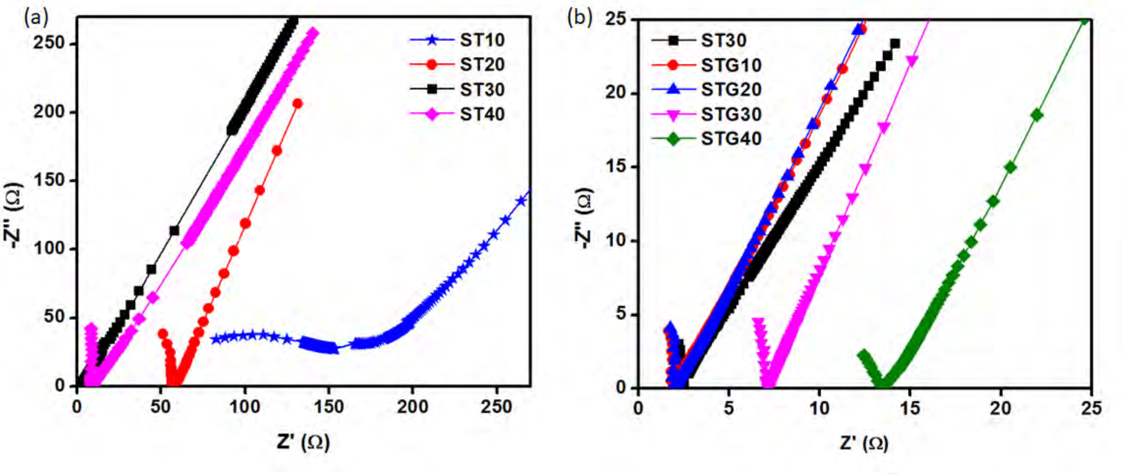


Figure 4.3: Nyquist plots of PVDF/LiClO$_4$/tetraglyme SPEs

Figure 4.4 describes the ionic conductivity of tetraglyme-free polymer electrolytes studied with different concentration of LiClO$_4$ (ST10 – ST40). Different mass ratios of PVDF-HFP to LiClO$_4$ studied to obtain the best mass ratio of PVDF-HFP to LiClO$_4$, which is to be used for tetraglyme-added polymer electrolytes.

The ionic conductivities of solid polymer electrolytes (SPEs) synthesized using PVDF-HFP with LiClO$_4$ salt increases with increasing percentage of LiClO$_4$ until reached maximum of 30 wt% LiClO$_4$. However, the ionic conductivity decreases at ST 40. This explains the ion aggregations that curbs the ions mobility and eventually reduces the ionic conductivity. These measurements serve as preliminary steps to investigate the effect of tetraglyme ratio in SPEs on its associated ionic conductivity. The mass ratio of PVDF-HFP and LiClO$_4$ salt in the investigated SPEs is described in Table 3.2.

Fundamentally, the ionic conductivity of the SPEs increases with increase in LiClO$_4$ concentration. The LiClO$_4$ salt dissociated into Li^+ cations and ClO_4^- anions upon mixing in PVDF-HFP/LiCIO$_4$ polymer matrix. The mobile charge carriers were then associated in the polymer electrolytes which led to ionic conduction process. From the above mentioned mechanism, it can be postulated that higher concentration of LiCIO$_4$ salt results in greater the number of free moving charge carriers, which led to higher ionic conductivity. However, low ionic conductivity of the SPEs at lower concentration of $LiClO_4$ certainly explains the relative presence of Li^+ cations available for ionic conduction in the SPE matrix reduced (Gohel & Kanchan, 2018; Ouhib et al., 2019).

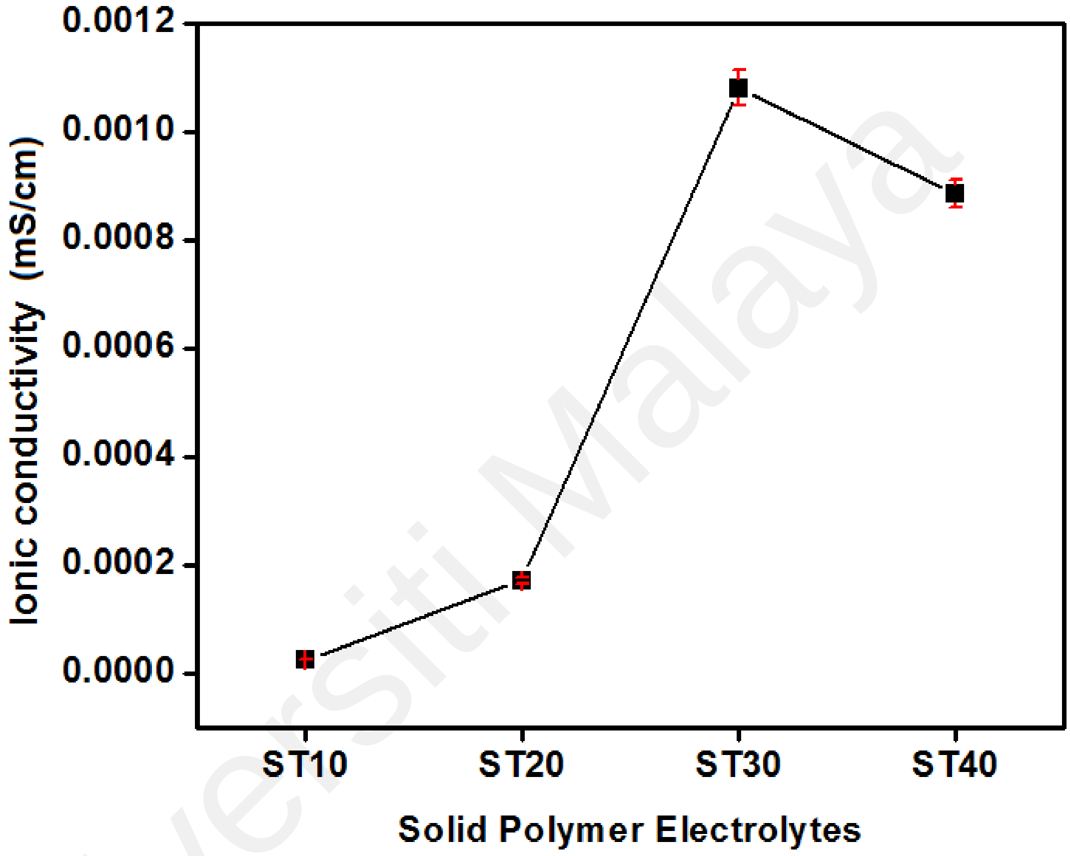


Figure 4.4: Ionic conductivity of PVDF-HFP/$LiClO_4$ SPE.

Figure 4.5 shows the ionic conductivity of PVDF-HFP with $LiClO_4$ salt at various wt % of tetraglyme. The details of sample labeling ST30(STG 0), STG10, STG20, STG30, and STG 40) has been described in Table 3.2, where ST30 has 0 wt% tetraglyme; STG10, STG20, STG30 and STG40 resembles 10, 20, 30, and 40 wt% of tetraglyme content.

From Figure 4.5, it can be observed that the ionic conductivity of PVDF-HFP/$LiClO_4$ mixture increased from 1.08 to 1.12 $mScm^{-1}$ upon inclusion of 10 wt.% tetraglyme

(STG10), and further increased to 1.34 Scm^{-1} when the weight percentage of the tetraglyme increased to 20 wt.% (STG20). The increase in ionic conductivity can be attributed to the plasticizing nature of tetraglyme additive, which soften the polymer and improved the ion transportation in the polymer phase. This aligned with previously-reported studies, where the ionic conductivity is significantly enhanced upon addition of tetraglyme additive into the SPE (Ouhib et al., 2019; Zhang et al., 2019). As the weight percentage of tetraglyme additive further increased to 30 and 40 wt.% (STG30 and STG40), the relative weight percentage of $LiClO_4$ salt reduced, which directly reduced the amount of Li^+ cations available for ionic conduction. Generally, the ionic conductivity of PVDF-HFP/$LiClO_4$ salt SPEs increased from ST30(STG0) to STG20 and reduced from STG20 to STG40.

Tetraglyme (tetraethylene glycol dimethyl ether) contains a glyme molecule that forms a complex ion with a Li^+ ion, $[Li(glyme)_1]^+$. Glyme molecules have strong solvating power due to chelating with a metal ion. Glymes is glycol diethers, which is miscible in both water and hydrocarbon solvents. Gylme consists of di, tri and tetraglyme according to their ether oxygen content. Tetraglyme binds more strongly with metal ions compared to di and triglyme. Effectively, glyme has the ability to solvate alkali cations. This is because glyme acts as a Lewis base and dissolves alkali salts, which forms Solvate Ionic Liquid complexes. Tetraglyme has the ability to form a complex ion due to the presence of lone pair electrons and therefore has the ability to form bidentate coordinate bonds with metal cations. An increase in ionic conductivity also relates to an increase in the concentration of $[Li(glyme)_1]^+$ complex ions. However, ionic conductivity is better at low concentration of tetraglyme and at further increase wt.% of tetraglyme at 30 % and beyond shows a decrease in ionic conductivity. This is mainly because high concentration of of tetraglyme causes rough morphology of Li ion deposition and dissolution cycling. This causes low Li cycling efficiency. Self-diffusion coefficient of each species in the solution decrease with the salt concentration (Bidin, Hon Ming, Omar, Ramesh, & Ramesh, 2018)

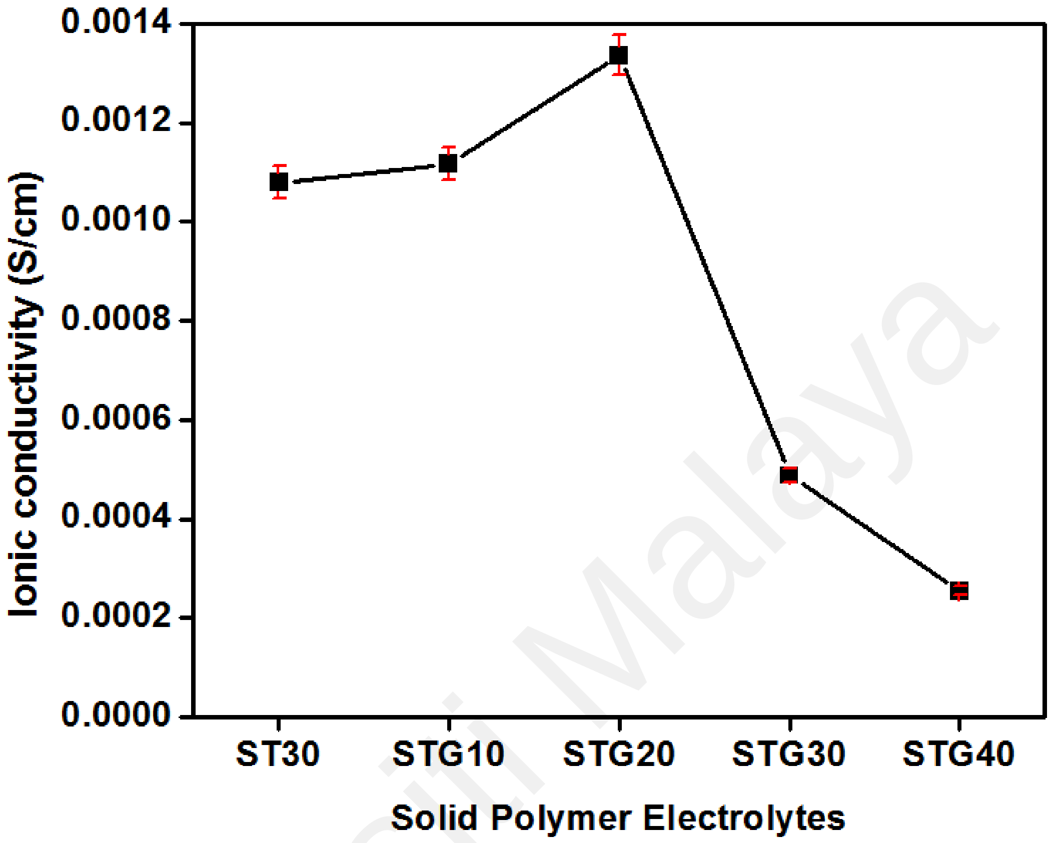


Figure 4.5: Ionic conductivity of PVDF-HFP/$LiClO_4$/tetraglyme SPE.

4.3.1 Temperature Dependent Ionic Conductivity

Temperature dependent ionic conductivity of SPE is critical in determining its key properties, such as the activation energy, and the temperature-dependability of ionic conductivity. Typically, there are two ionic mobility mechanisms in the temperature-dependent ionic conductivity of SPEs: Arrhenius mechanism and Vogel Tammann Fulcher (VTF) mechanism. In Arrhenius mechanism, log σ versus 1000/T graph is naturally linear/near-linear, reflecting its conduction model, where ionic particles disintegrated from segmental motion of polymer chain and diffused via hopping mechanism. On the other hand, in VTF mechanism, the log σ versus 1000/T graph nonlinear, reflecting its conduction model where hopping ionic particles were coupled from segmental motion of polymer chain. (Gohel & Kanchan, 2018; Okada, Ikeda, & Aniya, 2015; Perumal, Christopher Selvin, & Selvasekarapandian, 2018).

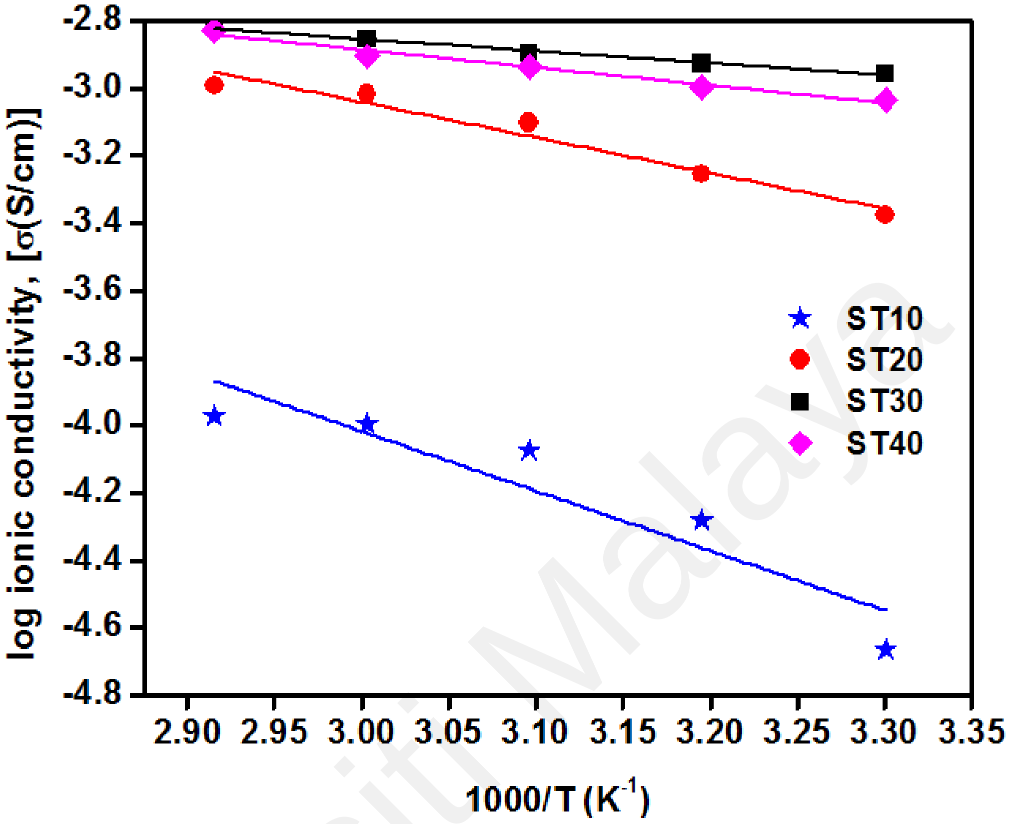


Figure 4.6: Temperature dependence of ionic conductivity of PVDF-HFP/LiClO4 SPE.

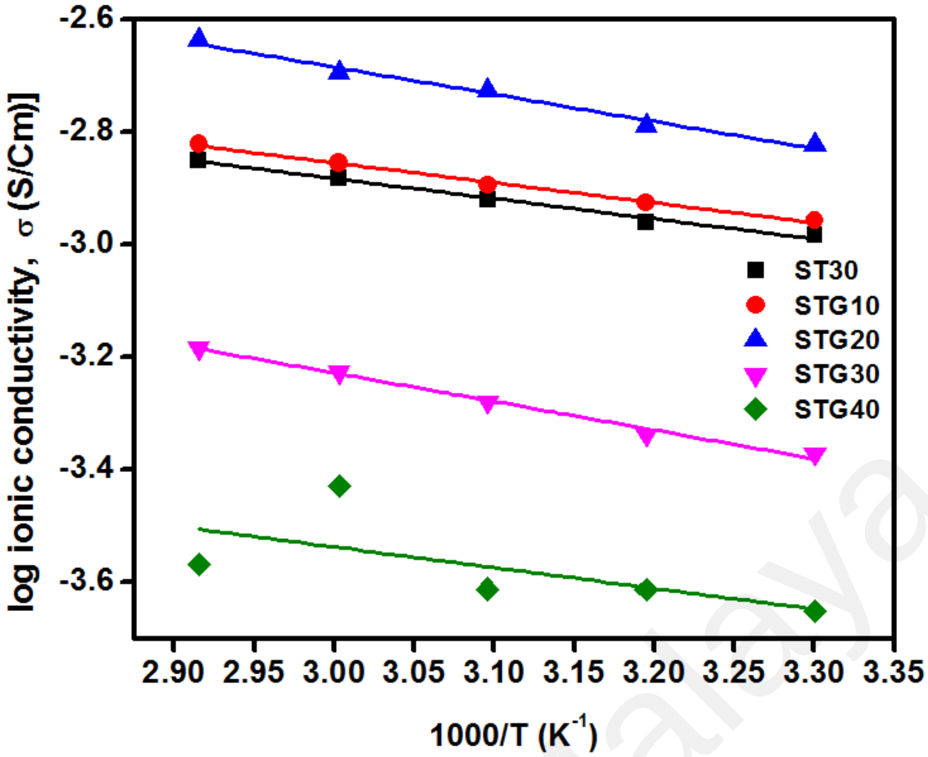


Figure 4.7: Temperature dependence of ionic conductivity of PVDF-HFP/LiClO4/tetraglyme SPE.

Figure 4.6 and 4.7 show the temperature dependence of ionic conductivity of PVDF-HFP/$LiClO_4$ and PVDF-HFP/$LiClO_4$-tetraglyme SPEs. From the plot, it is observed all SPEs exhibits increase in ionic conductivity as the temperature increases from 303 to 343K. When the temperature increases, the motion of ionic particles obtained a low-energy route for its motion, which increases the mobility of ionic particles in SPEs and their associated ionic conductivity (Gohel & Kanchan, 2018). At the same time, the kinetic energy gained by molecules in polymer at elevated temperatures disintegrates the low-energy bonding between oxygen atoms in pectin compound, and Li^+ cations (Perumal et al., 2018). Apart from the above mentioned possibilities, the concept of free volume also can be applied in explaining such phenomenon. At higher temperatures, the disintegrated polymer chains accommodate more free volume, increasing the movable space and mobilities of ion, leading to improved ionic conductivity. This will facilitate the movement of ions through the polymer matrix thereby increasing the conductivity of the SPEs (Isa et al., 2014). Combining the abovementioned mechanisms, it can be postulated that the increase in temperature further enhance the mobility of Li^+ cations in PVDF-HFP/$LiClO_4$ SPE, similar to the functional properties of tetraglyme additive as discussed in the previous section.

From Figure 4.6 and 4.7, it is observed that the log σ versus 1000/T plot follows a linear trend. This shows that the investigated PVDF-HFP/$LiClO_4$ SPE possesses Arrhenius behavior. The ionic conduction mechanism occurs via disintegration of the low-energy bonding between oxygen atoms in pectin compound, and Li^+ cations. The activation energy of the SPE can be computed using Arrhenius relation expressed in Equation 4.1:

$$\sigma = \sigma_0 exp\left(\frac{E_a}{kT}\right) \tag{4.1}$$

Where σ_0 is the pre-exponential factor, E_a is the activation energy, k is the Boltzmann constant and T is the temperature in Kelvin (Gohel & Kanchan, 2018; Jagadeesan et al., 2019). By fitting the linear plot in Figure 4.6 and 4.7 into Equation 4.1, the activation energy of the PVDF-HFP/$LiClO_4$ SPEs (STG30) is calculated to be 0.097 eV. The obtained activation energy compares favorably with the published studies on PVDF-HFP containing Li^+ cations (Gohel & Kanchan, 2017, 2018; Isa et al., 2014; Ulaganathan & Rajendran, 2010) ranges from 0.08 – 0.3 eV.

For typical ionic conduction in polymer-based SPEs, the activation energy correlates directly with its enthalpy of migration, which is the energy barrier where a particle (Li^+ cation in this case) should overcome in diffusion (Ouhib et al., 2019; Prabakaran, Mohanty, & Nayak, 2014). In this study, PVDF-HFP/$LiClO_4$ SPE with tetraglyme (sample STG30) exhibits low activation energy of 0.092 eV. This encouraging outcome can be attributed to the addition of tetraglyme, where the additives soften the polymer and improve ionic mobility, as discussed earlier. The softening of polymer matrix eases the diffusion of Li^+ cation in the matrix, which result in low activation energy. Nevertheless, the atomic interaction between Li^+ cations and PVDF-HFP polymer matrix shall be further investigated to have a comprehensive view of ionic motions in PVDF-HFP/$LiClO_4$ SPE.

4.4 Dielectric Studies

Dielectric study is carried out to describe about ion transport behavior and ionic/ molecular interactions. This was mainly due to ion hopping mechanism coupled with the segmental motion of the polymer chain. The broadband dielectric spectroscopy analysis of the PVDF-HFP: $LiClO_4$/tetraglyme electrolyte has been explained in view of the dielectric permittivity and dielectric modulus of the electrolytes. The dielectric properties were studied using real (Z') and Imaginary (Z") component of the complex impedance (Z*). Both Z' and Z" were used to calculate real(ε'), imaginary component (ε''), component of dielectric permittivity and loss tangent. Dielectric permittivity of the polymeric system presented by real and imaginary parts of the complex permittivity, ε_r^* which defined by the following Equation:

$$\varepsilon_r^* (\omega) = \varepsilon' (\omega) - j\varepsilon'' (\omega) \tag{4.2}$$

Where the real $\varepsilon' (\omega)$ is the dielectric constant and imaginary $\varepsilon'' (\omega)$ is the dielectric loss.

The dielectric constant explains the polarization of material that incurred during the formation of hetero-charge layer due to finite and reversible trapped ions accumulated at the electrode-electrolyte interface. The dielectric loss shows the energy lost due to oscillation of the ions and aligning of the dipoles of the charges for the each cycle of the applied electric field (Kumaran et al., 2018).

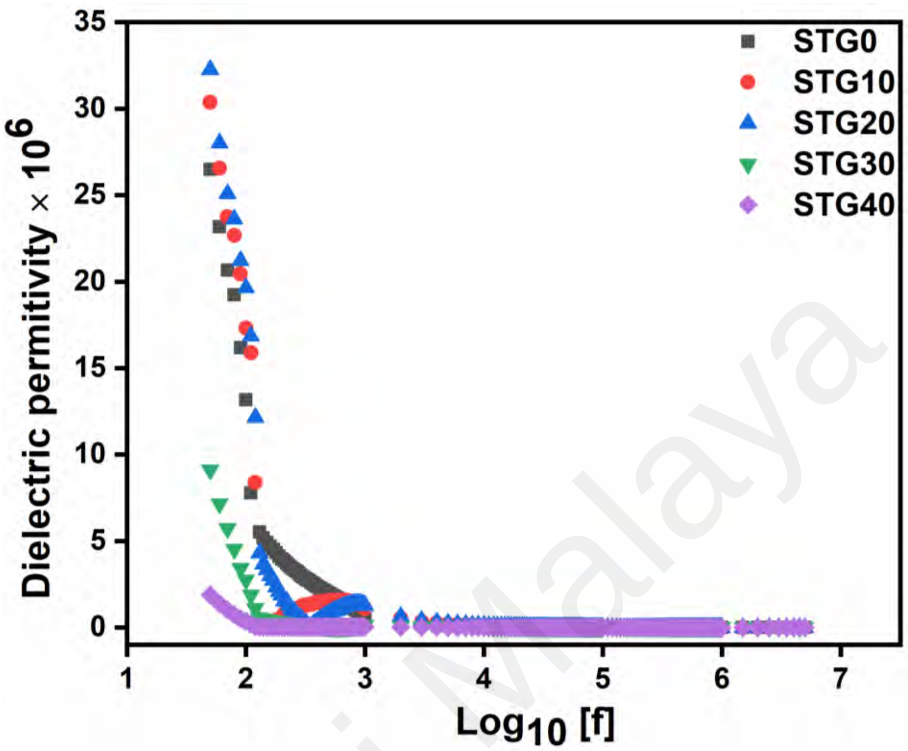


Figure 48: The dielectric permittivity (ε') versus log$_{10}$ [f] of different PVDF-HFP/LiClO$_4$/tetraglyme SPE at room temperature.

Figure 4.8 explains the relationship between the variation of real component which is dielectric constant ε' and frequency for SPE samples (STG 0, 10, 20, 30 and 40). The figure shows the values of dielectric constant ε' are high at a low frequency region at different wt.% of tetraglyme complexes. The dielectric constant provides measurement of reduction of coulomb interaction between the ion pairs. Hence, analysis of dielectric property provides the information such as characteristic of the ionic/molecular interaction of SPE. The values of dielectric constant ε' increases rapidly by polarization effect at low frequency region. High accumulation of charge carriers near the blocking electrodes due to free charges that build up at the interface between the material and electrodes. . Similarly, this also lead to increase in storage of dipoles electric charges per unit volume at low frequency region. When the frequency of applied alternating electric field was increased, the dielectric constant ε' decreased and showed a plateau at higher frequency region. This is mainly due to the periodic reversal of electric field occurs rapidly until there is no excess ion diffusion in the direction of the field. (Koduru et al., 2017).

The relationship of the dielectric loss ε'' with $\log_{10}$ [f] in Figure 4.9 shows the energy losses as the polarity of AC electric field reverses. The energy loss is due to the ion translational diffusion and the dipole orientation undergo deceleration and acceleration in the reverse directions. Eventually, the reverse polarization may cause the heating effect due to internal friction, which leads to dielectric loss as heat energy (Kumaran et al., 2018).

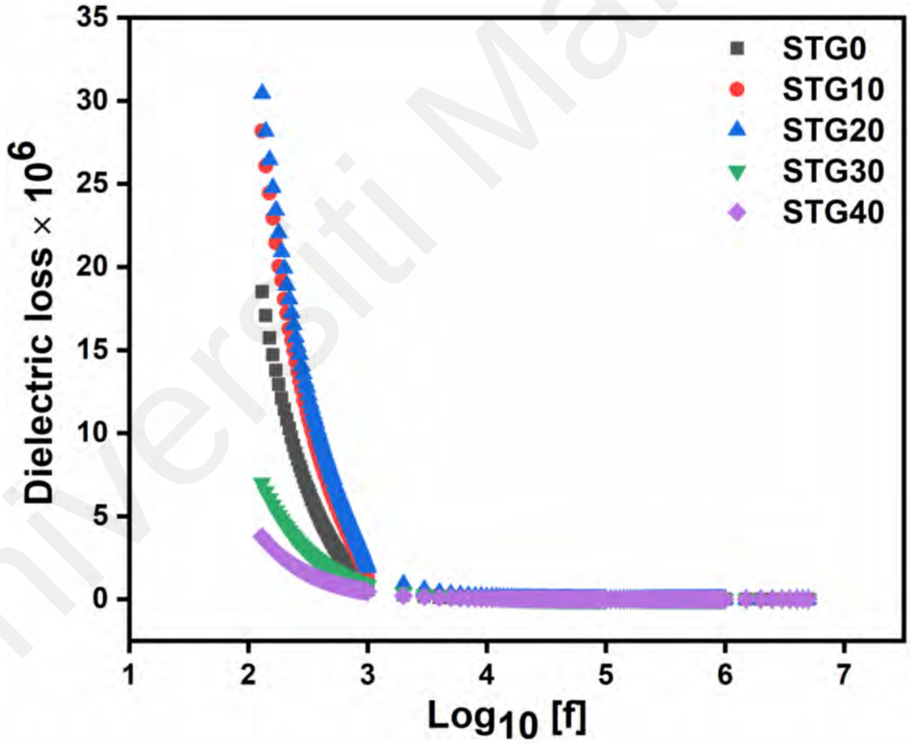


Figure 4.9: The dielectric loss (ε'') versus $\log_{10}$ [f] plot of different PVDF-HFP/LiClO$_4$/tetraglyme SPE at room temperature.

The dielectric loss increases with the addition of tetraglyme content. When there is large density of charge carriers undergo internal friction, thus generate huge amount of heat energy dissipation. However, at 30 wt.% of the tetraglyme concentration, dielectric loss showed a reducing value. As the concentration of tetraglyme goes beyond 30%, the dielectric showed further decrease. This reduced in dielectric loss is due to re-association of ion clusters (Kumaran et al., 2018).

The ratio of dielectric loss factor ε'' to the dielectric constant ε' is defined as loss tangent. It is given by Equation 4.3.

$$\tan\theta = \frac{\varepsilon''}{\varepsilon'} \tag{4.3}$$

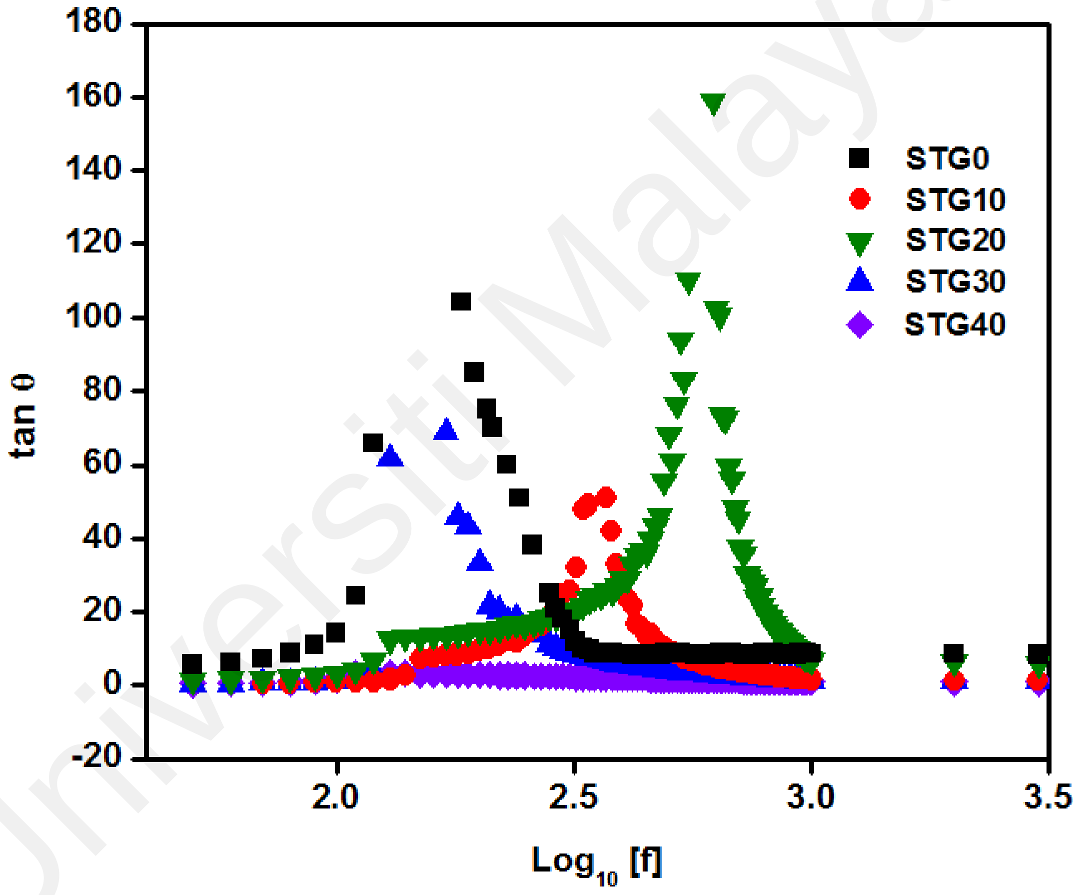


Figure 4.9: Variation of loss tangent versus $\log_{10}$ [f] plot of different PVDF-HFP/$LiClO_4$/tetraglyme SPE at room temperature.

Figure 4.10 shows loss tangent, tan δ curves for all the STG samples. Loss tangent, tan δ increases at lower frequency and eventually decreases at higher frequency region. Figure 4.10 also shows a frequency peak, which is the maximum value achieved f_m, in STG samples. The lost peak of tan θ describes the relaxation behavior in the polymer electrolytes. Relaxation behavior is a momentary delay as the charges and dipoles recover from their unperturbed state upon removal of AC stimulus. As the concentration of tetraglyme was incorporated, the amorphous region expands, and PVDF-HFP molecular structure became loose and weak. The polymeric chain becomes more flexible to orient, causing a ion polymer intermolecular interactions (Koduru et al., 2017). As the % of tetraglyme increases, the loss peak tan δ shifted towards higher frequency region with increasing salt content until 20%, thus reducing the relaxation time. It is often behave as the resonance effect of an oscillator. In general, a resonance dipolar relaxation is expected to occur when the frequency of the applied electric field is comparable to the characteristic or natural frequency of the dipoles (Kumaran et al., 2018).

By considering Debye Equation in an ideal case, and assuming the static dielectric constant and high frequency dielectric constant are almost the same, the relaxation time τ can be calculates from the frequency, $f_m$corresponding to the peak according to Equation 4.4.

$$\omega\tau = 2\pi\tau = 1 \tag{4.4}$$

Table 4.1: The peak frequency f_m, and the relaxation time τ designations.

Samples	Frequency, f_m (Hz)	Relaxation time,τ
STG 0	160	9.95×10^{-4}
STG 10	350	4.55×10^{-4}
STG 20	540	2.95×10^{-4}
STG 30	170	9.37×10^{-4}
STG 40	-	-

Table 4.1 shows that the lowest relaxation time 2.95×10^{-4} was achieved in STG 20 sample, which corresponds to the highest ionic conductivity, which agreeable with the conductivity results in Figure 4.5. The results for frequency f_m, for STG 40 was not derived as the peak was beyond the frequency range of measuring instrument due to low ionic conductivity.

The electric modulus, which introduced by Macedo et al is used to analyse the electrical relaxation processes. This analysis is carried out to understand the electrode polarization effect. The electric modulus (M^*) is defined by the Equation 4.4:

$$M^* = M' - jM'' = \frac{1}{\varepsilon_r^*} = \frac{1}{\varepsilon\prime - j\varepsilon''} \tag{4.4}$$

Where the M' and M'' are real and imaginary part of the complex electric modulus and it also explains the reciprocal of the complex relative permittivity as stated in 4.4.

In comparison, both plots of M' and M'' in Figure 4.11 and 4.12 show an increase at the higher frequency range and decrease at lower frequencies. They are well-defined dispersion peaks in M" plots which show features of an ionic conduction.

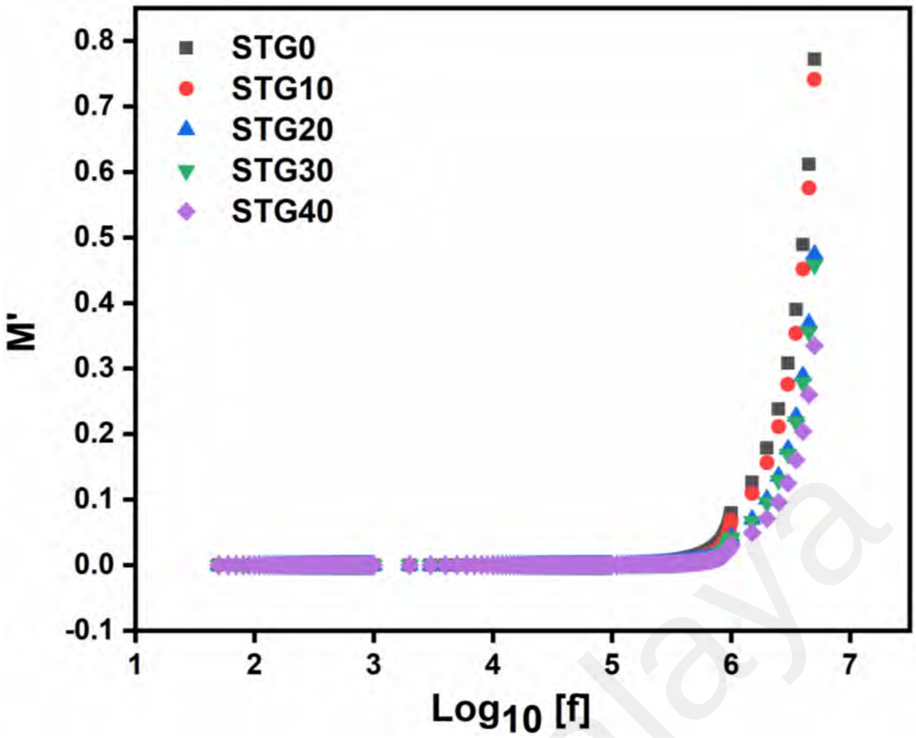


Figure 4.10: Variation of M' versus log f plot of PVDF-HFP/LiClO$_4$/tetraglyme SPE at room temperature.

In Figure 4.11, the trend shows that M' reaches zero at low frequency region, and this long tail is attributed to the large capacitance associated with the electrode polarisation. A similar results as A.K. Arof, over the higher frequency region, M' shows a sigmoidal shape for STG10 as the addition of tetraglyme, the overall spectra showed a shift to the right beyond the frequency window of this experiment, thus showing the dispersion part, which demonstrate the reverse conductivity trend (Kumaran et al., 2018).

Which can be described by the Kohlrausch-williams-Watts function given in Equation 4.5:

$$\varphi(t) = \varphi o exp(-\frac{t}{\tau})^{\beta} \; ; (0 < \beta < 1) \qquad (4.5)$$

Where τ and β are the conductivity relaxation time and the Kohlrausch exponent, respectively. The β parameter (corresponding to all the composition) has been estimated using the formula $\beta = 1.14$/full width at half maximum (FWHM), where the FWHM of the modulus peak displaying the stretched exponential function reveals the non-Debye behaviour of the materials which corresponds to long-time slow polarization and relation of hopping charges. As the increase in $LiClO_4$ salts, there was obvious increase in the value of β. This could be mainly due to an increase in charge carrier concentration.

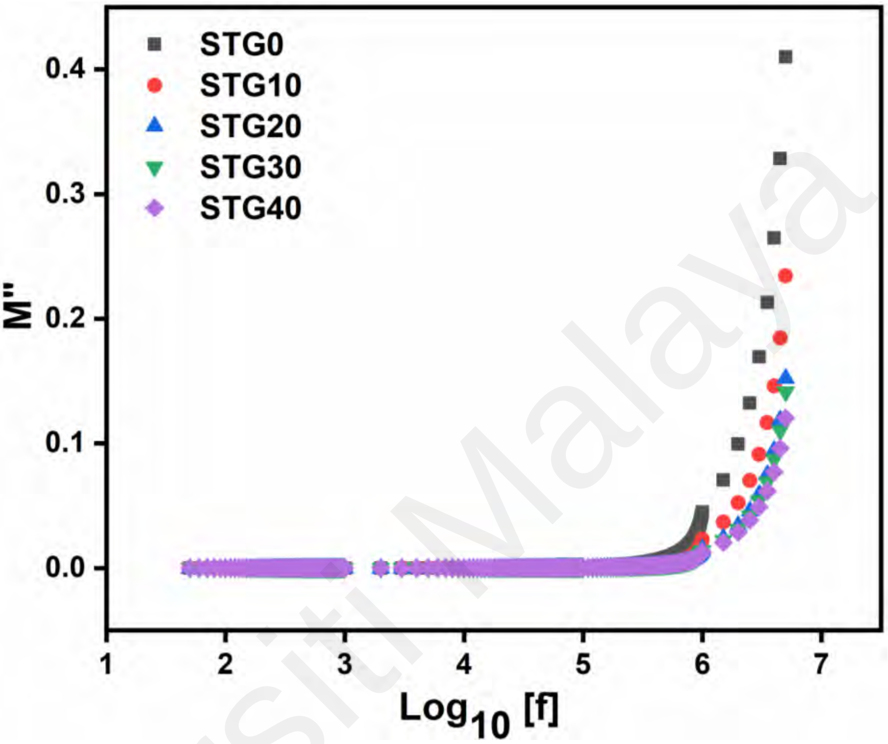


Figure 4.112: Variation of M" versus log f plot of PVDF-HFP/$LiClO_4$/tetraglyme SPE at room temperature.

4.5 Electrochemical Performance of EDLC

To explore the feasibility of PVDF-HFP/$LiClO_4$ SPEs in solid-state Electrical Double Layer Capacitors (EDLCs), Galvanostatic Charge-Discharge (GCD) performances of the SPEs are acquired. As described in Chapter 3, GCD testing is carried out by charging and discharging SPEs between two specified voltage points at a constant applied current. The obtained CV curve can be used to determine specific capacitance value (Cs) of SPEs

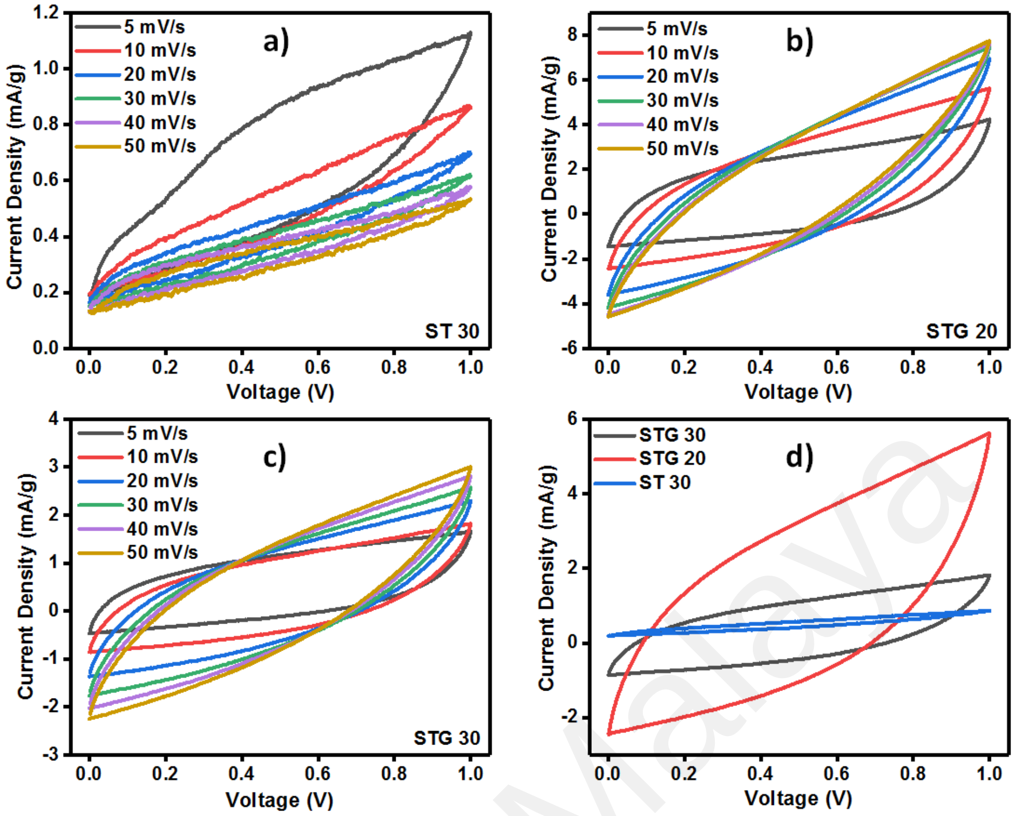


Figure 4.12: CVs of cells a) ST 30 (STG 0), b) STG 20 , c) STG 30, and d) comparison of CVs at 30 mV/s

The comparison of CV curves of PVDF-HFP/LiClO$_4$ SPEs at 30 mV/s for 0 wt.% tetraglyme (ST30), 20 wt.% tetraglyme (STG20) and 30%wt (STG30) tetraglyme based supercapacitor are shown in Figure 4.13 (a, b, & c). From Figure 4.13(b), it can be seen that STG20 SPE has wider integrated area in its CV curve as compared to ST30 (Figure 4.13 (a)) SPE. As indicated in Equation 4.2, this suggests that sample STG20 with 20 wt% tetraglyme additive possesses much higher specific capacitance as compared to sample ST30 with 0 wt% tetraglyme.

At various sweep rates, ST30 sample with 0 wt% tetraglyme exhibits randomized CV curve patterns, with irregular CV curve shapes and non-linear correlation between sweep rate and specific capacitance (Figure 4.13 (a)). Meanwhile, STG20 exhibits typical capacitance behaviors. From Figure 4.12(b), it can be observed that the CV curves of

STG20 have near-rectangular geometry. At the same time, the CV curves show mirror-image symmetry at the 0 mA/g current density line. These suggest the capacitive behavior of SPEs, aligned with the typical capacitive properties of EDLCs. At the same time, the near-rectangular shape of CV curves also suggest efficient ionic mobility and outstanding capacitance (Kumar, Pandey, & Hashmi, 2012). From the integrated area of the CV curves, it can be deduced that the specific capacitance of sample STG20 is 14.06 F/g increases with higher sweep rate, which aligns well with Equation 4.2 (Wang et al., 2018).

The capacitive behavior of EDLCs typically occurs in the electrochemical double layer (Helmholtz Layer) capacitor interlayer electrostatic forces. Attributing to the formation of dual-layer translational charges in the micro- and mesoporous structure of carbon-based polymer, EDLCs have high charging capability and low-lost charging-discharging cycles. To realize the application of SPEs in EDLCs, SPEs of high specific capacitance is required (Singh & Hashmi, 2017). From Figure 4.13, it can be observed that the specific capacitance of PVDF-HFP/$LiClO_4$ SPE increases upon addition of 20 wt% tetraglyme additive. The improvement in specific capacitance can be due to the improved mobility and lower activation energy of Li^+ cation in the PVDF-HFP/$LiClO_4$ matrix (Mauger et al., 2019), as discussed in section 4.1 and section 4.2. The improvement in specific capacitance yields from 0.11 F/g (ST 30) to 14.06 F/g (STG 20) shows promising potential of tetraglyme additive in PVDF-HFP/$LiClO_4$ SPEs, where the obtained outcomes can be further optimized to further realized its applicability in commercial EDLCs.

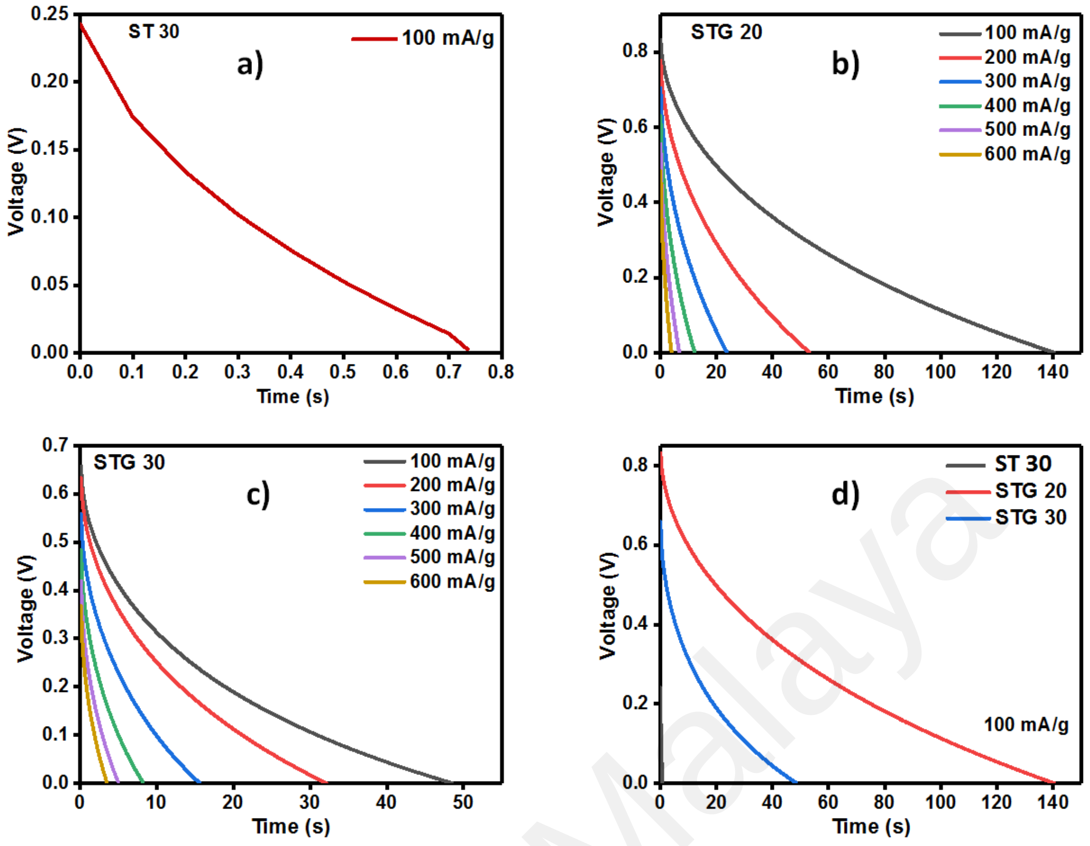


Figure 4.13: Galvanostatic discharge curves for EDLCs fabricated for both a) STG 20 and b) STG 30 SPEs at various current densities.

Figure 4.14 describes the galvanostatic discharge curves of the assembled supercapacitor cells at current densities of 100 mA/g, 200 mA/g, 300 mA/g, 400 mA/g, 500 mA/g and 600 mA/g at room temperature for the SPE sample with 0% wt, 20 wt.% and 30 wt.% of tetraglyme. It shows that 20 wt.% tetraglyme showed a best discharge time of the EDLC compared to ST30 and STG 30. This confirms that supercapacitors with 20 wt.% tetraglyme produced better capability of charge storage (Farah et al., 2019). From the electrochemical studies, STG 20 achieved the maximum specific capacitance of 14.06 F/g, which is larger than STG 30 (4.87 F/g) and ST30 (0.11 F/g) at 100 mA/g.

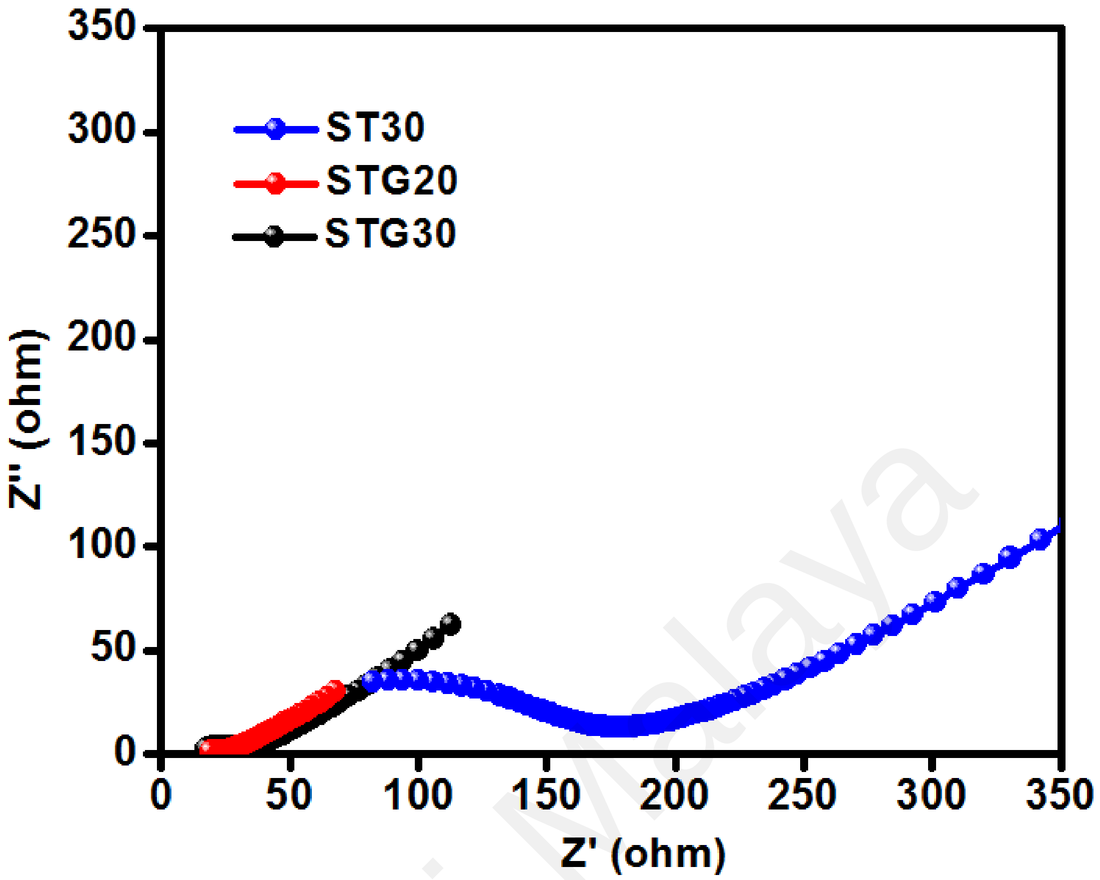


Figure 4.14: Nyquist Plots for EDLCs fabricated by using ST30, STG20 and STG30 SPE.

The EIS measurements (Nyquist plot) were plotted for ST30, STG20. STG30 supercapacitor cells in the range from 0.01 to 1 MHz, as shown in Figure 4.15. All three samples able to perform small semicircle at low frequency region and establish inclined spike at high frequency range. The first intersecting point of Nyquist plot to real axis at low frequency is studied as series resistance. This series resistance originated due to the internal resistance, resistance due to connecting wire and the connections. The Nyquist plot is known to have second intersecting plot (R_{ct}) against the real axis, which is due to the resistance of charge transfer between electrode and electrolyte. The plot shows an incline line as the frequency increases, which linked with capacitive behaviour of the device, which exhibits adsorption and intercalation charges. STG 20 SPE supercapacitor performed the highest spike indicates large charge accumulation at the electrode-electrolyte boundary (Farah et al., 2019).

4.6 Summary

Electrical and structural characterizations were carried out on PVDF-HFP/LiCIO$_4$ SPEs, and tetraglyme-based PVDF-HFP/LiCIO$_4$ SPEs with various weight percentages. The ionic conductivity of PVDF-HFP/LiCIO$_4$ SPEs increases from 1.08 to 1.12 x 10^{-7} Scm^{-1} when 10 wt.% of tetraglyme is added into the polymer matrix, reaching its peak at 1.34 Scm^{-1} (20 wt.%) before dropping to ~0.23 Scm^{-1} as the weight percentage of tetraglyme increases further to 40 wt.%. The temperature-dependent ionic conductivity of PVDF-HFP/LiCIO$_4$/tetraglyme matrix shows Arrhenius behavior, where low activation energy of 0.092 eV is obtained. The obtained FTIR outcomes contribute a preliminary understanding on the effect of tetraglyme and Li$^+$ ion addition towards the FTIR characteristics of PVDF-HFP. The shifting and reducing in intensity of the peaks indicate that the complexation between polymer PVDF-HFP and LiClO$_4$ and tetraglyme. XRD outcomes preliminary infers that Li$^+$ ions homogeneously dissolved in PVDF-HFP, which gives a positive impact on its ionic conductivity. The GCD characterizations on the PVDF-HFP/LiCIO$_4$/tetraglyme SPEs show that the addition of tetraglyme additives into PVDF-HFP/ LiCIO$_4$ matrix enhances its specific capacitance, as observed from the CV curves. From the electrochemical studies, STG 20 achieved the maximum specific capacitance of 14.06 F/g, which is larger than STG 30 (4.87 F/g) and ST30 (0.11 F/g) at 100 mA/g suggests fast transport of electrolyte ions. The improvement in specific capacitance of PVDF-HFP/LiCIO$_4$/tetraglyme SPEs demonstrates a promising insight, which can be further developed to enhance the applicability of PVDF-HFP/LiCIO$_4$ matrix in commercial EDLCs.

CHAPTER 5: CONCLUSION

5.1 Conclusion

The main purpose of this study is to find the most compatible ratio of tetraglyme blended with PVDF-HFP into the polymer electrolyte based $LiClO_4$ system. Effect of adding tetraglyme is investigated by varying different weight ratios (from 10% to 40%) of tetraglyme. Several important characterization studies have been done to study the electrical and electrochemical properties of the electrolyte. STG 20 achieved the highest ionic conductivity in the polymer blend system. Maximum ionic conductivity at room temperature is found to be 1.12×10^{-7} Scm^{-1} (ST 30) whereas with the addition of tetraglyme it is 1.34×10^{-3} Scm^{-1} for STG 20. XRD analysis confirms the STG20 has achieved the highest amorphous nature which gives a positive impact on its ionic conductivity. XRD also outcomes preliminary infers that Li^+ ions and tetraglyme additive homogeneously dissolved in PVDF-HFP, FTIR study reveals the shifting of the bands, signifying the formation of complex among PVDF-HFP, Li^+ ion and tetraglyme. From the electrochemical studies, STG 20 achieved the maximum specific capacitance of 14.06 F/g, which is larger than STG 30 (4.87 F/g) and ST30 (0.11 F/g) at 100 mA/g.

5.2 Future work

Further investigation can be carried out to improve the performances of copolymer PVDF-HFP/$LiClO_4$/tetraglymes for EDLC application. This can be done by incorporating nanoparticles such as carbon nanotubes (CNTs) and graphene oxides (GO). The addition of nanoparticles will be able to increase the stability and ionic conductivity of SPEs. Other than that, the SPE made of PVDF-HFP/$LiClO_4$/tetraglymes is also can be converted to gel polymer electrolyte (GPE) to enhance the conductivity of the polymer since SPE has lower ionic conductivity. GPE has a better contact with an electrode compared to the SPE. Besides that, the developed SPE also can be fabricated in other electrochemical devices such as battery, supercapacitor and supercapattery.

REFERENCES

Akiyama, Y., Sodaye, H., Shibahara, Y., Honda, Y., Tagawa, S., & Nishijima, S. (2010). Study on degradation process of polymer electrolyte by solution analysis. *Journal of Power Sources, 195*(18), 5915-5921.

Angulakshmi, N., Thomas, S., Nahm, K. S., Stephan, A. M., & Elizabeth, R. N. (2011). Electrochemical and mechanical properties of nanochitin-incorporated PVDF-HFP-based polymer electrolytes for lithium batteries. *Ionics*, *17*(5), 407-414.

Aziz, S. B., & Abidin, Z. H. Z. (2013). Electrical conduction mechanism in solid polymer electrolytes: new concepts to arrhenius equation. *Journal of Soft Matter, 2013*, 1-8

Aziz, S. B., Woo, T. J., Kadir, M., & Ahmed, H. M. (2018). A conceptual review on polymer electrolytes and ion transport models. *Journal of Science: Advanced Materials and Devices, 3*(1), 1-17.

Baskaran, R., Selvasekarapandian, S., Kuwata, N., Kawamura, J., & Hattori, T. (2006). Conductivity and thermal studies of blend polymer electrolytes based on PVAc–PMMA. *Solid state ionics, 177*(26-32), 2679-2682.

Baskaran, R., Selvasekarapandian, S., Kuwata, N., Kawamura, J., & Hattori, T. (2007). Structure, thermal and transport properties of PVAc–LiClO4 solid polymer electrolytes. *Journal of Physics and Chemistry of Solids, 68*(3), 407-412.

Bidin, M. Z., Hon Ming, N., Omar, F. S., Ramesh, K., & Ramesh, S. (2018). Solid terpolymer electrolyte based on poly (vinyl butyral-co-vinyl alcohol-co-vinyl acetate) incorporated with lithium salt and tetraglyme for EDLCs. *Journal of Applied Polymer Science, 135*(8), 45902(1-7).

Boota, M., & Gogotsi, Y. (2019). MXene—conducting polymer asymmetric pseudocapacitors. *Advanced Energy Materials, 9*(7), 1802917(1-8)

Braun, D., Cherdron, H., Rehahn, M., Ritter, H., & Voit, B. (2012). *Polymer synthesis: theory and practice: fundamentals, methods, experiments*: Springer Science & Business Media.

Chandra, A. (2016). Hot-pressed PEO-PVP blended solid polymer electrolytes: ion transport and battery application. *Polymer Bulletin, 73*(10), 2707-2718.

Chandra, M. V. L., Karthikeyan, S., Selvasekarapandian, S., Premalatha, M., & Monisha, S. (2017). Study of PVAc-PMMA-LiCl polymer blend electrolyte and the effect of plasticizer ethylene carbonate and nanofiller titania on PVAc-PMMA-LiCl polymer blend electrolyte. *Journal of Polymer Engineering, 37*(6), 617-631.

Chen, X., Xie, Y., Ling, Y., Zhao, J., Xu, Y., Tong, Y., . . . Wang, Y. (2020). Ionic liquid crystal induced morphological control of solid composite polymer electrolyte for lithium-ion batteries. *Materials & Design*, 108760 (1-8).

Choi, N.-S., & Park, J.-K. (2001). New polymer electrolytes based on PVC/PMMA blend for plastic lithium-ion batteries. *Electrochimica Acta, 46*(10-11), 1453-1459.

Cowie, J., & Spence, G. (1999). Novel single ion, comb-branched polymer electrolytes. *Solid State Ionics, 123*(1-4), 233-242.

Das, S., & Ghosh, A. (2017). Solid polymer electrolyte based on PVdF-HFP and ionic liquid embedded with TiO2 nanoparticle for electric double layer capacitor (EDLC) application. *Journal of The Electrochemical Society, 164*(13), F1348-F1353.

Ding, J., Chuy, C., & Holdcroft, S. (2002). Solid Polymer Electrolytes Based on Ionic Graft Polymers: Effect of Graft Chain Length on Nano-Structured, Ionic Networks. *Advanced Functional Materials, 12*(5), 389-394.

Devaux, D., Glé, D., Phan, T. N., Gigmes, D., Giroud, E., Deschamps, M., ... & Bouchet, R. (2015). Optimization of block copolymer electrolytes for lithium metal batteries. *Chemistry of Materials*, *27*(13), 4682-4692.

Fahmy, T., & Ahmed, M. (2001). Thermal induced structural change investigations in PVC/PEMA polymer blend. *Polymer Testing, 20*(5), 477-484.

Farah, N., Ng, H., Numan, A., Liew, C.-W., Latip, N., Ramesh, K., & Ramesh, S. (2019). Solid polymer electrolytes based on poly (vinyl alcohol) incorporated with sodium salt and ionic liquid for electrical double layer capacitor. *Materials Science and Engineering: B, 251*, 114468.

Guan, K. H., Farhana, N. K., Omar, F. S., Saidi, N. M., Bashir, S., Ramesh, S., & Ramesh, K. (2020). Influence of tetraglyme towards magnesium salt dissociation in solid polymer electrolyte for electric double layer capacitor. *Journal of Polymer Research, 27*(5).

Guilherme, L., Borges, R., Moraes, E. M. S., Silva, G. G., Pimenta, M., Marletta, A., & Silva, R. (2007). Ionic conductivity in polyethylene-b-poly (ethylene oxide)/lithium perchlorate solid polymer electrolytes. *Electrochimica Acta, 53*(4), 1503-1511.

Jannasch, P. (2000). Synthesis of novel aggregating comb-shaped polyethers for use as polymer electrolytes. *Macromolecules, 33*(23), 8604-8610.

Khanmirzaei, M. H., Ramesh, S., & Ramesh, K. (2015). Polymer electrolyte based dye-sensitized solar cell with rice starch and 1-methyl-3-propylimidazolium iodide ionic liquid. *Materials & Design, 85*, 833-837.

Koduru, H., Marino, L., Scarpelli, F., Petrov, A., Marinov, Y., Hadjichristov, G., . . . Scaramuzza, N. (2017). Structural and dielectric properties of NaIO4–complexed PEO/PVP blended solid polymer electrolytes. *Current Applied Physics, 17*(11), 1518-1531.

Kumar, M. S., & Bhat, D. K. (2009). Polyvinyl alcohol–polystyrene sulphonic acid blend electrolyte for supercapacitor application. *Physica B: Condensed Matter, 404*(8-11), 1143-1147.

Kumaran, V. S., Ng, H., Ramesh, S., Ramesh, K., Vengadaesvaran, B., & Numan, A. (2018). The conductivity and dielectric studies of solid polymer electrolytes based on poly (acrylamide-co-acrylic acid) doped with sodium iodide. *Ionics, 24*(7), 1947-1953.

Lee, L., Park, S.-J., & Kim, S. (2013). Effect of nano-sized barium titanate addition on PEO/PVDF blend-based composite polymer electrolytes. *Solid State Ionics, 234*, 19-24.

Li, S., Chen, Y.-M., Liang, W., Shao, Y., Liu, K., Nikolov, Z., & Zhu, Y. (2018). A superionic conductive, electrochemically stable dual-salt polymer electrolyte. *Joule, 2*(9), 1838-1856.

Mohan, K. R., Achari, V., Rao, V., & Sharma, A. (2011). Electrical and optical properties of (PEMA/PVC) polymer blend electrolyte doped with NaClO4. *Polymer Testing, 30*(8), 881-886.

Nicotera, I., Coppola, L., Oliviero, C., Castriota, M., & Cazzanelli, E. (2006). Investigation of ionic conduction and mechanical properties of PMMA–PVdF blend-based polymer electrolytes. *Solid State Ionics, 177*(5-6), 581-588.

Rahaman, M. H. A., Khandaker, M. U., Khan, Z. R., Kufian, M. Z., Noor, I. S. M., & Arof, A. K. (2014). Effect of gamma irradiation on poly (vinyledene difluoride)–lithium bis (oxalato) borate electrolyte. *Physical Chemistry Chemical Physics, 16*(23), 11527-11537.

Rajendran, S., Mahendran, O., & Kannan, R. (2002). Lithium ion conduction in plasticized PMMA–PVdF polymer blend electrolytes. *Materials Chemistry and Physics, 74*(1), 52-57.

Rajendran, S., Sivakumar, M., & Subadevi, R. (2004). Investigations on the effect of various plasticizers in PVA–PMMA solid polymer blend electrolytes. *Materials Letters, 58*(5), 641-649.

Rajendran, S., Sivakumar, M., Subadevi, R., & Nirmala, M. (2004). Characterization of PVA–PVdF based solid polymer blend electrolytes. *Physica B: Condensed Matter, 348*(1-4), 73-78.

Rajendran, S., & Uma, T. (2000). Conductivity studies on PVC/PMMA polymer blend electrolyte. *Materials Letters, 44*(3-4), 242-247.

Ramesh, S., & Wong, K. (2009). Conductivity, dielectric behaviour and thermal stability studies of lithium ion dissociation in poly (methyl methacrylate)-based gel polymer electrolytes. *Ionics, 15*(2), 249-254.

Singh, M. K., & Hashmi, S. (2017). Performance of solid-state hybrid supercapacitor with LiFePO 4/AC composite cathode and Li 4 Ti 5 O 12 as anode. *Ionics, 23*(10), 2931-2942.

Sivakumar, M., Subadevi, R., Rajendran, S., Wu, N.-L., & Lee, J.-Y. (2006). Electrochemical studies on [(1− x) PVA–xPMMA] solid polymer blend electrolytes complexed with LiBF4. *Materials Chemistry and Physics, 97*(2-3), 330-336.

Song, Y., Wu, S., Jing, X., Sun, J., & Chen, D. (1997). Thermal, mechanical and ionic conductive behaviour of gamma-radiation induced PEO/PVDF (SIN)-LiClO4 polymer electrolyte system. *Radiation Physics and Chemistry, 49*(5), 541-546.

Soo, P. P., Huang, B., Jang, Y. I., Chiang, Y. M., Sadoway, D. R., & Mayes, A. M. (1999). Rubbery block copolymer electrolytes for solid-state rechargeable lithium batteries. *Journal of The Electrochemical Society, 146*(1), 32-37.

Souquet, J.-L., Nascimento, M. L. F., & Rodrigues, A. C. M. (2010). Charge carrier concentration and mobility in alkali silicates. *The Journal of Chemical Physics, 132*(3), 034704.

Stephan, A. M., Nahm, K. S., Kulandainathan, M. A., Ravi, G., & Wilson, J. (2006). Poly (vinylidene fluoride-hexafluoropropylene)(PVdF-HFP) based composite electrolytes for lithium batteries. *European Polymer Journal, 42*(8), 1728-1734.

Stephan, A. M., Thirunakaran, R., Renganathan, N., Sundaram, V., Pitchumani, S., Muniyandi, N., . . . Ramamoorthy, P. (1999). A study on polymer blend electrolyte based on PVC/PMMA with lithium salt. *Journal of Power Sources, 81*, 752-758.

Su, N. C., Noor, S. A. M., Roslee, M. F., Mohamed, N. S., Ahmad, A., & Yahya, M. Z. A. (2019). Potential complexes of NaCF 3 SO 3-tetraethylene dimethyl glycol ether (tetraglyme)-based electrolytes for sodium rechargeable battery application. *Ionics*, *25*(2), 541-549.

Tamilselvi, P., & Hema, M. (2014). Conductivity studies of LiCF3SO3 doped PVA: PVdF blend polymer electrolyte. *Physica B: Condensed Matter, 437*, 53-57.

Tan, C. Y., Farhana, N., Saidi, N. M., Ramesh, S., & Ramesh, K. (2018). Conductivity, dielectric studies and structural properties of P (VA-co-PE) and its application in dye sensitized solar cell. *Organic Electronics, 56*, 116-124.

Tao, C., Gao, M.-H., Yin, B.-H., Li, B., Huang, Y.-P., Xu, G., & Bao, J.-J. (2017). A promising TPU/PEO blend polymer electrolyte for all-solid-state lithium ion batteries. *Electrochimica acta, 257*, 31-39.

Theerthagiri, J., Senthil, R., Buraidah, M., Madhavan, J., & Arof, A. K. (2015). Effect of tetrabutylammonium iodide content on PVDF-PMMA polymer blend electrolytes for dye-sensitized solar cells. *Ionics, 21*(10), 2889-2896.

Tiruye, G. A., Muñoz-Torrero, D., Palma, J., Anderson, M., & Marcilla, R. (2016). Performance of solid state supercapacitors based on polymer electrolytes containing different ionic liquids. *Journal of Power Sources, 326*, 560-568.

Ulaganathan, M., & Rajendran, S. (2010). Preparation and characterizations of PVAc/P (VdF-HFP)-based polymer blend electrolytes. *Ionics, 16*(6), 515-521.

Wilson, J., Ravi, G., & Kulandainathan, M. A. (2006). Electrochemical studies on inert filler incorporated poly (vinylidene fluoride-hexafluoropropylene)(PVDF-HFP) composite electrolytes. *Polimeros, 16*(2), 88-93.

Wright, P. V. (1975). Electrical conductivity in ionic complexes of poly (ethylene oxide). *British Polymer Journal, 7*(5), 319-327.

Wu, F., Feng, T., Bai, Y., Wu, C., Ye, L., & Feng, Z. (2009). Preparation and characterization of solid polymer electrolytes based on PHEMO and PVDF-HFP. *Solid State Ionics, 180*(9-10), 677-680.

Yang, Y., Zhou, C.-h., Xu, S., Hu, H., Chen, B.-l., Zhang, J., . . . Zhao, X.-z. (2008). Improved stability of quasi-solid-state dye-sensitized solar cell based on poly (ethylene oxide)–poly (vinylidene fluoride) polymer-blend electrolytes. *Journal of Power Sources, 185*(2), 1492-1498.

Ye, Y.-S., Rick, J., & Hwang, B.-J. (2012). Water soluble polymers as proton exchange membranes for fuel cells. *Polymers, 4*(2), 913-963.

Zhang, Z., Jin, J., Bautista, F., Lyons, L., Shariatzadeh, N., Sherlock, D., . . . West, R. (2004). Ion conductive characteristics of cross-linked network polysiloxane-based solid polymer electrolytes. *Solid State Ionics, 170*(3-4), 233-238.