CHAPTER 1

INTRODUCTION

1.1 INTRODUCTION

Solid state materials have become the driving force for the pace of today's society. It would be no exaggeration to say that we are in the midst of materials revolution. Material scientists have responded to the needs of the industry from time to time. Solid state devices are based on material modification and tailor-made production.

The development of polymeric systems with high ionic conductivity is one of the main objectives in polymer research. This is due to their potential application as an electrolyte and as a separator in electrochemical devices. Among the polymer electrolyte systems, solid polymer electrolytes have many advantages like high ionic conductivity, high energy density, solvent-free condition, leak-proof, wide electrochemical stability windows, ease of processability and light in weight. Generally, ionic conduction in polymer electrolytes is dominated by the amorphous elastomeric phase.

In the present study, greener alternatives were driven to fabricate biodegradable polymer electrolytes by employing naturally occurring polymer namely corn starch. This contraption was developed to be used in electrochemical devices such as solar cells, fuel cells, electrochromic windows, lithium batteries and electric double layer capacitors. This type of electronic devices require successively high ionic conducting medium that enables it to function at ambient temperature. The main objective of this work is to develop and characterize corn starch based polymer electrolytes (PEs) with lithium perchlorate (LiClO₄) as salt, silica (SiO₂) and barium titanate (BaTiO₃) as the composite fillers. All the samples were prepared via solution casting technique. A literature review giving state of the art about current development of polymer electrolytes, in particular, is presented in Chapter 2. Chapter 3 illustrates the preparation of PEs and experimental methods. Selection of characterization technique for the polymer electrolytes in present studies will be discussed as well.

The variation in the polymer electrolytes properties upon doping with different amounts of filler were evaluated by subjecting to several different types of characterization techniques that being tested on structural, electrical and thermal properties. The preliminary studies of surface morphology will be analyzed using scanning electron microscopy (SEM). The ionic conductivity of all the samples will be measured by impedance spectroscopy. Thermal properties are important in determining the suitability of the polymer electrolyte to be used in EDLC application. Therefore, differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) will be carried out. Prepared polymer electrolytes film will be subjected to degree of swelling test to determine the water solubilities of the polymer film.

The effect of LiClO₄, SiO₂ and BaTiO₃ upon addition into corn starch based polymer electrolyte systems will be presented in Chapter 4, 5 and 6 respectively. The electrolytes that exhibit the highest ionic conductivity will be used to fabricate the electrochemical cells. Prior to the EDLC analysis, working voltage of the samples will be measured by linear sweep voltammetry (LSV). The EDLC performance will be illustrated in chapter 7. Chapter 8 presents a complete discussion of the study and chapter 9 gives an overall conclusion with suggestion for future studies.

CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTION

The term 'polymer' was originated from the Greek word where the word *poly* correlates to 'many' while *mer* refers to 'part'. A polymer is a long-chain molecule composed of a large number of identical repeating units. Examples of natural polymers are cellulose, starch, pectin, chitin, protein and silk while artificial polymers include polystyrene, nylon, polyethylene, and polycarbonate. Generally, polymers are insulators since their conductivity is very low $(10^{-12} \text{ to } 10^{-18} \text{ S cm}^{-1})$. However, the development of polymer electrolyte has led to high ionic conductivity in polymers $(10^{-2} \text{ to } 10^{-4} \text{ S cm}^{-1})$ [Appetecchi *et al.*, 1999; Dias *et al.*, 2000].

2.2 POLYMER ELECTROLYTE

Polymer electrolyte may be defined as a solvent free system where the ionically conducting phase is formed by dissolving salts in a high molecular weight polar polymer matrix. Dissolution of the salt in a polymer matrix provides ions that contribute to ionic conductivity of the polymer electrolyte. The fundamental of ionic conduction in the polymer electrolytes is the covalent bonding between the polymer backbones with the ionizing groups from the low lattice energy metal salts. The dissolving of dopant salt forms both cation and anion component in the polymer. The ionic conduction of polymer electrolytes arises from strong Lewis acid-base interaction between cation and donor atom with rapid segmental motion of polymer matrix [Ganesan *et al.*, 2008].

In the late 1960s and early 1970s, research into new materials with high ionic mobility intensified. Polymer electrolyte was discovered as early as 1975 by Wright [Wright, 1975]. The flexibility of the polymeric material allows dimensions changes to be accommodated on intercalation/deintercalation but this is not possible with rigid electrolytes. This relatively latecomer of polymer electrolyte to the broader field of solid state ionics has attracted numerous interest on it.

Polymer electrolytes are widely used in the applications of electronic devices. This utilization was stimulated by a number of listed advantages that potentially offered by solid and gel polymer electrolytes when compared to their liquid counterparts: (1) excellent processability and flexibility that could enable the fabrication of ultra thin lithium cells so that high energy and power density could be achieved for versatile applications, (2) safer due to the absence of flammable organic solvents and the much lower reactivity toward lithium, (3) the possible prevention of the growth of lithium dendrite crystals upon cycling, (4) the high dimensional stability that could lead to the elimination of a separator, so further improvement in both energy density and manufacturing cost could be achieved due to the simplified cell configuration and enhanced packing efficiency. SPEs do possess other advantages such as being low profile, solvent free condition, flexible, light weight and also less chance for electrolytes leakage [Ramesh *et al.*, 2001; Dias *et al.*, 2000]. Polymer electrolyte is generally classified into three major types, namely solid polymer electrolyte, gel polymer electrolyte and composite polymer electrolyte.

2.2.1 Solid polymer electrolyte (SPE)

Polymer based solid electrolytes are of growing importance in solid state electrochemistry in view of their application, the most important of which is for high energy density batteries used in electric vehicle (EV), start-light-ignition (SLI), portable electronic and personal communication. The first suggestion for the use of poly(ethylene oxide), PEO based electrolyte came in 1975. Ever since Armand proposed the application of SPE to lithium batteries, the research and development effort has been made throughout the world. SPE serves three principal roles in lithium battery. Firstly it acts as electrode spacer that insulates the anode from the cathode in the battery. Secondly, it plays the role as lithium ion carriers to generate ionic conductivity which ions are transported between the anode and cathode during charging and discharging. It also works as binders to ensure good electrical contact with electrodes. Other than that, SPE possesses high specific energy, solvent-free, wide electrochemical stability window and ease of processability [Kim and Kim, 1999].

Most of the extensively studied solid polymer electrolytes are based on poly(ethylene oxide) (PEO) and lithium salts [Itoh *et al.*, 2003; Marzantowicz *et al.*, 2011; Sun *et al.*, 2000]. SPEs have improved safety for lithium battery compared to conventional liquid electrolytes, but they are well known to result with insufficient performance especially due to low ionic conductivity [Huang *et al.*, 2012; Hamaide *et al.*, 1993; Zhang *et al.*, 2011].

2.2.2 Gel polymer electrolyte (GPE)

The second category of polymer electrolyte is called gel polymer electrolyte which is neither liquid nor solid or conversely both liquid or solid. Gels possessed both cohesive properties of solids and the diffusive properties of liquids. GPE is obtained by dissolving the polymer host along with a dopant salt in a polar organic solvent or more commonly known as plasticizer. Some of the commonly used plasticizers are ethylene carbonate (EC) and propylene carbonate (PC) due to their high permittivity and high dielectric constant. Frequently used polymeric materials include poly(acrylonitrile), (PAN), and poly(vinylidene fluoride) (PVdF).

Recently, the utilization of room temperature ionic liquid (RTIL) has received an upsurge of interest to substitute the plasticizer. RTIL is a non-volatile room temperature molten salt which comprised of bulky, asymmetric organic cation and highly delocalized charge inorganic anions. It remains in a liquid form at ambient temperature as its unique characteristic. Ions in a gel electrolyte can travel either through the segmental motion of the ion-solvating polymer chains or through diffusion in solvent channels [Morita *et al.*, 2004]. This is attributed to the ion motions in the polymer framework are much faster compared to the liquid-phase solvent. Tien and Teng (2009) have developed gel polymer electrolytes that promoted the power performance of activated carbon electrodes by enhancing the transport of electrolyte ions inside and outside of the micropores.

One of the main advantages of gel polymer electrolytes is high ionic conductivity. Appetecchi and coworkers (1999) discovered that the addition of ethylene carbonatedimethyl carbonate (EC-DMC) into polyacrylonitrile (PAN) polymer electrolytes demonstrates high ionic conductivity and very good chemical and electrochemical stability. The maximum ionic conductivity obtained from the prepared samples at room temperature reached up to 10^{-2} S cm⁻¹. While the electrochemical window stability in the range of 4.3 - 4.5 V versus Li which is assumed as the breakdown voltage of the films. Moreover, poly(acrylonitrile-co-methyl methacrylate-co-styrene) (PAMS) based gel polymer electrolyte exhibits excellent mechanical strength and fabricated lithium cell shows high discharge capacity up to 142 mAhg⁻¹ [Kim *et al.*, 2000]. Long charge-discharge cycle life of more than 8000 cycles was exhibited by poly(methyl methacrylate) (PMMA)/LiClO₄ based gel polymer electrolytes [Osaka et al., 1997].

2.2.3 Composite polymer electrolyte (CPE)

However, the structural and mechanical stabilities of GPEs are inadequate because of the impregnation of a liquid electrolyte into a polymer system leads to the softening of the polymer. Composite polymer electrolyte on the other hand, is a subset of polymer electrolyte with an idea of incorporating electrochemically inert fillers into polymer matrices. Generally, high surface area particulate fillers such as ZrO₂, TiO₂, Al₂O₃ and hydrophobic fumed silica were incorporated into the polymer matrices and are called composite polymer electrolyte. The incorporation of fillers enhances the ionic conductivity at low temperatures, and improves the stability at the interface with electrodes. As illustrated in Fig. 2.1, the intimate contact at the electrolyte/electrode interface would tend to stabilize the interface and reduces interfacial resistance.



Figure 2.1: Schematic diagram of phases between electroactive material, binder and the electrolyte [Dias *et al.*, 2000].

These CPEs offer some attractive advantages such as superior interfacial contacts, highly flexible, improved lithium transportation, high ionic conductivity and better thermodynamic stability towards lithium and other alkali metals.

2.3 METHOD OF ENHANCING IONIC CONDUCTIVITY

Ionic conductivity is the main aspect to be concerned in polymer electrolytes. Numerous manipulations were attempted by a number of researchers to enhance the ionic conductivity of polymer electrolytes at ambient temperature. The enhancement of ionic conductivity can be done by means of polymer blending [Oh and Kim, 1999], addition of plasticizers [Aihara *et al.*, 1999], incorporating of ionic liquids and doping of ceramic fillers [Li *et al.*, 2011; Goldshtein *et al.*, 2012].

2.3.1 Polymer blending

Polymer blend is a physical mixture of two or more different polymers together. It is a feasible way to increase ionic conductivity because it offers the combined advantages of ease of preparation and easy control of physical properties within the definite compositional change [Rajendran *et al.*, 2002]. The conductivity enhancement through this contraption was induced by the increase in the amorphous elastomeric phase which is responsible in facilitating the lithium conducting ions. The properties of polymer blends depend on the physical and chemical properties of the participating polymers. If two different polymers are able to dissolve successfully in a common solvent, this polymer blends or intermixing of the dissolved polymers will occur due to the fast establishment of the thermodynamic equilibrium.

Polymer blends are gaining practical importance and scientific interest, as a result of the current emphasis on modifying existing synthesized polymers, rather than manufacturing new ones [Linares *et al.*, 1997]. Blending properties often exhibit properties that are superior compared to the properties of each individual component polymer [Rocco *et al.*, 1997]. The main advantages of blend-based systems are their simplicity of preparation and easy control of physical properties by compositional change [Choi *et al.*, 2001]. A polymer blend may be obtained by several methods like melt-mixing, coprecipitation and casting [Crispim *et al.*, 1999].

The conductivity enhancement through this contraption was induced by the increase in the amorphous elastomeric phase which is responsible in facilitating the lithium conducting ions (Li^+). This method also has significant effect on the thermal and mechanical properties of the polymer electrolytes (Rajendran *et al.*, 2001). This polymer blending technique also improves the properties of chitosan film that lack of water resistance and poor mechanical properties by blending with two thermally gelatinised corn starches (Xu *et al.*, 2005). The blending with corn starch component not only appears to be environmental friendly yet attained the desired properties.

2.3.2 Addition of plasticizer

The commonly used plasticizers are ethylene carbonate (EC), propylene carbonate (PC) and poly (ethylene glycol) (PEG) due to their high dielectric constant and low vapor pressure. By adding these plasticizers, the ionic conductivity of polymer electrolyte can be greatly enhanced [Masuda et al., 2006]. Plasticizers are widely incorporated in GPEs as additive due to the high salt-solvating power, high ion mobility and reduction in crystalline nature of the polymer matrix [Prosini *et al.*, 1997]. Nevertheless, the addition of plasticizers incurred low flash point, slow evaporation, and decrease in thermal, electrical and electrochemical stabilities of the samples. The disadvantages of adding plasticizers into polymer electrolytes system including narrow working voltage range and electrochemical stability window, high vapor pressure and poor interfacial stability with lithium electrodes [Raghavana *et al.*, 2010; Kim *et al.*, 2006; Pandey and Hashmi, 2009].

Over the years, plasticization has been known as one of the most effective way to improve the ionic conductivity of polymer electrolytes. The features of selecting a suitable plasticizer includes its higher dielectric constant than that of the pure polymer used, low volatility, low freezing point and high boiling point and its inert nature towards the electrodes (Kumar and Sekhon, 2004). The principal function of plasticizer is to reduce the modulus of polymer at the desired temperature. The increase in concentration of plasticizer causes the transition from the glassy state to rubbery state at lower temperature. This progressive transition improves the flexibility of polymer chains in the polymer matrix and reduces the viscosity of the polymer electrolytes. Consequently, the free volume in the polymer increases and the segmental motion of the polymer molecules is enhanced.

Oligomeric poly(ehytlene glycol) dimethylether (PEGDME) was used as plasticizer in poly(vinylidene fluoride)-hexafluoropropylene copolymers (PVdF-HFP) and the reported maximum ionic conductivity obtained at room temperature to be 2×10^{-4} S cm⁻¹ [Abraham *et al.*, 1997]. Other supporting evident on the reliability of plasticizer in enhancing the ionic conductivity can be visualized from the system composed of gelatin as a host polymer with two variables namely LiBF₄ and glycerol [Vieira and Pawlicka, 2010]. From this analysis it was identified that the effect of glycerol (plasticizer) in enhancing the ionic conductivity is more prominent than the effect obtained by varying the lithium salt content or the effect of the interaction of both variables. The highest conducting sample was identified for sample with the highest content of glycerol and lithium salt with the conductivity value of 2.29×10^{-5} S cm⁻¹.

The term plasticizer refers to a species, which will decrease the glass transition temperature, T_g of a polymer [Kim *et al.*, 2000; Henry *et al.*, 2002]. This effect is due to a reduction in the cohesive forces of attraction between polymer chains. The plasticizer

molecules penetrate into the polymer matrix and establish attractive forces between plasticizer molecules and the chain segments. This will increase the segmental mobility, thus enhancing ionic conductivity.

Through the addition of plasticizers to the polymer, the original structure of the polymer was changed into a less crystalline structure. It has been thoroughly investigated that ion migration mainly takes place in the amorphous part of the polymer and crystalline domains will impede ion mobility both by blocking the paths of ions and by reducing the overall polymer flexibility [Zhang *et al.*, 2000; Periasamy *et al.*, 1999].

The possible drawbacks of plasticized electrolytes can be attributed to the poor mechanical properties due to a high degree of plasticization and the reactivity of polar solvents towards lithium electrodes [Lewandowski and Stepnicak, 2001; Kim *et al.*, 2000]. It is reported that for electrolytes based on PMMA and PC, which acts as a solvent easily corrodes the lithium metal anode in an electrochemical cell [Yarovoy *et al.*, 1999]. A further disadvantage is that most plasticizers are volatile at room temperature and the material may rapidly revert to unplasticized, unenhanced state [Latham *et al.*, 1992].

2.3.3 Addition of ionic liquid

In the last decades, room temperature ionic liquid (RTIL) has received an upsurge interest to overcome those drawback of plasticizer. RTIL also known as green solvent is a non-volatile room temperature molten salt with low melting point (<100 °C). It is comprised of bulky, asymmetric organic cation such as ammoniums, phosphoniums, imidazoliums, pyridiniums and highly delocalized-charge inorganic anion, such as triflate (Tf), tetrafluoroborate (BF₄⁻), bis(trifluoromethylsulfonyl imide) (TFSI⁻) and

hexafluorophosphate (PF₆⁻) [Pandey and Hashmi, 2009]. The large interest on RTIL is mainly due to its wider electrochemical stability window (up to 6 V), wider decomposition temperature range, high conductivity, high thermal stability, non-toxicity, non-volatility and non-flammability [Hussey, 1998; Fannin et al., 1984]. Moreover, it serves as potential replacement for volatile organic compounds due to its ability to dissolve wide range of organic, inorganic and organometallic compounds. It still remains in liquid form in a wide temperature range and does not coordinate with metal complexes, enzymes and different organic substrates as its unique characteristic [Jain *et al.*, 2005]. Other intrinsic features are excellent safety performance and relatively high ionic conductivity due to high ion content [Marcilla *et al.*, 2006; Sekhon *et al.*, 2006]. However, the main drawbacks of RTIL are poor biodegradability and less cost effective.

The addition of ionic liquid has showed excellent reversible cyclability. The addition of N-methyl-N-propylpyrrolidinium bis(trifluoromethanesulfonyl)imide to lithiummetal polymer electrolyte batteries has resulted in a very promising improvement in performace at moderate temperature [Shin et al., 2006]. On the other hand, RTIL consisting *N*-alkyl-*N*-methylpyrrolidinium cations and bis(trifluoromethanesulfonyl)imide anions not only have a relatively high ionic conductivity, but also a wide electrochemical stability window [Shin et al., 2003; MacFarlane et al., 1999]. The overall cell efficiency and photoelectrochemical properties of dye-sensitized solar cell (DSSC) were enhanced upon addition of ionic liquid. Sirisopanaporn et al. (2009) had developed freestanding, transparent and flexible gel polymer electrolyte membranes by trapping N-n-butyl-Nethylpyrrolidinium N,N-bis(trifluoromethane) sulfonamide-lithium N.Nbis(trifluoromethane) sulfonamide (Py₂₄TFSI–LiTFSI) ionic liquid solutions in poly(vinylidene fluoride)-hexafluoropropylene copolymer (PVdF-co-HFP) matrices. The

resulting membranes exhibited high room temperature ionic conductivity from 0.34 to 0.94 mS cm⁻¹. These polymer electrolytes can operate up to 110 $^{\circ}$ C without degradation and did not show any ionic liquid leakage within 4 months storage time [Sirisopanaporn *et al.*, 2009].

2.3.4 Addition of ceramic filler

The enhancement of ionic conductivity can be done by adding ceramic fillers while improving the structural and mechanical stability of the polymer. Generally the fillers can be classified into two categories: active and passive. The active components comprised materials such as Li₃N and LiAlO₂. Due to the presence of lithium ions, these particles participate in the conduction process. The passive components comprise materials such as Al₂O₃, SiO₂, etc., which do not participate in the lithium transport processes [Kumar *et al.*, 2001].

Among the studies, introduction of ceramic fillers is one of the most successful ways. Researchers have recognized that adding inorganic fillers polymer electrolytes improves the ionic conductivity of the electrolytes [Walls *et al.*, 2000; Carriere *et al.*, 2001; Quartarone *et al.*, 1998; Appetcchi *et al.*, 2000]. B.Scrosati and co-workers (1991) stated that the addition of ceramic fillers, having the right particle size and composition limit, prevents crystallization and favors the amorphous, highly conducting structure of the polymer electrolyte. According to Qian and co-worker (2001), the addition of Al₂O₃ particles will decrease the glass transition temperature (T_g) and the degree of crystalline PEO phase (X_c) in PEO₁₀LiClO₄ system. The decrease of T_g and X_c will increase the flexibility of the PEO chain and so increase the ionic conductivity.

These improvements have been ascribed to the fillers that

- (1) Acted as solid plasticizers and lowered the crystalline of the polymer matrix [Chung *et al.*, 2001]
- (2) Increased ion mobility by providing additional conductive pathway due to formation of the Lewis acid-base interactions [Jayathilaka *et al.*, 2002]
- (3) Increased the number of charge carriers due to enhancement of the salt dissociation[Marcinek *et al.*, 2000a]

As reported in literature, the addition of ceramic fillers (such as SiO_2 , TiO_2 , Al_2O_3 , $LiAlO_2$) for the PEO-based electrolyte results in an enhancement of the ionic conductivity, an increase in transference numbers, and an improvement of the interfacial stability between the polymer electrolytes and the lithium metal electrode [Croce *et al.*, 1998; Croce *et al.*, 1999].

The addition of ceramic fillers to the plasticized polymer electrolyte reduces the rate of growth of the resistive layer on the Li surface [Marcinek *et al.*, 2000b; Lee *et al.*, 2000]. It was proposed that these ceramic fillers trap trace impurities such as water and oxygen to protect the electrode surface from corrosion [Walls *et al.*, 2000; Carriere *et al.*, 2001; Quartarone *et al.*, 1998; Appetcchi *et al.*, 2000]. The particles grain size has been found to be important for stability with a greater effect being found for smaller grain sizes. Smaller grains dispersed in the polymer are more effective at shielding the electrolytes from the lithium. The smaller particles are able to cover a greater surface area minimizing the area of lithium electrode exposed to species that give rise to passivation. In many cases, the particle size of the fillers maintained in the order of a few microns [Quartarone *et al.*, 1998].

The addition of Al_2O_3 increased the mechanical strength of the polymer electrolytes and the ionic conductivity reaches up to 10^{-4} S cm⁻¹ at room temperature. The lithium ionic transference number is greatly enhanced with the addition of Al_2O_3 [Tokuda and Watanabe, 2002].

2.4 CORN STARCH

Starch has attracted attention in recent years because it is found in abundance, renewable, low priced, biodegradable and biocompatible [Lopes *et al.*, 2003; Ma *et al.*, 2006]. Much effort has been made to develop biopolymer electrolytes by using natural polymer in order to overcome the shortcoming of synthetic polymer. Among different natural polymers, starch-based solid polymer electrolytes show good opto-electrochemical characteristics and can be applied to electrochemical devices [Pawlicka *et al.*, 2008]. Other than that, corn starch is widely explored in the field of drug delivery [Piskin, 2002], tissue engineering [Piskin, 2002] and shape memory polymers [Vechambre *et al.*, 2010].

Corn starch is the starch of the corn obtained from the endosperm of the corn kernel consisting of a large amount of glucose units joined together by glycosidic bond. Natural polymers such as chitosan, starch, cellulose have attracted numerous interest in the field of polymer electrolytes due to their wide availability, renewable nature, biodegradability, cost effective and superior electrical properties [Majid and Arof, 2007]. Corn starch appears to be a promising host polymer due to their superior mechanical and electrical properties [Finkenstadt and Willett, 2005]. Other features such as completely biodegradable and have good solubility properties as well as superior steel adhesion properties [Lopes *et al.*, 2003].

Corn starch is a semi-crystalline polymer composed of both linear amylose $\alpha(1,4)$ linked anhydroglucose unit and branched amylopectin $\alpha(1,6)$ linked anhydroglucose polysaccharide chain [Beninca *et al.*, 2008]. The proportion of amylose is around 25% while amylopectin will be around 75%. The amylose is mostly responsible in the conduction of Li⁺ cation due to the straight chain properties whereas the superior mechanical properties are obtained from amylopectin chains due to its high crystallinity nature. Fig. 2.2 shows the molecular structure of amylose and amylopectin chain.

Water and glycerol are widely used as plasticizers for starch an act as agents of polymeric network formation through the polymer-polymer and polymer-plasticizer interactions. These interactions are van der Waals forces and strong hydrogen bonds, which lead to the increase of toughness and strength of the starch plasticized with glycerol materials [Van Soest and Vliegenthart, 1997]. In the presence of water and plasticizers, starch can be processed into thermoplastic starch (TPS) [Shogren, 1992].

The preparation for corn starch based polymer electrolytes is always initiated by gelatinization of corn starch powder in distilled water at temperature of ~75 °C. This gelatinization steps unfold the macromolecules of carbohydrate polymer and is nonreversible reaction. Addition of ionic salt will form lewis acid-base bonding with the polymer matrix.



Amylose-linear polysaccharide



Amylopectin-highly branched polysaccharide

Figure 2.2: Structure of corn starch containing two different polysaccharide chains.

The anions are responsible in inducing the structural disorderliness in the corn starch matrix by unfolding the carbohydrate polymer. Cations are responsible in enhancing the ionic conductivity of the polymer electrolytes. Corn starch biopolymer electrolytes doped with 1-butyl-3methylimidazolium hexafluorophosphate shows good ionic conductivity up to 1.47×10^{-4} S cm⁻¹. The interaction between anhydroglucose ring of corn starch and LiPF₆ has been revealed from ATR-FTIR studies shows the suitability of corn starch as polymer electrolytes [Ramesh *et al.*, 2011]. Corn starch is also used as precursor to fabricate activated carbon for capacitor. It is a promising precursor of activated carbon for electrochemical capacitors [Li *et al.*, 2008].

2.5 LITHIUM PERCHLORATE

The criteria of choosing a salt is that it must have relatively low lattice energy (e.g. $<700 \text{ J mol}^{-1}$) and can form crystalline polymer-salt complexes at high salt concentrations [Papke *et al.*, 1086]. Lithium salt is preferably chosen by researchers in developing polymer electrolytes is mainly due to its small ionic radius, greatest electrochemical potential and largest energy content. Lithium perchlorate (LiClO₄) is comprised of a small sized cation and a large sized anion. Fig. 2.3 shows the molecular structure of LiClO₄.



Figure 2.3: Structure of LiClO₄

The incorporation of LiClO₄ salt into polyurethane/poly(vinylidene fluoride) shows wide electrochemical stability window up to 5 V versus Li [Santhosh *et al.*, 2006]. Good performance of LiClO₄ is obtained compared to LiPF₆ and LiCl [Fan *et al.*, 2009]. The crystallization of the polymer is suppressed by adding LiClO₄, so that the polymer does not crystallize to any appreciable extent at low temperatures [Nagae *et al.*, 1992]. Nagae and coworkers (1992) found that the ionization equilibrium of LiClO₄ to be:

$$2(\text{Li}^+\text{ClO}_4) \leftrightarrow (\text{Li}^+\text{ClO}_4)\text{Li} + \text{ClO}_4$$

Thus, $LiClO_4$ is chosen due to its good conductivity and is more favorable compared to other lithium salts due to the low interfacial resistance when lithium metal was used as anode. Moreover, $LiClO_4$ has high dissociation energy, thus it is readily soluble in most solvents.

2.6 SILICA

Silica has a molecular formula of SiO₂. It is a ceramic filler or also known as inert particle which is commonly used as solid plasticizer in polymer electrolytes to enhance ionic conductivity and structural modification [Xiong *et al.*, 2008]. As reported by [Wang et al., 2008], the addition of mesoporous silica greatly enhanced the transference number, t_{Li}^+ and ionic conductivity of the samples. The addition of SiO₂ ceramic filler into polyurethane acrylate polymer electrolytes has greatly enhanced the dynamic modulus by 150% and the interfacial stability between polymer electrolytes and lithium electrode [Jiang *et al.*, 2005]. Incorporation of silica aerogel powder into polyacrylonitrile polymer electrolyte shows excellent electrochemical stability and cyclability over the potential range of 0 – 4 V [Chen *et al.*, 2011].

The addition of SiO_2 which provides high surface area not only enhances the mechanical properties but also increases ionic conductivity [Nicotera *et al.*, 2006]. The particle size of SiO_2 influences the kinetics of PMMA chain and promotes localized amorphous regions and thus enhances the Li⁺ ion transport in the amorphous polymer

electrolytes [Ramesh and Liew, 2010]. Xiong and co-workers (2008) found that nano-SiO₂ deviates from a stable silicon-oxygen structure due to lack of oxygen in its interface. Because of its small size, large specific surface area, high surface energy, as well as a lot of unsaturated chemical bonds and hydroxyl groups on the surface, nano-SiO₂ is easily dispersed into macromolecular chains [Xiong *et al.*, 2008]. Fig. 2.4 shows the proposed network structure of nano-sized silica.



Figure 2.4: Tridimensional network of silica [Xiong *et al.*, 2008]

2.7 BARIUM TITANATE

Barium titanate is a strong ferroelectric ceramic filler with high dielectric constant. Sun and coworkers (2000) reported that the ferroelectric material, BaTiO₃, in PEO is effective in increasing ionic conductivity, especially at lower temperatures and to decrease the interfacial resistance between the lithium anode and polymer electrolyte. Furthermore, Bhide and Hariharan (2008) reported that an enhancement in the ionic conductivity of about two orders of magnitude is achieved by incorporating BaTiO₃ into PEO based polymer electrolytes. The addition of BaTiO₃ was effective in improving the mechanical strength and elasticity of the fully amorphous composite polymer electrolytes over a wide range of temperature [Wen *et al.*, 2003]. The strong acidic surface of BaTiO₃ filler competes with the cations to interact with the basic ether oxygen of the polymer. Such interaction reduces the ionic coupling of the oxygen and the cation thereby promoting dissociation of the salt and hence increase in ionic conductivity is observed [Forsyth *et al.*, 2002].

2.8 ELECTROCHEMICAL CAPACITOR (EC)

Capacitors which stores energy within the electrochemical double layer at the electrode/electrolyte interface are known as double layer capacitors, supercapacitors, ultracapacitors, power capacitors, gold capacitors or power cache. In older generation, electrostatic capacitor have low capacitance values which limits the use to low power applications or at most for short term memory back-up supplies. However, the development of EC occupies the niche amongst the other energy storage technologies that was previously vacant. EC is able to store large amount of energy than conventional capacitors, and are able to deliver more power than that of batteries. Fig. 2.5 shows the ragone plot of different energy storage technologies.



Figure 2.5: Ragone plot of various energy storage devices [Kötz and Carlen, 2000].

EC acts as intermediate power source between rechargeable batteries and conventional capacitors (CC). It fills the gap existing between batteries, fuel cells and CC [Lufrano and Staiti, 2004; Hashmi *et al.*, 2005]. In terms of specific energy and specific power, this gap covers several orders of magnitude.

However EC can be classified as redox capacitor, electrical double layer capacitor and hybrid capacitor. These classes of EC were based on the types of electrode materials employed and the charge storage mechanism at the electrode/electrolyte interfaces. Fig. 2.6 shows the taxonomy of EC.



Figure 2.6: Taxonomy of EC

Redox capacitors employed conducting polymer and metal oxides such as NiO_x, CoO_x, RuO₂ etc as electrode materials. Redox capacitors have shown several advantages for instance fast charge-discharge kinetics, low cost, suitable morphology, and fast doping-undoping processes. Some of the commonly used polymer for redox capacitors includes polyaniline (Pani) and polythiophene. Polyaniline is the most attractive *p*-dopable polymer due to its stability, controllable electrical conductivity and easy processability [Fusalba *et al.*, 2001; Belanger *et al.*, 2000; Hu and Chu, 2000]. For redox supercapacitors, the storage mechanism is faradaic [Hashmi *et al.*, 2007]. Faradaic process involves the transfer of charge between electrode and electrolyte such as oxidation-reduction reactions, electrosorption and intercalation process.

EDLC have a longer cycle life and higher power density compared to conventional rechargeable batteries. EDLC comprises of an electrolyte and two porous electrodes sandwiching the electrolyte [Kibi *et al.*, 1995]. Activated carbon, which has a high surface

area and is chemically stable, is generally used as the electrode material combining with some other active materials such as carbon black (CB) [Arof *et al.*, 2010]. Charge storage of EDLC is electrostatic in nature [Hashmi et al., 2005]. Electric charge is stored in the electric double-layer at the electrode/electrolyte interface when DC voltage is applied [Matsuda et al., 1999]. EDLC is safe because the storage mechanism is non-Faradaic and there are no transfer of charge between electrode and electrolyte but based on the accumulation of charges in electrical double layers [Ganesh *et al.*, 2008; Mitra *et al.*, 2001].

Hybrid capacitor combined both EDLC and redox capacitor properties. It was developed to manipulate the advantages and moderate the disadvantages of EDLC and redox capacitor to improve performance characteristics. Pani-LiPF₆ and active carbon electrodes hybrid capacitor shows better capacitor performance as compared to redox capacitor with two LiPF₆-doped polyaniline electrodes. The internal resistances and the equivalent series resistance of the hybrid type are smaller than those of the redox type [Ryu *et al.*, 2004].

2.8.1 Electrical Double Layer Capacitor (EDLC)

NEC Corporation and Panasonic in Japan have been commercializing EDLCs called "SuperCapacitor" since 1980. They are composed of activated carbon powders as the polarizable electrodes and an aqueous solution of sulfuric acid as the electrolyte. However the incorporation of aqueous solution as an electrolyte has many limitations such as leakage problems and difficulty in designing the capacitor. In recent years, polymer electrolyte capacitors have attracted considerable attention [Asmara *et al.*, 2011; Yang *et al.*, 2005;

Pandey *et al.*, 2011; Staiti *et al.*, 2002]. The application of polymer electrolytes to EDLC can lead to thin film cells and high reliability without leakage problems.

EDLC stores electrical energy in the interface between an electrolyte and a solid electrode (Helmholtz layer). Positive and negative ionic charges within the electrolyte accumulate at the surface of solid electrode and compensate for the electronic charge at the electrode surface. The charges accumulate at the interface between the surface of a conductor and an electrolytic solution as shown in Fig. 2.7. The accumulated charges hence form an electric double-layer, the separation of each layer being of the order of a few Angstroms.



Figure 2.7: The schematic sketch of electrical double layer capacitor [Emmenegger *et al.*, 2003]

2.8.2 Electrode material

The electrode material is crucial in order to achieve higher capacitance value. In this study, the electrode material employed to develop EDLC cells are BP20 as the carbonaceous/active material, carbon black to reduce the internal resistance in electrode and poly(vinylidene fluoride), (PVdF) as binder. BP20 was prepared from phenol resin. The information of BP20 as obtained from Kuraray website is listed in Table 2.1.

Table 2.1:	Properties of BP20 (from Kuraray website)
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Test parameter	Units	BP20
Iodine adsorption	mg/g	1700~1800
Benzene adsorption	Wt.%	45-55
Total surface area	m ² /g	1600~1700
рН	рН	5~8
Ash content	%	1.0 max
Diameter of particles	Microns	3~20

As reported by Arof et al., (2012) carbonaceous material derived from shells of mata kucing (Dimocarpus longan) fruit shows potential as candidate for active material in the electrode for EDLC application. According to Staiti et al., (2002), the mechanical stability of the electrodes can also be increased by adding the polymer electrolyte in the electrode composition. The use of carbon black (CB) in the electrode material can improve electrolyte/electrode contact as CB also acts as binder in the electrode [Latham et al., 2002]. CB which is added into the electrode mixture can enhance electron conduction and to

decrease the ohmic resistance of the electrode [Lust *et al.*, 2004]. Sheem *et al.* (2006) pointed that CB enhances the electrical conductivity by forming conducting bridges between particles of the active materials. Kibi and coroworkers (1996) stated that high rate charge/discharge characteristics are affected by the resistance of electrolyte phase in the pores of the electrode. The charge/discharge characteristics were improved by optimizing the pore-size distribution of the electrodes [Kibi *et al.*, 1996].

Multiwalled carbon nanotube (MWCNT) shows good performance in EDLC [Pandey et al., 2011]. The electrochemical stability window as estimated from cyclic voltammetry is found to be -2 to 2 V. The increase in specific surface area of carbon shows an increase in EDLC capacitance. Carbon nanotubes show promising electrochemical characteristics whereby the increase of the specific capacitance per surface area was achieved by increasing the active layer thickness and particularly the mass density [Emmenegger *et al.*, 2003].

The EDLC cells were fabricated using the activated carbon (BP20) as electrode, polymer electrolytes as separator and aluminium mesh as current collector electrode. Fig. 2.8 shows the configuration of EDLC cell.

2.8.3 Characterization of EDLC performance

Some of the common techniques used for EDLC characterization will be discuss in this section. Among the commonly used techniques are galvanostatic charge-discharge test, cyclic voltammetry and low frequency impedance. Galvanostatic charge-discharge is employed to investigate the capacitance of EDLC.



Figure 2.8: EDLC cell fabricated with aluminium mesh as collector electrode, activated carbon and separator [Kibi *et al.*, 1996].

Fig. 2.9 shows typical triangular charge-discharge profile for an EDLC with a small cell potential drop. The symmetric profile of EDLC cells containing Chi/EMImBF₄ and EMImBF₄ suggesting high Coulombic efficiency.



Figure 2.9: Charge discharge curves of test cells containing Chi/EMImBF₄ (-) and EMImBF₄ (--) at current densities of 2.5 mA cm⁻² [Yamagata *et al.*, 2012].

The fabrication of EDLC with chitosan based gel electrolytes maintained their coulombic efficiency at more than 99.9% up to 5000 cycles suggesting that the chitosan gel exhibits high retention of ionic liquid and high electrochemical stability [Yamagata *et al.*, 2012]. Fig. 2.10 shows the cyclic voltammogram of a capacitor based on MWCNT | PEO_{25} LiTf + 40 wt.% EMITf | MWCNT studied by Pandey and co-workers (2011).



Figure 2.10: Cyclic voltammogram of EDLC cell at room temperature [Pandey *et al.*, 2011].

A rectangular shape was obtained from cyclic voltammogram characteristics as shown in Fig. 2.10 suggesting that no Faradaic process occur in the capacitor with pure electrostatic behavior of capacitor. Low frequency impedance measurements enable the investigation of capacitive behavior of EDLC cell at low frequency. Fig. 2.11 shows the impedance spectra for EDLC cells with frequency range from 2 mHz to 100 kHz. The semicircle consists of the electrode resistance and capacitance of porous electrodes. Tien *et al.*, (2008) investigated the viability of liquid electrolyte and gel electrolyte as a membrane in EDLC cell by impedance spectroscopy. Following the semicircle with decreasing frequency, the plots transform to a vertical line reflecting a significant resistance for ion motion.



Figure 2.11: Nyquist plots for GE-EDLC and LE-EDLC [Tien *et al.*, 2008].

2.8.4 Applications of EDLCs

EDLCs have a number of desirable qualities that make them a lucrative option as energy storage devices. EDLCs have the capabilities of storing and releasing charge reversibly that make them to withstand a large number of charge/discharge cycles and are also able to charge/discharge quickly than that of batteries. EDLCs are having both high energy and power density. Some of the new application of EDLCs includes [Sharma and Bhatti, 2010]:

- 1) Memory back-up
- 2) Electric vehicles (EV)
- 3) Power quality
- 4) Battery improvement
- 5) Portable power supplies
- 6) Electrochemical actuators
- 7) Adjustable-speed drives
- 8) Renewable energy applications

CHAPTER 3

MATERIALS AND METHODS

3.1 MATERIALS

In this study, corn starch with a linear formula of $C_6H_{10}O_5$, obtained from Sigma-Aldrich, was used as polymer host. Lithium perchlorate salt, LiClO₄, with 99.99 % purity and less than 100 ppm total metallic purities was procured from Aldrich. Fumed silica (SiO₂) with 7 nm particle size was obtained from J.T. Baker. Inorganic filler Barium Titanate, BaTiO₃ was purchased from Aldrich. Distilled water was used to dissolve all the starting materials upon developing corn starch based polymer electrolytes. Activated carbon, BP20 and carbon black (Super P) was used to prepare the electrode for EDLC fabrication. Poly(vinylidene fluoride), (PVdF) from Aldrich was used as binder and the solvent N-methylpyrrolidone from Aldrich.

3.1 PREPARATION OF POLYMER ELECTROLYTES

Corn starch based polymer electrolytes were prepared by solution casting technique with distilled water as the solvent. The initial step in developing biodegradable polymer electrolytes was by dissolving an appropriate amount of corn starch powder in 20 mL of distilled water. The solution is then gelatinized under 80 \degree at constant stirring for 1 h

before adding appropriate amount of LiClO₄ salt and fillers. This is followed by a constant stirring and heating for 24 h to ensure homogeneity and complete dissolution of the polymer complexes. The viscous solution were then casted on a Petri dish and dried in the oven at 50 \degree for 24 h to produce free standing and mechanically stable films. Table 3.1, Table 3.2 and Table 3.3 summarize the composition ratio of 3 systems with its respective designation. The designations of the highest conducting compositions for all the three systems were bolded.

Composition (wt.%)		Designation for system
Corn starch	LiClO ₄	Designation for system
100	0	CS0
90	10	CS10
80	20	CS20
70	30	CS30
60	40	CS40
50	50	CS50

Table 3.1: Designation of corn starch-lithium perchlorate polymer electrolyte films

Composition (wt.%)			
Corn starch : LiClO ₄	SiO ₂	Designation for system	
(60:40 ratio)			
100	0	Si-0	
98	2	Si-2	
96	4	Si-4	
94	6	Si-6	
92	8	Si-8	
90	10	Si-10	

Table 3.2:Designation of corn starch-lithium perchlorate: SiO_2 polymer electrolyte films.

Table 3.3:Designation of Corn starch-lithium perchlorate:BaTiO3 polymer electrolyte
films.

Composition (wt.		
Corn starch : LiClO ₄	BaTiO ₃	Designation for system
(60:40 ratio)		
100	0	Ba-0
98	2	Ba-2
96	4	Ba-4
94	6	Ba-6
92	8	Ba-8
90	10	Ba-10

3.3 PREPARATION OF EDLC

The electrodes for EDLC were prepared by mixing a ratio of 8:1:1 of activated carbon : carbon black : PVdF in suitable amount of NMP solvent. The mixture is allowed to stir until homogeneous slurry was obtained and dipped coated on an aluminum mesh current collector. EDLC was constructed by sandwiching the polymer electrolyte film between two activated carbon cloth electrodes. Constructed EDLC cells were pressed under 200 mbar pressures to ensure good contact between electrodes and polymer electrolyte film.

3.4 INSTRUMENTATIONS AND TECHNIQUES

In this research work, different types of instrumentation and techniques were used to characterize the developed polymer electrolytes and fabricated EDLC cells.

3.4.1 Alternating current (AC) impedance spectroscopy

Conductivity in a material is determined by the ionic species concentration and ion jump rate functions between sites. In order to determine the ionic conductivity of the prepared polymer films, AC impedance spectroscopy were carried out. The impedance of the prepared films was measured using the HIOKI 3531 Z HI-TESTER in the frequency range from 50 Hz to 5 MHz and in the temperature from 25 to 80 °C. Prior to measurements, the thickness of the polymer electrolyte films were measured using a
micrometer screw gauge. The films were sandwiched between two stainless steel blocking electrodes which having an area of 4.9807 cm^2 . Three different portions from the same film were used to obtain the average conductivity value and its deviation.

The bulk resistance, R_b , can be determined from the diameter of the semicircle. This value is then used to calculate the ionic conductivity of the material via equation,

$$\sigma = \frac{L}{R_b A}$$

where,

$$\sigma$$
 = ionic conductivity in S cm⁻¹

- L = thickness of the sample in cm
- A = the area of the sample in cm^2
- $R_{\rm b}$ = bulk impedance in ohm

The conductivity obtained at different temperatures is plotted in the form of log σ T against 1000/T. This plot exhibits the Li⁺ ion conductivity mechanism in the polymer matrix which helps in the study of the conduction behavior. If the regression value of all the points in the plot is almost unity, the plot can be represented by a straight line and the conductivity can be represented by the Arrhenius equation.

$$\sigma(T) = \sigma_0 \exp\left(\frac{-E_a}{kT}\right)$$

Where,

 σ_0 = pre-exponential factor

 E_a = activation energy

k = Boltzmann constant (8.617 $\times 10^{-5} \text{ eVK}^{-1}$)

T = absolute temperature

3.4.2 Scanning electron microscopy (SEM)

Surface morphology features of the polymer electrolytes are very much associated to the ionic conductivity performance as it is the interface between two active electrodes permitting the conduction of Li^+ ions. In order to understand how the surface morphology of the polymer electrolyte films changes with doping with salt and filler, SEM study was carried out.

The micrographs for corn starch based polymer electrolytes were captured using Leica's SEM with the model S440 at an acceleration potential of 8 kV at room temperature. A thin layer of gold was coated on top of the samples surface prior capturing the surface images to prevent electrostatic charging when the samples surface being subjected with high energy beam of electron.

3.4.3 Differential scanning calorimetry (DSC)

A DSC instrument can measure the change in heat capacity, C_p , as a function of temperature. At a particular state of the material, C_p changes very slightly with temperature. However, when there is a change of physical state, such as melting, C_p would change drastically. This analysis accounts to the thermal properties of the polymer electrolytes which includes the glass transition temperature and melting temperature. The existence of crystalline peak and glass transition temperature are related to the crystallinity and amorphousity of the polymer electrolyte films.

Thermal properties were studied using TA Instrument Analysis which comprised of DSC Q200. The samples were cut from films that were prepared. These samples were encapsulated in standard aluminium pans supplied with the instrument with their cover. Prior to analysis, the samples were equilibrated at 105 °C for five minutes to remove any traces of water. The samples were then cooled rapidly to -50 °C and then reheated to 200 °C at a heating rate of 30.00 °C min⁻¹. Upon reaching 200 °C, the samples were allowed to cool to -50 °C and reheated again to 200 °C for a second cycle. This is to unveil the glass transition temperature slope from the broad crystalline peak. The entire heating process was done in a nitrogen atmosphere.

3.4.4 Thermogravimetric analyses (TGA)

Heat resistivity and thermal stability of the polymer electrolytes were determined by thermogravimetric analysis. With the aid of TGA thermogram, the information on the heat resistivity and thermal stability were obtained by referring to the weight loss of samples and decomposition temperature of the samples. From the weight loss measurement, we can identify the change in property of the polymer electrolytes. Thermogravimetric analyses were conducted with TA Q500 thermogravimeter under nitrogen atmosphere at the temperature ranging from 25 \degree to 600 \degree with the heating rate of 50 \degree min⁻¹.

3.4.5 Water solubilities test

This technique is used to determine the water resistivity of the membrane. The hydrophilic nature of the hydroxyl group in amylase and amylopectin allows water absorption, results in swelling and assists permeation in transporting through membrane. However, if too much water absorption occurs, then it may results in excessive mechanical fragility and morphological instability of membrane.

A 50 mm \times 50 mm polymer sheet film was weighed (W_0) and soaked in distilled water for five minutes. The polymer sheet film was then allowed to air dried and placed in dessicator until a constant weight was obtained (W_1).

The water solubilities (W_s) were calculated using following equation:

$$W_{s} = \frac{W_{0} - W_{1}}{W_{0}} \quad 100\%$$

3.4.6 Linear sweep voltammetry (LSV)

Linear sweep voltammetry was used to evaluate the electrochemical stability window of the corn starch polymer electrolyte films in order to determine the working voltage to be used in EDLC application. The CH-Instrument Model 600D electrochemical analyzer was used. The electrolytes were sandwiched between stainless steel blocking electrodes and measurements were performed in the range of -4 V to 4 V with 10 mVs⁻¹ scan rate.

3.4.7 Cyclic voltammetry (CV)

The knowledge on the electrochemical behaviors and nature of charge storage at the interface of anodic and cathodic regions were obtained by referring to the redox behavior in cyclic voltammogram. The electrochemical properties of polymer electrolytes were scrutinized by the aid of Autolab PGSTAT12 potentiostat-galvanostat in the voltage range between 0 to 1.0 V at 10 mVs⁻¹ scan rate. General Purpose Electrochemical System (GPES) software is used to plot the cyclic voltammogram in this study.

3.4.8 Galvanostatic charge-discharge analysis

This technique is used to evaluate the performance of EDLC cell galvanostatically. The fabricated EDLC cell was subjected to charge-discharge analysis. The knowledge of the internal resistance, cycle durability, capacitance value of the EDLC cell was obtained by referring to the charge-discharge profile. Galvanostatic charging-discharging test was performed in the voltage range between 0 to 1.0 V at a constant current of 0.5 mA by using Neware battery cycler.

3.4.9 Low frequency impedance spectroscopy

Low frequency impedance measurements were carried out using HIOKI 3532 Z HI-TESTER in the frequency range from 10 mHz to 100 kHz in room temperature. In the low frequency range, the nyquist plots of the impedance spectra analyses enable the evaluation of various parameters associated with the bulk properties of electrolytes and electrodeelectrolyte interactions.

CHAPTER 4

RESULTS AND DISCUSSION: SYSTEM I (Corn starch:LiClO₄)

4.1 SCANNING ELECTRON MICROSCOPY (SEM)

The structure and morphology of a polymer electrolyte film surface is an important property for the polymer electrolyte. The grain morphology and microstructure of the samples were investigated using SEM. The SEM micrograph of pure corn starch is shown in Fig. 4.1 (a). The entire cross-sectional region is totally uniform and the surface is smooth and without any impurities on it. This shows that, corn starch has completely gelatinized and dissolved in the solvent.

Fig. 4.1 (a-f) shows the SEM images of the prepared samples at magnification of \times 1000. From the homogeneous structure in pure corn starch, formation of slight crystalline LiClO₄ is observed in CS10. However, when more LiClO₄ was added, formation of rod-type crystalline on top of corn starch surface was clearly observed in CS20 and CS50. It is obvious that the introduction of LiClO₄ plays an important role in the morphology and distribution of particles.



Figure 4.1: Surface morphology for (a) CS0 (b) CS10 (c) CS20 (d) CS30 (e) CS40 and (f) CS50 from SEM.

CS20 shows a distribution of 50 μ m grain size and CS50 shows similar crystallite shape with grain size 7.5 to 40 μ m. The values of grain size were measured and tabulated in Table 4.1. The larger grain size in CS20 reduces the number density of ions and reduces the ionic mobility that could be due to ion traps in the polymer electrolytes.

Samples	$R_{ ext{ct}}\left(\Omega ight)$	Grain size (µm)	Pore (µm)
CS10	2125	-	-
CS20	450	50	-
CS30	320	2.5 - 10	2.5-5.0
CS40	126	2.5 - 12.5	-
CS50	250	7.5 - 40	2.5

Table 4.1:Charge transfer resistance, R_{ct} , grain size and pore size of corn starch-
LiClO₄ polymer electrolyte

Further addition of LiClO_4 gradually modifies the crystalline structure to a smaller spherulite structure. CS30 and CS40 show smaller spherulite size and even distribution on the surface. Generally, a smaller and uniform distribution of particle size allows easier penetration of electrolyte and shorter pathway for Li^+ ion diffusion [Uma *et al.*, 2005].

However, close inspection of CS30 and CS50 showed the existence of pores in its surface in the range of $2.5 - 5.0 \mu m$. The pore sizes are tabulated in Table 4.1. This is responsible to the increase in resistance to ion diffusion within the active material. Further investigation has been done with A.C. impedance spectroscopy.

4.2 A.C. IMPEDANCE SPECTROSCOPY

In order to understand how the ion transport was affected by grain size in polymer electrolyte, further analysis with impedance spectroscopy was required. In principle, the overall resistance of polymer electrolyte is composed of bulk resistance R_b and charge

transfer resistance R_{ct} . Fig.4.2 represents the nyquist plot and equivalent circuit inset for CS50. The steep capacitive impedance rising in low frequency region accompanied with high frequency semicircular features owing to the bulk and interfacial properties. The locus of the semicircle intercepts the real axis at R_b and R_{ct} as shown in the nyquist plot. Following the semicircle with decreasing frequency, the plots transform to a sloping line. A Warburg element Z_w is introduced in the circuit to emphasize the solid state diffusion of Liions in the active materials corresponding to the sloping line. Constant phase element has to be incorporated to represents the double layer capacitive behavior [Lu *et al.*, 2009].



Figure 4.2: Nyquist plot for CS50 at room temperature with equivalent circuit inset.

Besides the calculated grain size from SEM, the charge transfer resistance, R_{ct} values are also tabulated in Table 4.1. Here, we assume the resistances for ion migration through the grain shows a much pronounce influence on charge transfer resistance.

As observed from SEM micrograph, the resistance increased with bigger grain size. The concept of boundary layer is used to explain the mechanism of Li⁺ ions migration in electrolyte-electrode interface [Ramesh and Wong, 2008]. Assuming conduction will occur inside the grain and along the grain boundaries, the grain size will eventually affect the diffusion of ions along the grains. The smaller grain size eventually assists the ion migration and shortens the diffusion pathway, thus lower down the charge transfer resistance.

Ionic conductivity of the films was calculated using impedance spectra. To calculate the ionic conductivity of a thin film sample, the following relationship is used:

$$\sigma = \frac{L}{R_b A}$$

Where σ is the ionic conductivity in S cm⁻¹, l is the thickness of thin film sample in cm, R_b is the bulk resistance in Ω obtained from the Cole – Cole impedance plot and A is the surface area of the stainless-steel blocking electrodes in cm². The ionic conductivity depends on the overall ionic mobility and number of charge carriers. Fig. 4.3 shows the ionic conductivity as a function of weight percentages of LiClO₄ in Corn starch-LiClO₄ polymer electrolyte complexes at room temperature.



Figure 4.3: Variation of log ionic conductivity as a function of weight percentage of LiClO₄ salt at room temperature.

A maximum ionic conductivity of 1.55×10^{-6} S cm⁻¹ is obtained for Corn starch:LiClO₄ at a composition of 60:40 at room temperature. The increase in ionic conductivity with increasing amount of LiClO₄ is mainly due to the increase of ionic mobility and concentration of its mobile charge [Rajendran *et al.*, 2003]. Corn starch consists of amylopectin and amylose which contain an ether group and 3 hydroxyl groups [Mishra *et al.*, 1998]. When lithium salt dissociates, Li⁺ will be attracted to partially electronegative oxygen atom due to the lone pairs in oxygen atom. For the highest ionic conductiving polymer electrolyte, the ion mobility and number of charge carriers have reached the optimum level.

Further increase of LiClO_4 results in a drop in ionic conductivity due to its optimum level being achieved. It may be due to the fact that a high concentration of salt will produce more charged ions which raise the retarding effect of ion aggregates. The neutral ion pairs and formation of ion triplet [Ramesh *et al.*, 2002] reduces the free mobile ions and constraints the polymer segmental mobility which is needed for electrical conductivity. For the composition ratio of corn starch:LiClO₄ at 50:50, a drop in ionic conductivity of 8.91 \times 10⁻⁷ S/cm was observed at ambient temperature. When there is too much salt added, a charge overload occurs leading to the restricted ionic and polymer segmental mobility in a rigid matrix.

Fig. 4.4 shows the temperature dependence ionic conductivities of corn starch-LiClO₄ polymer electrolyte system investigated at temperature range of 25 $^{\circ}$ C to 80 $^{\circ}$ C.



Figure 4.4: Variation of log conductivity as function of temperature change for CS20, CS30, CS40 and CS50 polymer electrolytes.

As the temperature increases, the ionic conductivity increases as well. This is attributed to the expansion of polymer matrix when temperature increased. Expansion of polymer matrix results in the formation of free volume and unoccupied spaces for the migration of ions. With increasing temperature, the ionic conductivity increases according to ion hopping mechanism [Ramesh *et al.*, 2011].

Table 4.2 shows all the ionic conductivity values at room temperatures and 80 °C. According to Arrhenius theory, the nature of cation transport in the polymer electrolytes is quite similar to that in ionic crystals, where the ionic conductivity is enhanced through continuous hopping of Li^+ mobile ion into neighboring vacant sites.

Samples	Ionic Conductivity	Ionic Conductivity
	at 25 °C (S cm ⁻¹)	at 80 °C (S cm ⁻¹)
CS20	5.37×10^{-7}	5.92×10^{-6}
CS30	9.77×10^{-7}	1.11×10^{-4}
CS40	1.55×10^{-6}	1.28×10^{-4}
CS50	8.91 × 10 ⁻⁷	4.51 × 10 ⁻⁵

Table 4.2:Ionic conductivity of corn starch:LiClO₄ polymer electrolytes at room
temperature and 80 $^{\circ}$ C

4.3 DIFFERENTIAL SCANNING CALORIMETRY (DSC)

The thermal properties of samples are examined through differential scanning calorimetry (DSC) analysis. The glass transition temperature (T_g) of the polymer electrolytes system are evaluated from DSC results. Fig. 4.5 depicts T_g values at 55.52 °C and 56.04 °C for first and second heating cycle respectively, for pure corn starch there is no melting peak observed up to 140 °C. This indicates that, the pure corn starch film prepared is fully amorphous up to 140 °C.



Figure 4.5 DSC thermogram of pure corn starch showing 2 glass transition temperatures for 2 heating cycles.

Upon addition of 10 wt.% LiClO₄, T_g exhibits an abrupt increase. CS10 shows T_g of 122 °C which is suspected due to the salt formation of transient cross link between corn starch-LiClO₄ polymer matrix which restricts the segmental motion of the polymer chain, leading to an increase in T_g [Hou *et al.*, 2003]. T_g values for all the samples are tabulated in table 4.3.

Samples	Τ _g (℃)
CS0	56
CS10	122
CS20	124
CS30	73
CS40	64
CS50	90

Table 4.3:Glass transition temperature for corn starch: LiClO4 polymer electrolyte
films.

On the other hand, T_g decreases when more LiClO₄ is added from 122 °C to 124 °C, 73 °C and 64 °C for CS20, CS30 and CS40 respectively. LiClO₄ acts as a plasticizing agent which softens the polymer backbone and ultimately decreases the crystallinity of corn starch [Stephen and Nahm, 2006]. Fig. 4.6 depicts the DSC thermogram for CS20, CS30 and CS40. CS40 depicts the lowest T_g values of 64 °C. The T_g is related to the segmental flexibility of the host polymer and the disordered structure. Lower T_g value may be related to a possible enhancement in the segmental flexibility of polymeric chains and consequently reduces the resistance to transport electroactive substance and hence an increase in ionic conductivity. However, an increased in T_g value is observed from 64 to 90 is observed in CS40 and CS50. It could be rationalized due to the formation of crystalline LiClO₄ salt.



Figure 4.6: DSC thermogram of (a) CS20 (b) CS30 and (c) CS40 showing glass transition temperature.

4.4 THERMOGRAVIMETRIC ANALYSIS (TGA)

Thermogravimetric analysis (TGA) was carried out to investigate the decomposition temperature of the polymer film. Fig. 4.7 shows the overlay thermogravimetric curve for pure corn starch, CS20 and CS40. The percentage of weight loss that is obtained from the TGA graphs will be used to study the thermal stability of the polymer electrolytes. As observed from Fig. 4.7, the decomposition temperature decreased when more LiClO₄ salt is added into corn starch polymer matrix.



Figure 4.7 Thermogravimetric curve for (a) pure corn starch, (b) CS20 and (c) CS40.

The initial weight loss is a result of residual solvent evaporation or moisture absorbed when the samples were loaded. Volatilization of monomers and oligomers adsorbed in the matrix can also be responsible for this initial mass loss. The significant weight loss also known as decomposition temperature for the polymer electrolyte films is above 200 °C. Decomposition temperature and total weight loss for each system has been recapitulated in Table 4.4.

Samples	Decomposition temperature, $(\ \mathfrak{C})$	Total weight loss up to 600 °C, (wt.%)
CS0	237	84.36
CS10	251	81.6
CS20	242	77.75
CS30	241	76.39
CS40	238	65.83
CS50	225	78.61

Table 4.4:The maximum decomposition temperature and percentages of total weight
loss at 600 $^{\circ}$ C

As we can see from Table 4.4, decomposition temperature increases upon addition of 10 wt.% of LiClO₄ and decreases accordingly when more salt is added. This is in good agreement with the T_g values obtain from DSC analysis. As suggested earlier, polymer crosslink within the corn starch amylose and amylopectin matrix requires more heat energy to break the bond. Therefore, decomposition temperature of CS10 increases to 251 °C from 237 °C for CS0. A decrease in decomposition temperature is observed upon addition of more than 10 wt.% LiClO₄. Dissociated perchlorate ion ClO₄⁻ in polymer electrolytes did not show good stability at high temperature and induces faster decomposition [Song *et al.*, 2000 and Ferry *et al.*, 2000]. Consequently, CS50 shows the lowest decomposition temperature of 225 °C.

CHAPTER 5

RESULTS AND DISCUSSION: SYSTEM II (Corn starch-LiClO₄:SiO₂)

5.1 SCANNING ELECTRON MICROSCOPY (SEM)

The grain morphology and microstructure of the samples were investigated using Scanning electron miscoscopy (SEM). Figures below show the morphology (SEM) of the prepared films Si-4 (Fig. 5.1) and Si-10 (Fig. 5.2) at magnification of \times 1500.



Figure 5.1: SEM image of Si-4 (magnification 1500 ×)



Figure 5.2: SEM image of Si-10 (Magnification 1500 ×)

From the results, we can observe that when excessive nano-silica is added into the system, they tend to aggregate to form a larger grain. Upon addition of nano silica into the system, the particles grow as platelet-like to form a grain size between 1 and 5 μ m. A different morphology is observed in Si-10 with interconnected sphere particles as a result of agglomeration with grain size about 5-8 μ m. The larger grain size reduced the number density of ions and reduced the ionic mobility that could be due to ion traps and blocking of ion in the polymer electrolytes. From the SEM morphology, we can observe the presence of SiO₂ will induce larger grain size. The larger grain size can be related to higher crystallinity in the polymer matrix which can decrease the ionic conductivity of the polymer electrolytes.

5.2 A.C. IMPEDANCE SPECTROSCOPY

The ionic conductivity for various compositions of nano-sized fumed silica incorporated in corn starch-LiClO₄ polymer electrolyte films were studied using impedance spectra. Impedance spectroscopy provides a better understanding in the conduction mechanism, mobility and carrier generation processes. In order to calculate the ionic conductivity of a thin film sample, the following relationship is used:

$$\sigma = \left(\frac{l}{R_b A}\right)$$

Where σ is the conductivity in S cm⁻¹, l is the thickness of thin film sample in cm, R_b is the bulk resistance in Ω obtained from the Cole – Cole impedance plot and A is the surface area of the stainless-steel blocking electrodes in cm².

Fig. 5.3 depicts the variation of log ionic conductivity values as a function of nanosized silica concentration. The ionic conductivity increases upon addition of nano-sized silica in Corn starch-LiClO₄ polymer electrolytes.

As can be seen, Si-4 exhibits highest ionic conductivity of 1.23×10^{-4} S cm⁻¹ at ambient temperature. The increase in the ionic conductivity with increasing nano-sized silica can be related to the weakening of the polyether-cation association induced by the nano-sized silica particles and the high interface area between the matrix and the dispersion of nano-sized silica particles [Lu *et al.*, 2009].



Figure 5.3: The variation of log ionic conductivity values as a function of nano-sized silica concentration.

It is believed that the charged nature of the surface of fumed silica promotes dissociation of aggregate ion and undissociated salt into free moving ions which increase the conductivity of polymer films [Ramesh and Lu, 2008]. Consequently, ionic conductivity increases due to formation of highly conducting interfacial layer between the particles of nano-silica and bulk electrolytes. This increase can be attributed to the conducting pathways that repeatedly keep forming [Sharma and Sekhon, 2007].

However the ionic conductivity does not continue to rise indefinitely with increasing concentration of nano-sized silica. In fact, it falls once the concentration of nano-sized silica is over an optimal value. Further increase in silica content results in the blocking of existing conducting pathways and the possible of conglomeration of the excess silica. This will reduce the polymer-filler interface and hence reduces the conducting pathways which hinder the motion of mobile ions [Ramesh and Lu, 2008]. Other than that,

nano-sized silica forms C-O-Si bond with corn starch reducing the bonding sites for the movement of mobile ions [Yu *et al.*, 2006]. Thus, excessive nano-sized silica eventually reduces the bonding sites for Li⁺ and constraints the movement of mobile ion which leads to decrease in ionic conductivity. The above findings are in agreement with those described in the literature, where it has been observed that a rise in conductivity occurs as the concentration of inorganic filler increases followed by a decrease in conductivity values for higher concentration [Pitawala *et al.*, 2007; Thakur *et al.*, 2010; Wen *et al.*, 2003].

An understanding on the mechanism of ion conduction in polymer electrolytes was established by relying on temperature dependent ionic conductivity. The linear variation in temperature dependent ionic conductivity is suggestive of an Arrhenius-type thermally activated process. With increasing temperature, the ionic conductivity increases according to ion hopping mechanism [Gray, 1997]. Activation energy, E_a , was calculated using the slope obtained by linear fitting the curves from log σ versus 1000/T graph. This is based on the Arrhenius rule,

$$\sigma(T) = \sigma_0 \exp\left(\frac{-E_a}{kT}\right)$$

Where σ_0 is the pre-exponential factor, E_a is the activation energy, k is the Boltzmann constant, and T is absolute temperature. The calculated activation energy for Si-0, Si-4 and Si-10 is 0.64, 0.25 and 0.0234 eV, respectively. The higher activation energy value signifies more energy is required to promote the dissociation of Li⁺/polymer bond in silica free sample.

Fig. 5.4 depicts the temperature dependent ionic conductivity values for Si-0, Si-4 and Si-10. The increase in ionic conductivity with temperature can be linked to the decrease in viscosity hence, increased chain flexibility. The regression values close to unity suggesting that the temperature dependent ionic conductivity for all the complexes obeys the Arrhenius rule. The nature of cation transport that obey Arrhenius rule is quite similar to that in ionic crystals, where the conduction of ions is by ion hopping into neighboring vacant sites and hence, increases the ionic conductivity to a higher value.



Figure 5.4: Arrhenius plots for the conductivity of (a) Si-0, (b) Si-4 and (c) Si-10

Si-10 did not show appreciable increases in ionic conductivity as the temperature increases. This can be rationalized to the blocking of ion migration in the polymer matrix where the large and bulky grain size from the agglomeration of silica particles block the conduction of charge carriers. Table 5.1 summarizes the ionic conductivity values, the activation energy (E_a) values and regression (R) values for selected samples.

	Ionic cond	luctivity, σ		
Designation	S/e	cm	Activation energy, $E_a (eV)$	Regression value, R
	(25 °C)	(70 ℃)	-	
Si-0	1.55E-05	4.22E-04	0.64	0.9952
Si-4	1.23E-04	5.02E-04	0.25-	0.9817
Si-10	5.59E-05	6.00E-05	0.0234	0.9915

Table 5.1: Data on ionic conductivity-temperature studies for Si-0, Si-4 and Si-10

5.3 DIFFERENTIAL SCANNING CALORIMETRY (DSC)

The glass transition temperature (T_g) of solid polymer electrolytes are determined by using DSC analysis. The deviation of T_g with silica content are shown in Fig. 5.5. With the increase in the concentration of silica, the T_g values of polymer electrolytes are raised. The increase in T_g is attributed to the formation of transient cross link between silica and corn starch-LiClO₄ polymer matrix which restricts the segmental motion of the polymer chain, leading to an increase in T_g [Hou *et al.*, 2003].



Figure 5.5: Glass transition temperature for silica added corn starch-LiClO₄ polymer electrolyte system.

Based on Fig. 5.5, one can easily find that T_g increases remarkably with content of nano silica increased, which will reduce the chain segment and consequently reduce the resistance to transport electroactive substance and hence a drop in ionic conductivity.

Maximum ionic conductivity as a function of silica content is generally explained by the increase of T_g competing with increase in the number of charge carriers. The decrease in ionic mobility due to the increment of T_g seems to predominate over the increase in the number of charge carrier ions at high silica content. Thus, ionic conductivity data passes through the maximum value and thereafter, decreases as silica concentration increases.

5.4 THERMOGRAVIMETRIC ANALYSIS (TGA)

Thermal stability can be determined by using TGA where the weight loss of the sample will be observed over the temperature range of 20-600 °C. TGA thermograms of Si-0, Si-4 and Si-10 are shown in Fig. 5.6, Fig. 5.7, and Fig. 5.8 respectively. The initial weight loss for Si-0 up to 118 °C is around 15%. However the intensity of weight loss increases sharply up to 48% at a higher temperature of 237 °C. The first degradation step is attributed to the loss of water molecules. The prolonged weight loss due to solvent evaporation is most likely due to some of the water molecules becoming entrapped in small cavities formed in corn starch polymer matrix upon gelatinization, where it is hard for them to diffuse out from the sample. The thermal decomposition of corn starch polymer main chain was shown in second weight loss.



Figure 5.6: TGA thermogram for Si-0



Figure 5.7: TGA thermogram for Si-4



Figure 5.8: TGA thermogram for Si-10

With the addition of 4 wt.% fumed silica as in Si-4, the sample has a comparatively larger initial weight loss approximately up to 20% compared to Si-0. The weight loss increases sharply up to 48% at a higher temperature of 244 $\$ compared to Si-0. The Hydroxyl group on the surface of nano silica increased the moisture absorption where the initial weight loss can be due to evaporation of water molecules. The second weight loss begins at a temperature of 244 $\$ which is the maximum weight loss reflecting the decomposition of polymer main chain.

Si-10 shows similar properties as Si-4 with around 20% initial weight loss which is suspected from the contribution of hydrophilicity of SiO₂ particles. The second weight loss for Si-10 is around 50% indicating consistent corn starch polymer content in the film prepared. However the decomposition temperature increases with higher content of nano silica in the polymer matrix. Si-10 starts to decompose at 257.7 °C which is higher than Si-4 and Si-0 indicating better thermal stability. This behavior can be explained on the basis of strengthening of the C-O bond, caused by the transient crosslink of silica with the oxygen atom [Santhosh *et al.*, 2006]. This is in good agreement with DSC results showing that higher T_g and higher decomposition temperature can be obtained by higher content of nano silica. The above analysis reveals that, the addition of nano silica restrict the segmental motion of the polymer chain and thus increased the T_g and decomposition temperature of the polymer electrolyte system.

5.5 DEGREE OF SWELLING

The hydrophilic nature of the hydroxyl group in amylose and amylopectin allows water absorption, results in swelling and assists permeation in transporting through membrane. However, if too much water absorption occurs, it may result in excessive mechanical fragility and morphological instability of membrane. Table 5.2 shows the water solubilities of the samples prepared. The addition of nano-silica into the system reduced the percentage of water solubility in the membrane from 50.44% for Si-0 to 29.57% for Si-10. This can be explained by the cross linking between corn starch and nano-silica. Meanwhile, as the cross-linking density increases, it limits the polymer chain mobility and leads towards a denser membrane structure as well as a smaller free volume, which results in a smaller hydrophilic channel. The network structure formed by combining nano-silica with starch prevented the water molecules from dissolving, improved the water resistance of the film. This is in good agreement as describe in thermal analysis, when more nano-silica is added into the system the silica will restrict the segmental mobility of the main chain polymer and thus leading to higher decomposition temperature and T_g value.

Designation	Water solubilities, $W_{\rm s}(\%)$
Si-0	50.44
Si-2	45.29
Si-4	43.31
Si-6	40.19
Si-8	39.59
Si-10	29.57

Table 5.2:	Water solublities of	corn starch-LiClO ₄)/SiO ₂	polymer electrolyte films
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Chapter 6

RESULTS AND DISCUSSION: SYSTEM III (Corn stach-LiClO₄:BaTiO₃)

6.1 SCANNING ELECTRON MICROSCOPY (SEM)

SEM images of Ba-2, Ba-6 and Ba-10 are shown in Fig. 6.1, Fig. 6.2 and Fig. 6.3, respectively. From the SEM images, we can observe that when nano-sized BaTiO₃ is introduced into the polymer matrix, LiClO₄ tend to aggregate to form larger piece of particles. As shown in Fig. 6.1, Ba-2 shows a large aggregate particle where its grain size is around 25 μ m. The addition of BaTiO₃ penetrates the polymer electrolyte system and dissociates excess LiClO₄ which adsorb on the surface of polymer electrolyte. The dissociation of salt due to the addition of BaTiO₃ particles has formed a large conductive aggregate which provide extra pathway for ion migration [Sun *et al.*, 2000]. Consequently, the ionic conductivity improves for composite polymer electrolytes.

Ba-6 shows more LiClO₄ salt dissociates form on the surface of the polymer matrix. The formation of more crystallite on top of the surface is suspected to increase the crytallinity of the corn starch polymer. These aggregate particles of BaTiO₃-LiClO₄ form a new ion conduction pathway instead of cation Li^+ hopping in the vacant Li-O bond in corn starch polymer backbone. The ferromagnetism of BaTiO₃ facilitates faster salt dissociation of LiClO₄ into ionic species which responsible for higher ionic conductivity. Therefore, an increase in ionic conductivity is expected when more BaTiO₃ is added into the system. Ba-10 shows homogeneous distribution of BaTiO₃-LiClO₄ aggregate particles on the surface of corn starch. As more BaTiO₃ is added into the polymer electrolyte system, excess LiClO₄ will have more platforms to bond which facilitates the dissociation. As compared to Ba-2, due to the lesser amount of BaTiO₃ contain in the system, only a few aggregates are formed around the surface of corn starch. Ba-10 shows a large and thick aggregate formation where agglomeration of filler particles at high concentration of BaTiO₃ [Bhide and Hariharan, 2008]. The interaction between ionic species and fillers on the surface is responsible for the increase in ionic conductivity due to the creation of additional sites for ionic migration. Close inspection of Ba-10 morphological behavior explores the presence of tail like chain segments on the particles. This is responsible for the high ionic conductivity of samples [Fan et al., 2003].



Figure 6.1: SEM micrograph for Ba-2



Figure 6.2: SEM micrograph for Ba-6



Figure 6.3: SEM micrograph for Ba-10

6.2 A.C. IMPEDANCE SPECTROSCOPY

The temperature dependence ionic conductivities of composite polymer electrolyte films were investigated at temperature range of 25 $^{\circ}$ to 75 $^{\circ}$. Table 6.1 shows the ionic conductivity for all prepared composite polymer electrolytes. The results clearly illustrate that the ionic conductivity of the polymer electrolytes significantly improved from 10⁻⁶ to 10⁻⁴ with increase concentration of BaTiO₃ concentration up to 10 wt.% at room temperature.

Ionic conductivity at 25 $^{\circ}$ C	Ionic conductivity at 75 $^{\circ}$ C
$(S \text{ cm}^{-1})$	$(S \text{ cm}^{-1})$
4.58×10^{-6}	5.09×10^{-3}
5.39×10^{-6}	8.81 $\times 10^{-3}$
1.99×10^{-5}	8.86 ×10 ⁻³
2.08×10^{-5}	1.00×10^{-2}
1.84×10^{-4}	1.28×10^{-2}
	Ionic conductivity at 25 °C (S cm ⁻¹) 4.58×10^{-6} 5.39×10^{-6} 1.99×10^{-5} 2.08×10^{-5} 1.84×10^{-4}

Table 6.1:Ionic conductivity values for the corn starch-LiClO₄-BaTiO₃ polymer
electrolytes

This observation was accounted to the dissociation of $LiClO_4$ in corn starch matrix by weakening the inter-ion Coulomb force between the anions and cations, making more availability of Li^+ ions. This is mainly due to the ferromagnetism nature of BaTiO₃ which promotes faster dissociation of $LiClO_4$ salt. The general expression of ionic conductivity of a homogeneous polymer electrolyte is shown as

$$\sigma(\mathbf{T}) = \sum n_i q_i \mu_i$$

Where n_i = number of charge carrier

 $q_{\rm i}$ = charge of ion

 μ_i = mobility of ion

Based on the equation, mobility of charge carriers are the main aspects that could affect the ionic conductivity. The ionic conductivity is strongly controlled by the mobility of ion and number of charge carrier. The ionic conductivity increase gradually with the concentration of BaTiO₃ added. Addition of BaTiO₃ promotes decoupling of lithium salt, hence increased the amount of charge carriers and eventually leads to higher ionic conductivity.

Ba-10 which contains 10 wt.% of BaTiO₃ shows the highest ionic conductivity. An ionic conductivity of 1.84×10^{-4} S cm⁻¹ has been achieved by Ba-10 at room temperature. This can be explained by the effect of amylose and amylopectin segregation and the electrostatic forces originated from the dipole moments in the BaTiO₃ particles. Owing to the acidic surface of BaTiO₃, it competes with the cations to interact with the basic ether oxygen of the polymer matrix [Kim and Kim, 1999]. Consequently, the ionic coupling of the oxygen and cation have been reduced which promotes faster dissociation of the salt [Wu *et al.*, 2011]. The spontaneous polarization of BaTiO₃ facilitates dissociation of the salt whereby a highly conductive layer formed around BaTiO₃ particles which create extra pathways for ion migration [Burke, 2000]. These interactions increase the contents of free
charge carriers in the electrolytes and enhanced the ionic conductivity of the nanocomposite polymer electrolytes.

Fig. 6.4 depicts the plot of logarithm σ against 1000/T for Ba-2, Ba-8 and Ba-10. As can be seen, the ionic conductivity of composite polymer electrolytes increases as the temperature increases. This is attributed to the expansion of polymer matrix when temperature increased. Expansion of polymer matrix results in the formation of free volume and unoccupied spaces for the migration of ions.

However, the ionic conductivity data exhibits two distinct behaviors. Ba-2 exhibit Arrhenius type behavior while Ba-8 and Ba-10 are expected to obey VTF (Vogel-Tamman-Fulcher) relation. According to Arrhenius rules, the ionic conductivity increases when temperature increases due to ion hopping mechanism [Hashmi *et al.*, 2007].

Ionic conductivity data for Ba-8 and Ba-10 shows two distinct regions marked by a sluggish transition around 50 °C. A tendency of curvature was observed above the softening point and this is believed to obey the VTF relation. This type of behavior exhibited by the conductivity data is often attributed to the segmental motion-assisted ionic transport in the elastomeric rich phase. The addition of BaTiO₃ had altered the way of ion diffusion in the polymer matrix. The results obtained show good agreement with literature at 10 wt.% of BaTiO₃ incorporated into poly(ethylene oxide): LiN(CF₃SO₂)₂ polymer electrolyte system shows VTF relation behavior [Itoh *et al.*, 2003]. In the present investigation, at lower concentration of the filler particles, formation of lewis acid-base interactions promoting the dissociation of lithium salt and increased the number of mobile charge carriers available [Ulaganathan *et al.*, 2011]. On the other hand, when too much of filler is added, the formation of highly conductive pathway is favorable. The migrating ion

species can now travel along the highly conducting pathway giving rise to the increase in ionic conductivity.



Figure 6.4: Variation of log ionic conductivity as a function of temperature for Ba-2, Ba-8 and Ba-10.

6.3 DIFFERENTIAL SCANNING CALORIMETRY (DSC)

The various thermal properties such as glass transition temperature (T_g), and melting temperature of crystalline phase (T_m) of the polymer electrolytes system evaluated from the Diffrential scanning calorimetry (DSC) results are summarized in Table 6.2. A drop in T_g from 64.4 °C for Ba-0 to 17.8 °C for Ba-2 is observed, suggesting an enhancement in the flexibility of polymer chain. As the T_g is related to the segmental flexibility of the host polymer and the disordered structure, the result may be related to a possible enhancement in the segmental flexibility of polymeric chains of the electrolyte due to addition of nano BaTiO₃. The maximum conductivity is obtained for the composition exhibiting lowest T_g value, suggesting that the addition of filler increases the amorphous phase content of the polymer [Johan *et al.*, 2011]. However the role played by the filler needs a special consideration. The varied amount of BaTiO₃ does not vary T_g value significantly. A closer comparison of the conductivity and DSC results of the filler-added samples points towards the existence of a second conductivity mechanism instead of involving the polymer host directly.

Corn starch is mainly composed of two homopolymers which are amylase and amylopectin [Pareta and Edirisinghe, 2006]. In the presence of LiClO₄, Li⁺ ion will attached to ether group on amylase and amylopectin chain. The addition of BaTiO₃ ceramic fillers influences the attraction of ether group on corn starch and Li⁺ ion. BaTiO₃ is a typical ferroelectric material with high dielectric constant was dispersed in the amylase and amylopectin matrix. The electrostatic force originated from the dipole moments in the BaTiO₃ particles causing to weaken the Li⁺-O interaction in the carbohydrate polymer electrolyte chain [Takeuchi *et al.*, 199]. Conclusively, The addition of filler creates extra migrating pathway for Li⁺ ions due to the Lewis acid-base type interactions with O/OH surface group on BaTiO₃ grains. These interactions would be able to provide transient sites for ionic hopping, consequently providing additional conductivity pathways for ion migration [Pitawala *et al.*, 2007].

Designation	Glass transition temperature, T_g (°C)	Melting point, $T_{\rm m}$ (°C)
Ba-0	64.4	-
Ba-2	17.8	86.1
Ba-4	17.4	84.9
Ba-6	17.3	80.6
Ba-8	17.4	84.9
Ba-10	17.2	-

 Table 6.2:
 Thermal properties of the corn starch-LiClO₄-BaTiO₃ polymer electrolytes

Fig. 6.5 shows DSC thermogram showing crystalline melting temperature of Ba-2, Ba-8 and Ba-10. The endothermic peaks corresponding to the melting of crystalline phase (T_m) are observed in Ba-2 and Ba-8. The occurrence of melting peak in the samples containing BaTiO₃ nano-fillers could be rationalized to the trapping of water molecule crystal by the nano-filler or polymer-salt crystalline complexes [Marzantowicz et al., 2011]. No endothermic peak is observed in Ba-10 indicating that an amorphous phase is obtained up to 150 °C.



Figure 6.5: DSC thermograms of (a) Ba-2, (b) Ba-8 and (c) Ba-10 showing crystalline melting temperature

6.4 THERMOGRAVIMETRIC ANALYSIS (TGA)

Thermogravimetric analysis was carried out to investigate the decomposition temperature of the polymer film. The decomposition temperature decreased as small amount of BaTiO₃ is doped into corn starch polymer electrolytes. Due to the ferromagnetic nature of BaTiO₃, it competes with the cation to interact with the basic ether oxygen of the polymer. Hence, crosslinked nature in cornstarch matrix reduced due to lesser amount of available cation. However when more BaTiO₃ are introduced into the polymer electrolytes, decomposition temperature of the corn starch main chain increases. The decomposition temperature for Ba-10 increased from 228 \degree to 260 \degree compared to Ba-2 as shown in

Table 6.3. From the results obtained, the weight loss has been reduced after excess addition of BaTiO₃ due to the saturated amount of filler particle in the polymer chain which restricts the segmental motion of the polymer. As we can see from SEM microgram, the aggregates of Ba-10 grain particles become larger are in good agreement with TGA results where Ba-10 shows the highest decomposition temperature. About 30% residue remained after the heating at 600 °C, which could be attributed to the residue of crosslinked polymer, lithium salt and BaTiO₃ fillers [Chung *et al.*, 2004].

Table 6.3:Decomposition temperature and total weight loss value obtained from TGA
thermogram analysis for corn starch-LiClO₄-BaTiO₃ polymer electrolytes.

Designation	Decomposition temperature, ($^{\circ}$ C)	Total weight loss at 600 $^{\circ}$ C (%)	
Ba-2	228	78.40	
Ba-4	265	77.39	
Ba-6	258	77.35	
Ba-8	259	75.47	
Ba-10	260	72.82	

Fig. 6.6 shows the TGA thermograms for Ba-2, Ba-6 and Ba-10 up to 600 °C. There are two main weight change transition occur in the TGA plot. First weight transition is in the range of 50 - 100 °C which is mainly due to solvent removal and moisture elimination in the polymer. Second transition occurs around 225 - 260 °C was attributed to the decomposition of amylase and amylopectin of corn starch. It was found that, the heat resistivity of the system increases with increasing concentration of BaTiO₃. Decomposition

temperature of Ba-2 increased from 228 °C to 258 °C and 260 °C for Ba-6 and Ba-10, respectively. The crosslinking effect from BaTiO₃ with corn starch polymer backbone enhanced the bond strength and thus more heat energy is needed to break the bond. Thermal stability of the system has been improved gradually with increasing concentration of BaTiO₃ as well. Total weight loss at 600 °C for Ba-2 is found to decrease from 78.40 °C to 77.35 °C and 72.82 °C for Ba-6 and Ba-10, respectively. Hence it can be concluded that, the effect of doping BaTiO₃ filler into corn starch polymer electrolyte system increased the heat resistivity and thermal stability of the film making it suitable in electronic device application.



Figure 6.6: TGA plot for (a) Ba-2, (b) Ba-6 and (c) Ba-10 showing different decomposition temperatures

6.5 DEGREE OF SWELLING

Solubility test is important to determine the water resistivity of the membrane. The hydrophilic nature of the hydroxyl group in amylose and amylopectin allows water absorption, results in swelling and assists permeation in transporting through membrane. However, if too much water absorption occurs, then it may result in excessive mechanical fragility and morphological instability of membrane. Fig. 6.7 shows the variation of water solubilities as a function of BaTiO₃ content. The addition of BaTiO₃ into the system reduced the total weight loss percentage of the polymer from 50.44% to 40.82% for Ba-0 and Ba-2 respectively. Ba-10 shows the lowest water solubility around 19.63%. The addition of ceramic fillers into the polymer system reduced the penetration of water molecule into corn starch-LiClO₄ polymer electrolyte. As more ceramic fillers are deposited, it limits the polymer chain mobility and leads towards a denser membrane structure as well as a smaller free volume, which results in a smaller hydrophilic channel. The network structure formed by combining BaTiO₃ with starch prevented the water molecules from dissolving, improved the water resistance of the film.



Figure 6.7: Variation of water solubilities as a function of BaTiO₃ content.

Chapter 7

Characteristics of electrical double layer capacitor

7.1 INTRODUCTION

In the last decade, electrochemical capacitors have attracted numerous interests as alternative energy storage systems compared to conventional capacitors and secondary batteries. The electric double layer capacitor (EDLC) has been widely used as memory back-up devices in many fields of electric equipments. The development of environmental friendly energy storage device is the main objective in this research.

In this chapter, the highest conducting polymer electrolyte from each system is used to fabricate EDLC cells using activated carbon as electrode. The characteristics of the EDLCs were studied using linear sweep voltammetry, cyclic voltammetry, low frequency impedance and galvanostatic charge discharge cycling to evaluate the capacitance value, electrochemical stability, internal resistance, maximum energy and power that can be delivered by the EDLC.

7.1 LINEAR SWEEP VOLTAMMETRY (LSV)

The electrochemical stability of the polymer electrolyte has been determined by using linear sweep voltammetry (LSV) before the fabrication of EDLC in order to determine the working voltage range. The measurements were carried out using the CH- Instrument Model 600D electrochemical analyzer. Fig. 7.1, 7.2 and 7.3 depict the voltammogram scan for CS40, Si-4 and Ba-10 from -4 V to 4 V with scan rate of 10 mVs⁻¹ by using stainless steel as blocking electrodes.



Figure 7.1: Linear Sweep Voltammetry curve of CS40

The electrochemical stability of CS40, Si-4 and Ba-10 has been found as 3.1, 2.7 and 3.1 V, respectively. The current onset is assumed to be the polymer electrolyte film breakdown voltage. Prior to the charge-discharge cycling test, the working voltage must be determined below this breakdown voltage to prevent the voltage decomposition of the polymer electrolyte. Hence, concluding it as no appreciable current flow is observed in the polymer electrolyte study in the range of -1 to 1 V as the working voltage for EDLC cell in this study.



Figure 7.2: Linear Sweep Voltammetry curve of Si-4



Figure 7.3: Linear Sweep Voltammetry curve of Ba-10

7.2 CYCLIC VOLTAMMETRY (CV)

Cyclic voltammetry is useful to understand the electrochemical behavior of EDLC during charge discharge process. In this study, cyclic voltammetry (CV) is carried out by using Autolab PGSTAT 12 potentiostat/galvanostat in conjunction with the General Purpose Electrochemical System (GPES) software to investigate the electrochemical behavior and nature of charge storage at the interface of anodic and cathodic regions [Hashmi *et al.*, 2007].

Fig. 7.4 shows the difference scan rate for CS40 in the range of 0 to 1.0 V. The large different in capacitive current is observed indicates that the scan rate of CV gives an effect on EDLC performance.



Figure 7.4: Cyclic voltammogram of the EDLC with CS40 polymer electrolyte.

An ideal capacitor with no resistance would display a rectangular shape where non-Faradaic reactions take place over the potential range of operation [Frackowiak and B éguin, 2001]. A parallelogram like shape is attributed to the distributed capacity effect that occurs when the exterior surface of porous electrodes charges or discharges faster than the interior and when the electrode resistance is non-uniform [Tanahashi, 2005]. Fig. 7.4 shows at lower scan rate the shape of the cyclic voltammogram is most likely to be rectangular, however at higher scan rate the shape would deviate to an oval-like shape. This can be attributed to the large internal resistance of solid polymer electrolyte. At high scan rate, the charge carriers have insufficient time to charge to the electrode surface due to the blocking of internal resistance where at lower scan rate the diffusion of ions have sufficient times to align accordingly to the polarity respectively.

Fig. 7.5 depicts the cyclic voltammograms for the capacitors with CS40 and Si-4 at 10 mVs^{-1} and room temperature.



Figure 7.5: Cyclic voltammograms of (a) CS40 and (b) Si-4 at 10 mVs⁻¹

The values of the capacitance calculated according to equation:

$$C = jv^{-1}$$

Where C is capacitance (F), *j* is average current (A) and *v* is scan rate (V s⁻¹). In a symmetrical two-electrode system the specific capacitance $C_{\rm m}$ (F g⁻¹) for an activated carbon can be obtained from the capacitance of the cell C by equation

$$C_m = \frac{2C}{m}$$

Where *m* is the weight (g) per electrode. Si-4 depicts higher current peak compared to CS40 as shown in Fig. 7.5 which eventually shows higher calculated capacitance value. Fig. 7.5 exhibited almost perfect horizontal plateau indicating ion diffusion occurs at a fairly constant rate with minor impact from ohmic resistance [Ganesh *et al.*, 2008]. This can be attributed to the formation of a homogenous and ideally polarizable double layer formed at the interface [Chung *et al.*, 2004]. The CV curves discrepancy from a box-like shape is assigned to the internal resistance and carbon porosity, which produces a current dependence of potential [Tien *et al.*, 2008; Niu *et al.*, 2006].

Fig. 7.6 depicts the cyclic voltammogram for the capacitor with Ba-10 in the range of -1 to 1 V at 10 mVs⁻¹ and room temperature.



Figure 7.6: Cyclic voltammogram for Ba-10 at 10 mVs⁻¹ at room temperature.

The behavior observed is comparable to rectangular shape where no redox peaks are observed. This can be attributed to the formation of a homogenous and ideally polarizable double layer formed at the interface [Ganesh *et al.*, 2008]. The voltammograms exhibited almost perfect horizontal plateau indicating ion diffusion occurs at a fairly constant rate with minor impact from ohmic resistance [Tien *et al.*, 2008]. The discharge current shows an almost plateau feature on the return path. This can be attributed to the formation of homogeneous and ideally polarizable double layer formed at the interface [Ganesh *et al.*, 2008].

7.3 GALVANOSTATIC CHARGE DISCHARGE CHARACTERFISTICS

The charge-discharge characteristics of the EDLC cells are evaluated galvanostatically. Working voltage of an EDLC cell is largely dependent on the electrolyte breakdown voltage, while internal resistance and capacitance depends on the electrode and conductivity of electrolyte. In this work, the voltage limits were set between 0 to 1.0 V to avoid the decomposition of the polymer electrolytes and constant current was applied during charge and discharge.

Fig. 7.7 shows the charge-discharge profile for EDLC cells for CS40 and Si-4 at constant current of 0.5 mA in the range of 0 and 1.0 V. Fig. 7.8 shows the charge discharge curves for the fabricated EDLC cell at current density of 4.0 mA cm⁻² with a maximum cell potential of 1.0 V. The charge and discharge characteristics have been found to be almost symmetrical indicates their high Coulombic efficiency. The initial jump/drop in the voltage while charging and discharging each cell has been observed, which is due to ohmic resistance (R_t), referred as equivalent series resistance (ESR) of the cells.



Figure 7.7: The charge discharge curves for EDLC cell of (a) CS40 and (b) Si-4 in the range of 0 - 1 V with constant current 0.5 mA.

The discharge characteristics have been found to be almost linear, which confirms the capacitive behavior of the EDLC cell. However these curves do not show the perfect "inverse V shape" for charging and discharging. ESR can be calculated from the voltage drop or IR_{drop} while discharging the EDLC as shown by the equation:

$$ESR = \frac{IR_{drop}}{i}$$

Where, IR_{drop} is the voltage drop upon discharge while *i* is the discharge current.



Figure 7.8: The charge discharge curves for EDLC cell of Ba-10 in the range of 0 - 1 V with constant current density 4.0 mA cm⁻².

The time required for charging or discharging for the capacitors was nearly identical at this low current density. This reflects similar ultimate charge-storage capacities. The cell capacitance is deduced from the discharge curve with

$$C = \frac{2\mathsf{D}I}{\mathsf{D}V \times m}$$

Where, C is the specific cell capacitance (F g⁻¹), ΔI is the discharge current in amperes (A), ΔV is the voltage scan and *m* is the mass of electrode. The energy stored in a capacitor was calculated as

$$E = 0.5 \text{ CV}^2$$

Where, C is the specific capacitance and V is the working voltage. The power (P) was calculated as

$$P = \frac{V^2}{4ESR}$$

Where, *V* is the working voltage and *ESR* is equivalent series resistance. Calculated results are presented in Table 7.1, Table 7.2 and Table 7.3 for CS40, Si-4 and Ba-10, respectively.

 Table 7.1 Main EDLC results for devices with CS40.

	CS 40		
	Impedance Spectroscopy	Cyclic Voltammetry	Charge- discharge
Specific Capacitance (F g ⁻¹)	5.33	5.42	7.09
Energy density (W h kg ⁻¹)	-	-	0.668
Power density (W kg ⁻¹)	-	-	106.9

 Table 7.2 Main EDLC results for devices with Si-4.

	Si-4		
	Impedance Spectroscopy	Cyclic Voltammetry	Charge- discharge
Specific Capacitance (F g ⁻¹)	9.29	8.71	9.83
Energy density (W h kg ⁻¹)	-	-	0.902
Power density (W kg ⁻¹)	-	-	135.0

Table 7.3 Main EDLC results for devices with Ba-10.

	Ba-10		
	Impedance Spectroscopy	Cyclic Voltammetry	Charge- discharge
Specific Capacitance (F g ⁻¹)	13.95	13.41	16.22
Energy density (W h kg ⁻¹)	-	-	1.380
Power density (W kg ⁻¹)	-	-	238.3

Ba-10 shows the highest energy density and power density obtained from charge discharge test compared to CS40 and Si-4. It could be rationalized to the higher ionic conductivity of Ba-10 polymer electrolyte compared to CS40 and Si-4. In order to split apart anode from contacting cathode, polymer electrolyte is needed as a membrane separator to avoid short circuit. However, this membrane separator is required to have high ionic conductivity in order to allow charge carrier to move freely. Therefore, high ionic conductivity is one of the main criteria in fabricating high capacitance EDLC.

The advantage of EDLC compared to conventional energy storage devices like lithium batteries is its long cycle life. Cycling test was performed to evaluate cycle durability of the fabricated EDLC cells. Here we summarize the dependence of coulombic efficiency on cycle number. Coulombic efficiency (η) is calculated as

$$h = \frac{C_d}{C_c} \quad 100\%$$

Where, C_c and C_d are the charge and discharge capacitance at each cycle, respectively. Fig. 7.9, Fig. 7.10 and Fig. 7.11 indicates the fabricated cells containing CS40, Si-4 and Ba-10, maintained their coulombic efficiency at ~ 90 % throughout 500 cycles, suggesting that the proper interfacial contacts between both electrode and electrolytes.



Figure 7.9: Variation of coulombic efficiency and voltage drop with CS40 as a function of cycle number.



Figure 7.10: Variation of coulombic efficiency and voltage drop with (b) Si-4 as a function of cycle number.



Figure 7.11: Variation of coulombic efficiency and voltage drop with Ba-10 as a function of cycle number.

EDLC containing CS40 shows an average voltage drop of 0.15 V over 500 cycles. As mentioned earlier, voltage drop is directly proportional to ESR. CS40 shows stable performance over 500 cycles where the resistance of the EDLC cell did not increase over long cycle tests which is suitable candidates for EDLC application.

A decrease in voltage drop from 0.2 to 0.1 V in the initial 100 cycles and stable up to 500 cycles has been observed in Si-4 suggesting that the EDLC cells are stable under these charge-discharge conditions. The initial drop of voltage shows the decrease in internal resistance of the cell. It could be due the formation of Faradaic pseudo-capacity around the electrode and electrolyte interface and hence lower the resistance for ion migration [Lewandowski and Olejniczak, 2007].

Ba-10 performed well in EDLC cell over 500 cycles as well. The voltage drop of EDLC containing Ba-10 maintained around 0.2 V over 500 cycles. This might be due to the larger grain size which restricts the mobility of cation from migrating to respective polarity electrode as observed in SEM morphology.

7.4 LOW FREQUENCY IMPEDANCE SPECTROSCOPY

Complex impedance spectra for both fabricated CS40, Si-4 and Ba-10 cells are shown in Fig. 7.12. Impedance spectroscopy enables the evaluation of various parameters associated with the bulk properties of electrolytes and electrode-electrolyte interactions. The nyquist plots of the impedance spectra analyses show a semicircle nature at high frequency region (100kHz - 1Hz) and a line inclined to the real axis in the low frequency region (1Hz - 10mHz).



Figure 7.12: Nyquist impedance plot for EDLC containing (a) CS40, (b) Si-4 and (c) Ba-10 with equivalent circuit is shown in inset

The impedance in the high-frequency region reflects the bulk properties of the electrolytes and the charge transfer process at the electrode-electrolyte interface of the newly assembled supercapacitors. Bulk resistance, R_b and Charge transfer resistance, R_{ct} can be determined from plotting a locus of the semicircle intercepts the real axis at R_b and R_b+R_{ct} in the nyquist plot. The contact situation between the electrode and electrolyte can be characterized through high frequency region. This information is especially important to solid polymer electrolyte due to the contact issue between electrode and electrolyte.

Resistance of ion migration in the corn starch based biopolymer electrolyte can be determined from R_{ct} of the cell. A Warburg diffusion element is introduced in the circuit to emphasize the resistance for ion diffusion in micropores [Tien *et al.*, 2008]. Hence pore resistance, R_p is incorporated to replace Warburg element.

Total resistance, R_t can be determined from IR drop. Thus, pore resistance R_p can be obtained by subtracting R_b and R_{ct} from R_t . All the values of different resistance components for the cells are summarized in Table 7.4.

Si-4 shows the highest value of R_b and R_p compared to CS40 and Ba-10. This is in good agreement that higher voltage drop is observed for Si-4 in the initial charge-discharge profile. The addition of silica increased the internal resistance of the devices where the migration of the Li⁺ ions faces a greater resistance due to larger pore size.

Table 7.4: The overall resistance (R_t) , bulk resistance (R_b) , charge transfer resistance (R_{ct}) and resistance of ion migration in carbon micropores (R_p) of CS40, Si-4 and Ba-10 EDLC devices.

EDLC cells		Resista	nce (Ω)	
	Rt	R _b	R _{ct}	R _p
CS40	363	172	45	146
Si-4	463	200	55	208
Ba-10	257	97	25	135

However as explained earlier, the ferromagnetism of this silica helps to dissociate the aggregate ion and undissociated salt to achieve higher ionic conductivity hence higher capacitance value is obtained. Ba-10 shows the lowest overall resistance (R_t), bulk resistance (R_b), charge transfer resistance (R_{ct}) and resistance of ion migration in carbon micropores (R_p) compared to CS40 and Si-4. This is in good agreement with capacitance value obtained from CV, charge discharge and impedance spectroscopy where Ba-10 shows the highest capacitance value compared to CS40 and Si-4. Therefore, we can conclude that, higher ionic conductivity shows higher capacitance value of fabricated EDLC cells.

Fig. 7.13 shows the specific capacitance for CS40, Si-4 and Ba-10 plotted as functions of frequency. The specific capacitance for EDLCs from impedance spectra can be calculated by using the following relationship:

$$C_{cell} = -\frac{1}{2\rho fz"}$$

Where Z" is the imaginary impedance (Ω) and f is the frequency (Hz). Capacitance rises at lower frequency when the frequency increases can be related to electrode polarization effect [Mishra and Rao, 1998]. Hence at higher frequencies, the capacitor behaves like a pure resistor and at low frequencies it shows capacitive behavior. The specific capacitance calculated from cyclic voltammetry, galvanostatic charge-discharge and impedance spectroscopy are shown in Table 7.1, Table 7.2 and Table 7.3 for CS40, Si-4 and Ba-10 respectively.



Figure 7.13: Specific Capacitance versus frequency plots for EDLC cells (a) CS40, (b) Si-4 and (c) Ba-10

7.5 COMPARISON OF EDLC FABRICATED WITH LITERATURE

In this study, the fabricated EDLC cells show good performance and maintained their coulombic efficiency at ~ 90% during 500 charge discharge cycles, suggesting that the proper interfacial contacts between both electrode and electrolytes and good electrochemical stability. A comparison of the EDLCs in this work with other studies was made and shown in Table 7.5. The entire listed quotes are solid state EDLCs fabricated with solid polymer electrolytes. This suggests that, corn starch biopolymer electrolytes show comparable and promising EDLC performance.

Active material	Electrolytes	Working voltage (V)	Capacitance (F g ⁻¹)	Reference
Carbon	Nafion/PTFE composite polymer	0-2	16.0	[Subramaniam <i>et al.</i> , 2011]
Activated carbon (BP20)	MC/NH ₄ NO ₃ /PE G200	0-0.85	38.0	[Shuhaimi <i>et</i> <i>al.</i> , 2012]
Carbon cloth	PU/EC/PC/LiCl O ₄	0-1	5.5	[Latham <i>et al.,</i> 2002]
Carbon black pearls 2000	(PEO- NPPP) ₁₁ /LiClO ₄	0-1	17.0	[Lavall <i>et al.,</i> 2008]
Activated carbon (BP20)	Corn starch/LiClO4/ BaTiO3	0-1	16.2	Current study

Table 7.5: Capacitance of EDLCs using different solid polymer electrolytes

CHAPTER 8

DISCUSSION

8.0 **DISCUSSION**

The aim of this study is to develop and characterize corn starch based polymer electrolyte with salt and filler added. The composition with the highest ionic conductivity from each system would then be used to fabricate EDLC cell. The successful breakthrough in this field would mean enormous benefit to the field of energy sources and green energy. In the last decade, biodegradable polymer is replacing the synthetic polymer in various filed of application. In line with our aim, we have successfully developed corn starch based polymer electrolytes with LiClO₄ as salt and SiO₂ and BaTiO₃ as fillers. All the samples were prepared by solution casting technique. Subsequently, EDLC cells with the highest ionic conductivity membrane from each system have successfully fabricated.

Scanning electron microscopy was used to investigate the surface morphology of the polymer electrolytes. The structure and morphology of a polymer electrolyte film surface is an important property for the polymer electrolyte. As mentioned earlier in chapter 4, the SEM micrograms show that the addition of LiClO₄ increases the crystallinity of the polymer electrolyte. The addition of excess LiClO₄ salt would form undissociated crystalline salt on the surface of polymer. The bulky size of this crystalline salt increases the charge transfer resistance of the polymer film during ion conduction mechanism. This undissociated salt would eventually become barriers which reduces the ionic conductivity of the film. However, the introduction of filler has changed the morphology of the polymer electrolyte. Fillers help to dissociate undissociated LiClO_4 and created new ion migration pathway. The addition of 4 wt.% of silica induces the growth of platelet like particles with grain size between 1 and 5 µm. When more silica is added into the system, the fillers tend to aggregate together forming large and bulky particles. The larger grain size reduced the number density of ions and reduced the ionic mobility that could be due to ion trap in the polymer electrolytes.

Similar observation was observed in $BaTiO_3$ fillers. The addition of $BaTiO_3$ penetrates the polymer electrolyte system and dissociates excess $LiClO_4$ which adsorb on the surface of polymer electrolyte. The dissociation of salt due to the addition of $BaTiO_3$ particles has formed a large conductive aggregate which provide extra pathway for ion migration [14]. The interaction between ionic species and fillers on the surface is responsible for the increase in ionic conductivity due to the creation of additional sites for ionic migration.

From the SEM morphology, we can observe that the addition of excess $LiClO_4$ created undissociated crystalline salt on the surface of polymer electrolyte which increases the crystallinity and reduces the ionic conductivity. The presence of SiO_2 and $BaTiO_3$ fillers play a role that helps to dissociate excess $LiClO_4$ salt.

An important factor in the development of polymer electrolyte is the ionic conductivity. The ionic conductivity value of corn starch was enhanced by addition of LiClO₄ as salt. The highest ionic conductivity obtained for corn starch:LiClO₄ complexes is 1.55×10^{-6} S cm⁻¹ for 40 wt.% of LiClO₄ at room temperature. The increase of salt in the polymer complex increases the number of charge carrier and ionic mobility. Thus, the ionic

conductivity increases with the salt content. However, the ionic conductivity decreases upon reaching the optimum concentration of salt concentration due to the formation of ion aggregate and decrease in ionic mobility. In order to improve the existing ionic conductivity values of corn starch: $LiClO_4$ complexes, SiO_2 and $BaTiO_3$ were added.

The increase in the ionic conductivity with increasing silica concentration can be related to the charged nature of the interface of silica promotes the dissociation of aggregate ion and undissociated salt into free moving ions. The highest ionic conductivity of 1.23×10^{-4} S cm⁻¹ was achieved with the addition of 4 wt.% of SiO₂ into the corn starch polymer electrolyte system at room temperature. The addition of BaTiO₃ filler shows better performance where at 10 wt.% of BaTiO₃, ionic conductivity value of 1.84×10^{-4} S cm⁻¹ was achieved at room temperature. This might be due to the higher ferroelectric value of BaTiO₃ compared to SiO₂ particle. The above discussion clearly shows that the addition of fillers (SiO₂ and BaTiO₃) increases the ionic conductivity values.

Temperature dependence conductivities of corn starch-LiClO₄ polymer electrolyte system investigated at temperature range of 25 °C up to 80 °C. According to Arrhenius theory, the nature of cation transport in the polymer electrolytes is quite similar to that in ionic crystals, where the ionic conductivity is enhanced through continuous hopping of Li⁺ mobile ions into neighboring vacant sites. Maximum ionic conductivity obtained for CS40 at 80 °C was 1.28×10^{-4} S cm⁻¹.

Si-4 shows increase in ionic conductivity with increasing temperature. The regression values close to unity suggesting that the temperature dependent ionic conductivity obey the Arrhenius rule. The highest ionic conductivity achieved with Si-4 was 5.02×10^{-4} S cm⁻¹ which is higher compared to CS40. This is mainly due to the

addition of silica soften the polymer backbone where the segmental motion of the corn starch polymer matrix increases.

Ba-10 is expected to obey VTF (Vogel-Tamman-Fulcher) relation which is different conduction mechanism compared to CS40 and Si-4. This is attributed to the segmental motion-assisted ionic transport in the elastomeric rich phase. The addition of BaTiO₃ had altered the way of ion diffusion in the polymer matrix. The highest ionic conductivity obtained for Ba-10 is 1.28×10^{-2} S cm⁻¹ at 75 °C. Ba-10 shows significantly better ionic conductivity compared to Si-4 and CS40.

Based on the discussed results, a possible conduction mechanism was proposed for CS40 and Si-4. Ion hopping mechanism is favored in CS40 and Si-4 due to the temperature dependence ionic conductivity obeys the Arrhenius rule. However Ba-10 is expected to obey VTF relation where segmental motion assisted ionic transport mechanism is favored.

CS40 shows the lowest T_g value of 64 °C among corn starch: LiClO₄ system as shown in DSC studies. This is attributed to the higher segmental flexibility of the polymer backbone and lower resistance to ion hopping and hence higher ionic conductivity. T_g values obtained for Si-4 and Ba-10 are 87 °C and 17 °C, respectively. Ba-10 shows the lowest T_g value as compared to CS40 and Si-4. The decrease in T_g value may possibly due to the acid-base interaction between the Li⁺ ion of the LiClO₄ and oxygen in the BaTiO₃. The absence of endothermic peak was observed from the DSC studies further confirmed the amorphous nature of Ba-10. This further confirms the conduction mechanism as mentioned earlier where Ba-10 obeys VTF nature can be rationalized to the low T_g value of the polymer electrolyte. TGA was used to determine the thermal stability and heat resistivity of the film. The decomposition temperature of CS40, Si-4 and Ba-10 are 238 $\$ 256 $\$ and 260 $\$ respectively. Owing to the TGA analyses, we can conclude that the thermal stability increases with the addition of filler. The decomposition temperature increases as filler was added into the system due to the crosslinking nature of the filler with the corn starch polymer matrix. This interaction strengthens the bond and thus more heat is needed in order to break the bond. Therefore, Ba-10 shows the highest thermal stability and heat. High thermal stability is desired for good EDLC performance to avoid the decomposition of the membrane when the EDLC is performing at high temperature.

The prepared polymer electrolytes are subjected to water solubilities test. The water solubilities for CS40, Si-4 and Ba-10 are 50.44, 43.31 and 19.63% respectively. CS40 shows the highest water solubilities. This properties are not favored in the fabrication of EDLC due to the moisture may congest the polymer film under the process of charging and discharging. Other than that, if too much water absorption occurs, it may results in excessive mechanical fragility and morphological instability of membrane. The addition of BaTiO₃ into the system significantly improves the water resistivity.

CS40, Si-4 and Ba-10 were chosen as membrane separators in fabricating EDLC cells due to its high ionic conductivity among the polymer electrolyte system. The fabricated EDLC cells containing these membranes were used for cyclic voltammetry, galvanostatic charge discharge and low frequency impedance test. Prior to the capacitance testing, this membrane has to go through linear sweep voltammetry to ensure their working voltage is within the range to avoid voltage decomposition of membrane. The electrochemical stability window of CS40, Si-4 and Ba-10 has been found in the range of 3.1, 2.7 and 3.1 V, respectively.

Cyclic voltammetry was carried out to investigate the electrochemical behavior and nature of charge storage at the interface of anodic and cathodic regions. No appreciable peak was observed during charging and discharging from the cyclic voltammogram for CS40, Si-4 and Ba-10 signify that it is suitable for EDLC application. The CV curve for Ba-10 shows a rectangular shape compared to Si-4 and CS40 which are more like a parallelogram. This might be due to the internal resistance of Si-4 and CS40 is much higher. The capacitance value calculated from CV for CS40, Si-4 and Ba-10 are 5.42, 8.71 and 13.41 F g^{-1} , respectively.

Galvanostatic charge-discharge was carried out for the fabricated cells. Ba-10 shows highest capacitance value and cyclic stability up to 500 cycles compare to CS40 and Si-4. This is mainly due to the highest ionic conductivity of Ba-10 polymer electrolyte. The high ionic conductivity shows better ion mobility, higher number of charge carrier which eases the transportation of charge in the EDLC system. However all the fabricated EDLC cells show ~90% coulombic efficiency suggesting that proper interfacial contacts between polymer membranes with the electrode material.

Low frequency impedance at the range of 10 mHz to 100 kHz enable the evaluation of capacitance nature of the fabricated EDLC cells. Based on the resistance calculated from this method, Ba-10 shows the lowest resistance compared to CS40 and Si-4. The lowest internal cell resistance of Ba-10 which is another main reason proposed for the enhancement in the EDLC cell capacitance value.

The incorporation of filler into corn starch: $LiClO_4$ polymer electrolytes significantly enhances the electrochemical properties and mechanical properties of the system. From the above analyses on filler incorporation in corn starch based polymer

electrolytes, we can conclude that SiO_2 and $BaTiO_3$ has brought the ionic conductivity of polymer electrolytes into the useful dominion for materials in EDLC application with improved structural, thermal and mechanical properties. From the EDLC performance studies, Ba-10 can be considered as potential candidates for use in EDLC application.

CHAPTER 9

CONCLUSION

9.1 CONCLUSION AND SUGGESNTIONS FOR FUTURE STUDY

The urge of developing sustainable and clean energy has become the driving force in the advances in green technology. In view of this, we have used natural biodegradable polymer namely corn starch as the host polymer in the present study. Corn starch is a carbohydrate polymer which composed of amylase and amylopectin structure. We have prepared 3 corn starch based polymer electrolyte systems.

We have performed studies to investigate the surface morphology of corn starch:LiClO₄ polymer electrolytes. From the SEM study, we can notice that the addition of LiClO₄ promotes the growth of crystalline salt on the surface of corn starch polymer. By adding appropriate amount of filler concentration, it promotes the dissociation of excess LiClO₄ salt. However, if too much filler is added, the particles tend to agglomerate and form bulkier particles which block the migration of ions.

The highest ionic conductivity value obtained from corn starch:LiClO₄ complexes was further improved by incorporating fillers. By adding silica, the ionic conductivity increases form 1.55×10^{-6} S cm⁻¹ to 1.23×10^{-4} S cm⁻¹ for Si-4. Furthermore, the incorporation of BaTiO₃ increases the ionic conductivity of Ba-10 to 1.84×10^{-4} S cm⁻¹ which is higher compared to Si-4. This reveals greater dispersion of BaTiO₃ in corn starch polymer electrolytes. Temperature dependence conductivity studies disclose CS40 and Si-4 obeys Arrhenius rule while Ba-10 exhibits VTF nature.

DSC and TGA analysis further confirm the incorporation of filler increases the bond strength within polymer matrix and thereby increases thermal stability and heat resistivity. The interaction between the lithium cation of the lithium salt and oxygen in the silica through an acid-base interaction resulted in an increase in T_g value of the polymer electrolyte. This may be due to the hydrogen bonding of silica with corn starch structure enhances the bond strength and thus an increase in T_g value is observed. However, by incorporating BaTiO₃, the T_g value of CS40 drops. This is possibly due to the disruption of crystalline structure of corn starch to a more amorphous nature leading to a decrease in T_g value. Through TGA analysis, filler added samples were found to exhibit improved thermal stability.

The water solubilities for CS40, Si-4 and Ba-10 are 50.44, 43.31 and 19.63% respectively. By doping small amount of fillers into the polymer electrolyte, the water resistance of the film improves remarkably due to the stronger bond formation.

The films that exhibit highest ionic conductivity from corn starch:LiClO₄ , corn starch:LiClO₄:SiO₂ and corn starch:LiClO₄:BaTiO₃ systems have been used as electrolytes to fabricate electrochemical cells. From LSV studies, all the samples exhibit wide electrochemical stability window which is suitable for EDLC performance studies. From the CV studies, the fabricated EDLC cells with CS40, Si-4 and Ba-10 as electrolyte did not show any appreciable peaks upon charging and discharging signify that it is suitable for EDLC application.

From the galvanostatic charge discharge analysis, the addition of filler improves the discharge capacitance of the EDLC cells. An increase of 38% discharge capacitance from Si-4 is observed comparing to CS40 which is 9.83 and 7.09 F g^{-1} respectively. The addition
of BaTiO₃ tremendously increases the discharge capacitance of CS40 from 9.83 F g^{-1} to 16.22 F g^{-1} . Ba-10 shows The highest capacitance value and cycling stability up to 500 cycles compared to CS40 and Si-4 attributed to the high ionic conductivity of the electrolyte which have better ionic mobility and higher number of charge carriers.

In order to study the capacitance nature of the fabricated EDLC cells, low frequency impedance studies were carried out. Ba-10 shows notable lower internal cell resistance compared to CS40 and Si-4 which is another main reason proposed for the enhancement in the EDLC cell capacitance value. For practical application of this work, much attention should be given to the interfacial adhesion between polymer electrolyte film and electrode. Further improvements such as incorporation of plasticizers namely, ethylene carbonate (EC), dimethyl carbonate (DMC), and diethyl carbonate (DEC) or ionic liquid would elevate the performance of the cell by decreasing the crystallinity of the polymer electrolyte. The enhancement in the electrode material for higher efficiency might bring us one step closer towards practical application and commercialization.

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