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Highly Conductive Solid Polymer Electrolytes: Poly(ethylene oxide)/LITFSI Blends

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ABSTRACT

CHEMISTRY

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HIGHLY CONDUCTIVE SOLID POLYMER ELECTROLYTES: POLY(ETHYLENE
OXIDE)/LITFSI BLENDS

Committee Chair: Ishrat M. Khan, Ph.D.

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In this study, highly ionic conductive solid polymer electrolytes have been prepared by blending high molecular weight polyethylene oxide (PEO: MW 35,000 and 100,000) and bis(trifluoromethane)sulfonamide lithium (LiTFSI) salt. The ionic conductivities were determined for several compositions of the blends at different temperatures. A maximum ionic conductivity of $9.45 \times 10^{-6} \text{ S cm}^{-1}$ at 25 °C has been obtained for the blends containing PEO-35,000/LiTFSI at an ethylene oxide to lithium salt ratio (EO/Li⁺) of 5, whereas a maximum ionic conductivity $7.7 \times 10^{-6} \text{ S cm}^{-1}$ at 25 °C was observed for the PEO-100,000/LiTFSI blend at EO/Li⁺ mole ratio of 5. For all the blends, increasing the temperature resulted in enhanced ionic conductivity. Furthermore, addition of tris(pentafluorophenyl)borane (TPFPB) increased the conductivities at 25 °C. The overall conclusion of the study is that using LiTFSI and the TPFPB in the blends results in ionic conductivities suitable for use in Li-air and/or Li-ion batteries.

HIGHLY CONDUCTIVE SOLID POLYMER ELECTROLYTES: POLY(ETHYLENE
OXIDE)/LITFSI BLENDS

A THESIS

SUBMITTED TO THE FACULTY OF CLARK ATLANTA UNIVERSITY

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR

THE DEGREE OF MASTER OF SCIENCE

BY

ZAHRA ALQURAINI

DEPARTMENT OF CHEMISTRY

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LIST OF ABBREVIATIONS

DME	1,2-dimethoxyethane
DSC	Differential Scanning Calorimetry
EV	Electric vehicle
G	Gram
H EV	Hybrid electric vehicle
LiTf	Lithium triflate
LITFSI	Bis(trifluoromethane)sulfonimide Lithium salt
MW	Molecular weight
NMR	Nuclear Magnetic Resonance
ORR	Oxygen reduction reaction
PB	Prussian blue
PEG	Polyethylene glycol
PEGDME	Polyethylene glycol dimethyl ether
PEO	Polyethylene oxide
PHOS	Poly(hydroxylstyrene)

PS- <i>b</i> -PEO	Poly(styrene- <i>b</i> -ethylene oxide)
PS	Polystyrene
S cm ⁻¹	Siemens per centimetre
SPE	Solid-like polymer electrolyte
THF	Tetrahydrofuran
TPFPB	Tris(pentafluorophenyl)borane
Σ	Conductivity

CHAPTER I

INTRODUCTION

Rapid economic development and increasing industrialization has significantly increased the demand and usage of fossil fuels. The increased usage of fossil fuels is contributing to increased carbon dioxide gas emissions which are responsible for global climate change. In order to meet with energy usage demand and minimize carbon dioxide emissions, the only approach is to develop innovative renewable energy sources. The recent research and development in this area is showing that alternative energy sources are becoming viable options and will start contributing to a clean energy economy.¹ Use of clean energy will require newer higher energy density storage devices such as Lithium-ion (Li-ion) batteries and the futuristic Lithium-Air (Li-air) batteries. The high energy storage devices have found application in new generation electric vehicles and aircraft such as the Boeing 787.

1.1 Metal-Air Batteries

During the search for more efficient and higher energy storage systems, metal-air batteries have received immense attention.² They are usually comprised of four parts: metal anode, electrolyte, separator and air cathode (Figure 1). Among metal-air batteries, Li-air, Na-air, K-air and Zn-air batteries are regarded as rechargeable ones. The separator acts as an insulator which allows only the transfer of ions. During the discharge

procedure, oxidation occurs at the metal anode and oxygen reduction reaction (ORR) occurs at the air cathode. Metal-air batteries show high specific capacity due to the open battery design that employs air as the reactant.

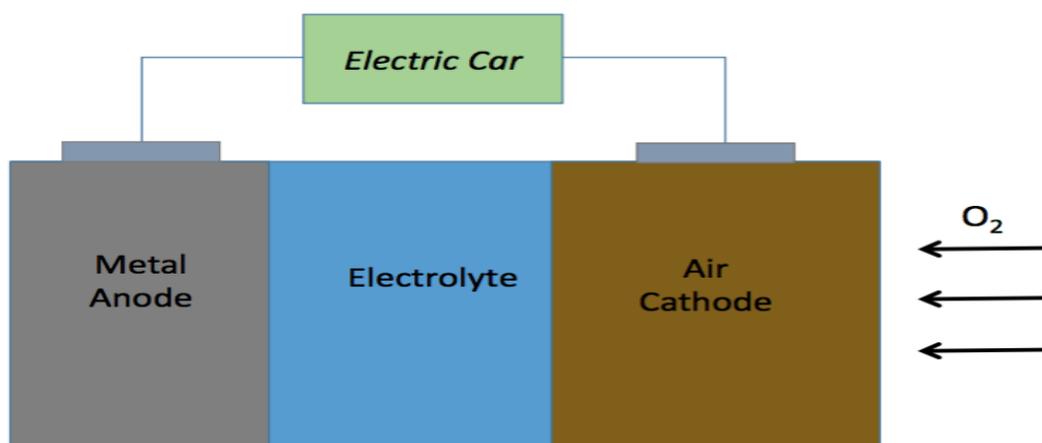


Figure 1. Schematic configuration of metal-air batteries.

1.2 Potassium-Based Batteries

Among alkali metal elements, potassium salts are commonly used as both supporting electrolytes and electro active species, due to their high conductivity, low cost, abundance, and uncomplicated electrochemical performance. Potassium batteries are at the infancy stage, and practical ideas and solutions will evolve in time. The first prototype of a potassium battery was introduced in 2004 by Eftekhari, utilizing a Prussian blue (PB) cathode.³ Since then, PB and its analogues have been widely employed as low-cost cathode materials in batteries.⁴ Ether-based electrolytes are relatively stable, and are also applied to K-air batteries. Currently, 1,2-dimethoxyethane (DME) are used as the electrolyte solvent for K-air batteries and show good stability.

1.3 Sodium-Based Batteries

Several research groups have reported sodium-ion based polymer electrolytes consisting of polyethylene oxide (PEO) complexed with NaPF₆, NaSCN, NaI, NaCF₃SO₃, and NaClO₄.^{5,6} Bhattacharya et al. reported the effect of combined sodium anion (NaI, NaCH₃COO, and NaSCN) doping in PEO-based polymer electrolytes.⁷ However, the ion conduction mechanism in solid-like polymer electrolytes (SPEs) is not entirely understood. Hence, a better understanding of the ion conduction mechanisms will guide the development of high conductivity SPEs at ambient temperature, which essential for practical applications. The ionic mobility in such complex systems is calculated through the number of charge carriers. There are some estimation methods for the number of charge carriers based on the data obtained from the impedance spectra over a broad frequency range.⁸ A recent study reported the conductivity of PEO-Nascent polymer electrolyte films as a function of salt content.⁹ The conductivity decreased with increasing weight percent of salt, whereas the dielectric constant first shows an initial decrease followed by an increase as the salt content in increased to 5% by weight. The maximum ionic conductivity and number of charge carriers are 9.86×10^{-6} S/m and 1.21×10^{20} m⁻³, respectively, for weight the percent ratio 95:05 in PEO:NaSCN polymer salt complex.

1.4 Lithium-Based Batteries

Lithium is one of the most important metals for performance effectiveness and power density of batteries. Over the past several years, significant research and

development has been carried out on lithium/air (Li-air) secondary batteries. Lithium-air batteries show extraordinary potential for the highest specific energy density among all galvanic cells. Additionally, the scientific and engineering community is significantly interested in Li-air batteries because of their potential application as the of high energy density rechargeable batteries for hybrid electric vehicles (HEVs) and next-generation aircrafts.¹⁰ In this context, the extensive investigations into the practical use of high energy density solvent-free batteries have encouraged the research in the area of solid-like polymer electrolytes (SPEs) for both Lithium-ion and Lithium-air batteries.¹¹ To develop a suitable Li-air battery for electric vehicles, a numerous issues associated with the electrolyte, the Li anode, and the air electrode, need to be addressed and solved to improve performance cyclability of the Lithium-air cells.

Li-ion and Li-air batteries are high density energy storage devices. Their common range of high battery voltage is 3V–3.6V and the value of the voltage of Li-ion and Li-air batteries is double that of a manganese dry cell which means using two of manganese dry cells gives the same power of using one of ether air or ion battery. Lightweight with high energy density is another feature of theses batteries. The main difference between Li-ion and Li-air battery is that the latter uses oxygen gas and the former uses intercalated lithium compound as the cathode.^{12,13}

The electrolyte medium in both batteries is usually organic which is a good media for Li ion movement.^{14,15} Electrolytes should be non-volatile, suitable for fabrication into thin films, non-flammable, and should possess high safety. The cathode, anode, and electrolyte are used to convert chemical energy into electrical energy through reversible

Redox reactions.^{16,17} An oxidation reaction in both batteries take place at the negative electrode during discharge of lithium batteries.^{18,19} During charging, the electrons move towards the positive electrode via the external circuit.^{20,21}

Current Li-air batteries utilize liquid, organic electrolytes that come with several shortcomings that limit their widespread usage in large load applications, such as in electric vehicles and in stationary power applications. These liabilities are safety related and include electrolyte leakage, decomposition, flammability, and a propensity to develop catastrophic short circuits.

1.5 Polymer Electrolytes: Polyethylene Glycol (PEG) and Polyethylene Oxide (PEO)

Ion transport in polymer electrolytes takes place via ion hopping from polymer chain to chain assisted by the local segmental motion of the polymer chains facilitated by inter- and intra-polymer transitions between coordinating sites. The most widespread polymeric structures employed to prepare liquid and solid polymer/salt electrolytes are PEG and PEO. The ethylene oxide (abbreviated as EO yielding the repeat unit $\text{CH}_2\text{CH}_2\text{O}$) is the fundamental repeating unit in both structures of PEG and PEO, but they vary in their molecular weights. Normally, lower molecular weight polymers are called PEG and the higher molecular weights are called PEO. PEG and PEO are excellent polymers for dissolving high concentrations of many salts to form polymer electrolytes and have a high degree of flexibility in PEO chain.²² The polymers dissolve the metal ions by interactions between the oxygen lone pair and the cation. Since lithium is the smallest cation, the polymer is most effective in dissolving PEG.

These substances are amphiphilic and soluble in water as well as in numerous organic solvents. Low molecular weight (MW<1,000) PEGs are viscous and colorless liquids, whereas high molecular weight PEGs are white waxy solids with melting points relative to their molecular weights with a maximum of about 67 °C.²³ PEGs are also available in three geometries: *Branched* PEGs have 3–10 PEG chains emerging from a central core, *Star* PEGs have 10–100 chains emerging from a central core and *Comb* PEGs have multiple PEG chains usually grafted onto a polymer backbone. The structure of high molecular weight PEO is shown in Figure 2.

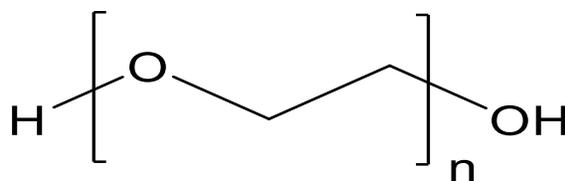


Figure 2. The chemical structure of high molecular weight PEO.

PEG is non-toxic and is approved by the FDA for use as an excipient or as a carrier in diverse pharmaceuticals, foods, and cosmetics.²⁵ The majority of PEGs with MW <1,000 are quickly eliminated from the body unchanged with clearance rates inversely proportional to their molecular weight.²⁶ This characteristic, in addition to the accessibility to PEGs with an extensive array of functional groups, led to the wide utility of PEGs in biomedical fields: drug delivery, tissue engineering, surface functionalization, and other applications.

PEO complexed with numerous salts of cations like lithium, sodium and silver have been reported due to yielding solid electrolytes with low glass transition temperatures (T_g) coupled with easy fabrication e.g. film creation by solution casting. Li and Khan have prepared SPEs with high ionic conductivity by blending high molecular weight PEO (MW 600,000) and poly(2-vinylpyridine) (MW 200,000) or poly(4-vinylpyridine) (MW 50,000) and LiClO_4 .²⁷ The PEO (85%)/poly(2-vinylpyridine)(15%)/ LiClO_4 blend at an ethylene oxide/ Li^+ mole ratio of 10 exhibits an ionic conductivity value of $1.0 \times 10^{-5} \text{ S cm}^{-1}$ at 25°C and is an elastomeric material with dimensional stability.²⁷ These properties are suitable for application of the blends as the solid polymer electrolytes in solid state batteries. In particular, the reported study utilizes ion-dipole interaction to break down ion aggregates and significantly increase the fraction of ions which are mobile and thus contributes to ionic conductivity.

In this context, polymer electrolytes based on block copolymers present specific advantages owing to the simultaneous existence of both the soft and hard phases. The soft phase is used for ion transport, while the hard phase provides dimensional and mechanical stability. Based on these properties, major research has been conducted on poly(styrene-*b*-ethylene oxide) (PS-*b*-PEO) copolymers doped with Li salts.^{28,29} Zardalidis et al. demonstrated that densely grafted PEO chains on a poly(hydroxystyrene) (PHOS) backbone (PHOS-*g*-PEO) as well as block copolymers with polystyrene (PS) (PS-*b*-(PHOS-*g*-PEO)) can produce Li ion conductivities that are greater than that of the electrolytes based on the homopolymers (Figure 3).³⁰ The design diminishes the propensity of PEO chains for crystallization with added Lithium triflate

(LiTf) as the salt. At the same time PS-*b*-(PHOS-*g*-PEO)/LiTf electrolytes show improved mechanical properties.

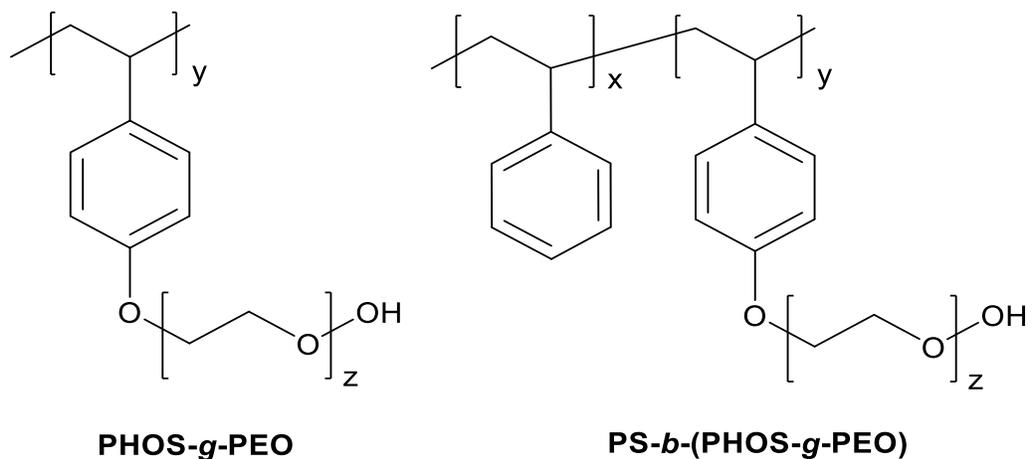


Figure 3. The chemical structures of the grafted poly(hydroxystyrene) (PHOS) with PEO (left) and of its block copolymer with polystyrene (PS) (PS-*b*-(PHOS-*g*-PEO)).

1.6 Properties of Low and High Molecular Weight PEGs/PEOs

The ionic conductivity of a polymer is dependent upon both the molecular weight of the polymer and its morphology. Polymers with lower glass transition temperatures have larger degree of segmental motion and thus can transport the ions faster within the matrix. This is due to the fact that the ions in the polymer move, assisted by the local fluid-like environment.³¹ The conductivity is dependent upon the intensity of segmental motion; more intense segmental motion leads to higher conductivity. Studies have shown that the polymer diffusion coefficients can be correlated with polymer segmental motion and are inversely proportional to its molecular weight. According to Yukio et al., the conductivity increases with a decreasing PEO molecular weight, as well as an increasing PEG content. A PEG having a molecular weight of 400, when added to high molecular

weight PEO (600,000) to create a 50/50 blend system and with 10% by weight lithium triflate content show a conductivity maximum value of $3 \times 10^{-3} \text{ S cm}^{-1}$ at 25 °C.³² On the other hand, high molecular weight PEO (>20,000) show ionic conductivity only around $10^{-7} \text{ S cm}^{-1}$ at 25 °C which is not suitable for either lithium-air or lithium-ion batteries. Since the early the days of investigation of polymer electrolytes, it has been known that the presence of crystalline phases significantly affects their properties. For electrolytes based on PEO matrix, crystallization of either PEO or stoichiometric complexes of PEO and salt in most cases leads to a decrease of conductivity. This is because high molecular weight PEO is crystalline and crystalline domains are not suitable for ion-transport as such domains do not possess considerable segmental motion.

The aim of the study reported in this thesis was to determine the ionic conductivity of blends of high molecular weight poly(ethylene oxide) (PEO, MW 35,000) as well as poly(ethylene oxide) (PEO, MW 100,000) with different concentrations of bis(trifluoromethane)sulfonamide lithium salt (LiTFSI). In addition, the ionic conductivity upon the addition of tris(pentafluorophenyl)borane (TPFB) to these blends has been studied.^{33,34} The goal of this study is to understand the effect of plasticization of the PEO by the large bis(trifluoromethane)sulfonamide anion and also the effect of the TPFB on the ionic conductivity.

CHAPTER II

LITERATURE REVIEW

Li-ion batteries are the batteries of choice for replacing conventional energy storage technologies for countless applications. As the scientific and engineering communities seek to enhance energy densities in Li-ion batteries and investigate advanced “beyond lithium ion” technologies, there is a major interest in replacing conventional intercalation anodes with Li metal. Li is the lightest metal, possesses metallic electronic conductivity and provides superior improvement in specific capacities relative to conventional intercalation anodes. The drawback with Li metal is its high oxidizing character; it will react with water, oxygen, and most aprotic electrolytes suited for Li-ion batteries.³⁵ Moreover, it does not homogeneously plate and strip, which results in the formation of dendritic structures that can eventually span the electrolyte region and short-circuit the cell, leading to serious safety hazards.^{36,37} Several research groups have reported on the ionic conductivity of polymer electrolytes and alkali metal salts which are now being used in lithium-ion batteries.³⁸⁻⁴⁰

2.1 Rationale for the Development of Advanced Li-Air Batteries

Li-air batteries have a great potential to be applied as high energy density rechargeable batteries with storage properties which will be far superior to Li-ion batteries.⁴¹ The Li-air batteries are attractive not only because of the higher energy

density but also their stability for longer periods. Furthermore, they can operate under extreme temperatures.^{42,43} The calculated energy density of the Li-air battery system, excluding oxygen, is similar to that of gasoline/air (11,140 Wh kg⁻¹). Consequently, this system could be employed to develop a higher specific energy density battery compared to the batteries currently used in electric vehicles (700 Wh kg⁻¹).⁴⁴ Therefore, the Li-air battery has fifteen-fold higher specific energy potential than Li-ion battery. Further pros of Li-air battery are total discharge and regeneration of Li atoms.

On the other hand, the Li-air battery is not compatible with presently accessible electrolytes because of decomposition and reactivity of Li metal. An additional drawback is the existence of the porous cathode, which must only permit oxygen gas transport. Li₂O₂ is produced as a result of the oxygen reduction that also results in oxygen radical anion formation.⁴⁵ The oxygen radical anion degrades the currently used organic electrolytes. To develop a suitable Li-air battery for electric vehicles, a number of issues associated with the electrolyte, the Li anode, and the air electrode needs to be addressed.

2.2 Developments in Novel Li Battery Electrolytes

The development of new electrolyte systems for Li batteries is an active area of research. The purpose is to decrease the toxicity and cost and to increase the safety and performance of Li batteries. The most commonly used polymer electrolytes in lithium-air batteries are based on PEO and Li salts due to their high conductivity.⁴⁶ Two types of the Li-air secondary batteries have been developed: a non-aqueous and an aqueous electrolyte system. Bruce et al. reported attractive results for the cells with the non-

aqueous electrolyte of LiPF_4 in propylene carbonate and a nano-carbon particle with a MnO_2 catalyst.^{47,48} A high reversible cathode capacity greater than 400 mAh g^{-1} after 10 cycles was reported. This capacity is about three times greater than that of the cathode in a traditional Li-ion battery. Nevertheless, this system showed a high polarization, particularly in the course charging. This high polarization results in a decrease in the energy conversion efficiency. The energy losses in charging and discharging have to be decreased for effective applications such as in electric vehicles. To decrease the high polarization, a more active catalyst for the oxidation of Li_2O_2 or Li_2O needs to be developed, or a new electrolyte should be employed.

Zhang et al. have reported a water stable Li metal electrode which consists of a Li metal, a polymer electrolyte, and a water stable lithium conducting glass ceramics, $\text{Li}_{1+x+y}\text{Ti}_{2-x}\text{Al}_x\text{P}_{3-y}\text{Si}_y\text{O}_{12}$ (LTAP).⁴⁹ They used a polymer electrolyte as a buffer layer to protect Li metal and the glass ceramics, because the LTAP is unstable in direct contact with Li metal. These kinds of water-stable Li metal electrodes could be potentially employed for the Li-air secondary batteries as the anode. The stability of LTAP in alkaline aqueous solutions with and without LiCl has been studied by Shimonishi et al.⁵⁰ A major conductivity decrease of the LTAP plate immersed in 0.057 M LiOH aqueous solution at 50°C for 3 weeks was observed.

Studies have also been reported on solvents with high dielectric constants to increase both the solubility of the salts and conductivity of the electrolytes.⁵¹ In addition, there have been reports on the use of cation complexing agents such as crown ethers and

cryptands as additives to increase the conductivity of the electrolyte by decreasing the ion aggregates.⁵² The use of anion receptors has been shown to be a more attractive approach for developing a stable electrolyte. Both the conductivity and cation transference number of the electrolyte can be increased when an anion receptor is used, because anion receptors enhance the dissociation of ion pairs and increase population of free cations in an electrolyte.

LiF is barely soluble in organic solvents, so the possibility of using LiF as a salt in a lithium battery electrolyte has never been explored. The complexing of F⁻ by the boron-based anion receptor tris(pentafluorophenyl) borane (TPFB) promotes the dissolution of LiF in organic solvents. LiF has been successfully used as a salt in a novel, highly conductive, non-aqueous electrolyte in a rechargeable Li/LiMn₂O₄ cell.⁵³ This was accomplished by using LiF with a new boron-based anion receptor additive in a 1,2-dimethoxyethane (DME) solvent. The additive increases the solubility of LiF in DME to as high as 1.0 M and results in a conductivity of $6.8 \times 10^{-3} \text{ S cm}^{-1}$ at 25 °C.

2.3 Polymer Electrolytes Comprising High Molecular Weight PEO with Bis(trifluoromethane)sulfonamide Lithium Salt (PEO/LiTFSI System)

The choice of materials for solid electrolytes applied in rechargeable Li-ion cells is usually based on the value of their ionic conductivity, electrochemical stability, mechanical properties and the ratio of charge transported by Li ions to the overall charge transport (the cation transference number, t^+). Unfortunately, for most electrolytes based on polymers with dissolved Li salts, the t^+ values are found to be low (<0.5). Apart from

decrease of efficiency of charge transport process in the cell, low t^+ can possibly lead to unwanted precipitation of salt at the anode and depletion of electrolyte at cathode.⁵⁴

PEO forms stoichiometric crystalline complexes with LiTFSI salt (PEO-LiTFSI), of molar ratios EO:Li = 6:1, 3:1 and 2:1.^{55,56} The molecular structure of PEO₃:LiTFSI crystalline complex has been determined using X-ray diffraction. LiTFSI is the preferred Li salt for PEO-based polymers, because the Li⁺ cations supply the electro-active species in the electrolyte, and TFSI anions exert a plasticizing effect on the polymer. It possesses outstanding electrochemical properties, as well as high thermal and chemical stability. The stability increases its safety, as well as performance during its applications in various areas such as automobiles, electronics, power tools, etc. The salt can be easily obtained in the pure form i.e. purity of 99.99%, with a melting point of around 234–238 °C. Employing LiTFSI as the salt in the electrolytes batteries with high performance, safety, reduced cost and charging time have been developed.

The interface resistance of Li metal and polymer electrolyte in a water-stable Li electrode is the main contributor to the cell resistance and an important factor in initiating lithium dendrite formation.⁵⁷⁻⁵⁹ Reduction of the interface resistance and increased Li ion transference number were observed by adding poly(ethylene glycol) dimethyl ether (PEGDME) to PEO₁₈-LiTFSI,⁶⁰ indicating that PEGDME reduces the coordination of Li ions with EO units of the high MW PEO matrix. The net result is enhanced mobility of Li⁺ ions which is possible because of decreased ion aggregation. The molecular weight of PEGDME is usually 500, which illustrates that the use of low molecular weight oligomer ethers as plasticizers was beneficial to enhance the transport properties of polymer

electrolytes. The PEO₁₈LiTFSI-2PEGDME electrolyte exhibited a Li-ion conductivity of $8.91 \times 10^{-4} \text{ S cm}^{-1}$ at 60 °C, and a low interfacial resistance in contact with Li (Figure 4).⁶¹

An electrolyte consisting of PEGDME and LiCF₃SO₃ salt in a lithium metal/polymer/LiFePO₄ cell delivered a stable capacity of 150 mAh g⁻¹.⁶²

Pożyczka et al. have estimated the values of t^+ of polymer electrolytes representing high molecular weight PEO:LiTFSI system.⁶³ It has been found that the values obtained for electrolytes with low and moderate amount of salt (molar ratio EO:Li between 50:1 and 5:1) are all below 0.2. The t^+ initially decrease with rising concentration of salt, but after passing a minimum at molar ratio EO:Li of around 6:1, a considerable increase is recorded. Such behavior can be interpreted either in terms of formation of PEO:salt complexes, or formation of ionic aggregates.

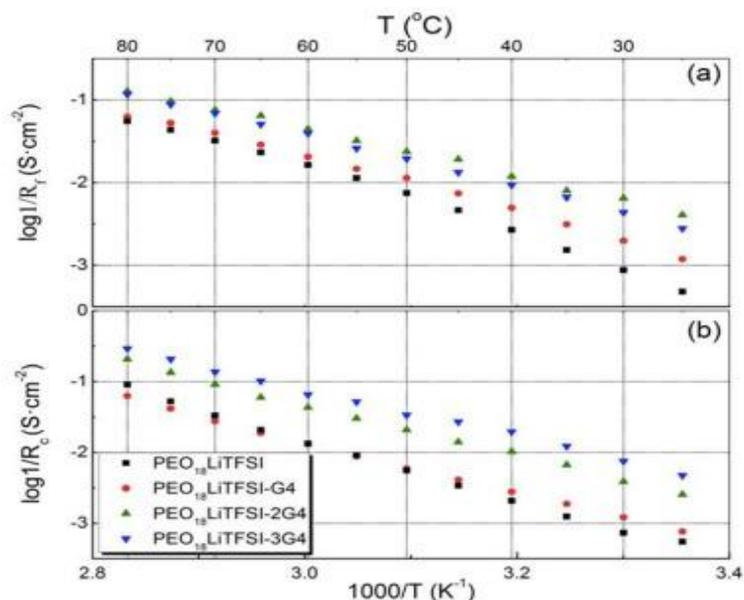


Figure 4. Temperature dependence of the resistance of a passivation film (SEI) formed on the Li electrode surface by the reaction of Li with the polymer electrolyte, and the charge transfer resistance for Li/PEO₁₈LiTFSI-*x*G₄/Li.

2.4 Ionic Conductivity of LiTFSI Blends in the Presence of Boron Compounds

The addition of boron compounds increases the conductivity of electrolytes as the degree of ionic aggregation decreases. Moreover, Boron compounds are anion receptors via acid-base interactions.⁶⁴ Tris(pentafluorophenyl)borane (TPFPB, $(C_6F_5)_3B$) is a white, volatile solid which contains of three pentafluorophenyl groups attached in a "paddle-wheel" style to the central boron; the BC_3 core is planar (Figure 5). The features of versatility and relative inertness of the B–C bonds of TPFPB make it an ideal Lewis acid. TPFPB, a representative anion receptor, tends to not only coordinate around anions but also dissolve the resistant components of the solid electrolyte interphase (SEI) film.

Several research groups studied TPFPB as an electrolyte additive for Li battery systems and reported enhanced battery performance.⁶⁵⁻⁶⁷ Lewis acids including TPFPB and related boron esters have been predicted to dissolve LiF, Li_2O , and Li_2O_2 , which are usually insoluble in carbonate-based solvents.⁶⁸ Notably, it was shown that TPFPB can partially dissolve insoluble lithium-oxygen substances generated at the air cathode and thus, a more active carbon surface could be exposed for further oxygen reduction reaction (ORR) during the discharge procedure.⁶⁹ The TPFPB anion receptor binds to peroxide anion and yields a thermodynamically stable species that can be electrochemically oxidized with kinetics that are superior to the oxidation of solid Li_2O_2 on a microporous carbon cathode.⁷⁰ In addition, the superoxide radical yields the TPFPB-peroxide anion complex via the disproportionation mechanism.

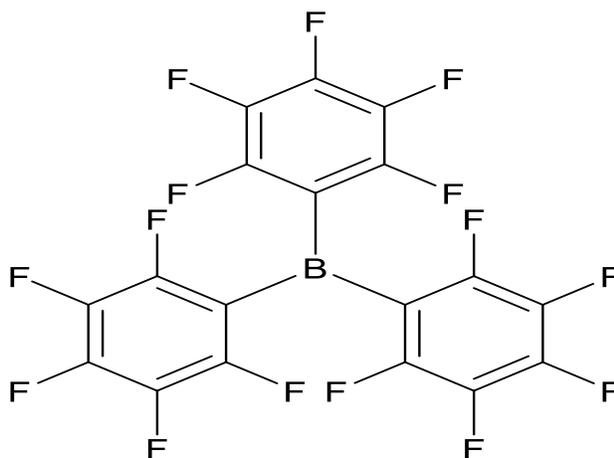


Figure 5. The chemical structure of Tris(pentafluorophenyl)borane.

CHAPTER III

MATERIALS AND METHODS

3.1 Materials

Poly(ethylene oxide)(MW 35,000) and (MW 100,000) were purchased from Sigma Aldrich Chemical Company and freeze dried prior to use. Tetrahydrofuran (THF) was purchased from Sigma Aldrich Chemical Company and was purified by distillation from sodium and benzophenone just before use. LiTFSI salt was acquired from Sigma Aldrich Chemical Company and dried in a vacuum oven at 50 °C before use. Benzene was purchased from Fisher Chemical Company. Chloroform-D (99.8%) for NMR was received from Acros Organics Company.

3.2 Instrumentation

A KEITHLEY 6430 instrument was used to measure the resistance of the samples. Resistance of the samples was determined by the two probe methods. The probes were made of copper and the samples were sandwiched between the copper plates under nitrogen gas. Measurements were carried out 25, 40, 55 and 70 °C. The measurements were carried out both during the heating and cooling cycles. Each resistance measurement was repeated 8 times. Conductivity was calculated from the resistance according to the following equation:

$$\sigma = \frac{D}{A} \times R \quad (1)$$

Where σ is conductivity, D is the thickness of the sample, A is the area of the sample, and R is resistance.

3.3 Methods

3.3.1 Preparation of PEO (MW 35,000)/LiTFSI Blends and PEO (MW 100,000)/LiTFSI Blends

Blends of PEO (MW 35,000) or PEO (MW 100,000) and LiTFSI were prepared by dissolving the components in 10 mL of THF with continuous stirring. LiTFSI salt was dried in vacuum oven at 50 °C. The blends were vigorously stirred for one day at room temperature and the solvent was evaporated under nitrogen gas. Subsequently, the blends were dried in a vacuum oven for 4 days at 50 °C following which the conductivity was measured at 25, 40, 55 and 70 °C. The prepared compositions of the blends of are listed in Tables 1 and 2. The salt content in the blends is as a mole ratio of EO repeat unit to Li salt (EO/Li⁺).

Table 1. PEO-35,000/LiTFSI Blend Compositions

Polymer	Salt	Mole ratio EO/Salt
1 g of PEO (MW 35,000)	LiTFSI salt	2
1 g of PEO (MW 35,000)	LiTFSI salt	5
1 g of PEO (MW 35,000)	LiTFSI salt	10
1 g of PEO (MW 35,000)	LiTFSI salt	15
1 g of PEO (MW 35,000)	LiTFSI salt	25

Table 2. PEO-100,000/LiTFSI Blend Compositions

Polymer	Salt	Mole ratio EO/Salt
1 g of PEO (MW 100,000)	LiTFSI salt	2
1 g of PEO (MW 100,000)	LiTFSI salt	5
1 g of PEO (MW 100,000)	LiTFSI salt	10
1 g of PEO (MW 100,000)	LiTFSI salt	15
1 g of PEO (MW 100,000)	LiTFSI salt	25

3.3.2 Preparation of PEO (MW 35,000)/LiTFSI/TPFPB Blends and PEO (MW 100,000)/LiTFSI/TPFPB Blends

PEO (35,000)/LiTFSI/TPFPB and PEO (100,000)/LiTFSI/TPFPB blends, respectively were prepared by dissolving the components in 10 mL of THF followed by stirring for 1 day. The solvent was removed by evaporation under an N₂ stream. The blends were dried for 4 days at 50 °C. After drying the blends, conductivity was measured at four different temperatures 25 °C, 40°C, 55°C and 70°C. Approximately 1.0 g of the blends of PEO (MW 35,000) and PEO (MW 100,000) were prepared and the compositions of the blends are listed in Tables 3 and 4, respectively.

Table 3. PEO-35,000/LiTFSI/TPFPB Salt Blends

Polymer	Boron compound	Weight ratio PEO/TPFPB	EO/Li ⁺
PEO (MW 35,000)	TPFPB	9:1	5
PEO (MW 35,000)	TPFPB	9:1	10

Table 4. PEO-100,000/LiTFSI/TPFPB Salt Blends

Polymer	Boron compound	Weight ratio PEO/TPFPB	EO/Li ⁺
PEO (MW 100,000)	TPFPB	9:1	5
PEO (MW 100,000)	TPFPB	9:1	10

3.3.3 Differential Scanning Calorimetry (DSC)

DSC has been performed on TA instruments DSC Q2000 at a heating rate of 10 °C/min in the temperature range of -80 to 250 °C. The DSC was calibrated using Indium under a nitrogen atmosphere. The samples (7–10 mg) were weighed and sealed in Tzero hermetic aluminum sample pans. Further, they were quenched prior to obtaining the thermograms. The samples have been heated to 250 °C and subsequently cooled to -80 °C ahead of acquiring the heating cycle at 10 °C. The glass transition temperatures have been reported from the second heating cycle. In addition, the heating rates in the first and second heating cycles stayed the same. Melting Point of PEO-100,000 is 65–67 °C.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 PEO/LiTFSI Blends

The blends of PEO with LiTFSI were prepared by solution processing using THF as the solvent. The molecular weights of the PEO used were 100,000 and 35,000. The compositions of the blends prepared are listed in Table 1 and 2. The LiTFSI salt in the blends is reported as the mole ratio of EO repeat units to Li⁺ (EO/Li⁺). The resistance of the blends was measured using the two probe method at 25, 40, 55 and 70 °C. To ensure reproducibility, the measurements were carried out both during the heating and cooling cycles. The conductivity (σ) was calculated using the following equation:

$$\sigma = 1/ RA \quad (2)$$

Where, R and A are the resistivity and thickness, respectively. The ionic conductivity values are listed in Tables 5–8.

4.1.1 Ionic Conductivity of PEO (MW 35,000)/LiTFSI Blends

In Table 5, the ionic conductivities of PEO-35000/LiTFSI blend are shown. At 25 °C, the maximum conductivity ($3.2 \times 10^{-6} \text{ S cm}^{-1}$) was obtained at an EO/Li⁺ mole ratio of 5, whereas, the maximum ionic conductivity was obtained at an EO/Li⁺ mole ratio of 25 at 70 °C. As seen from the plot in Figure 6, the conductivity increases as the salt content is increased and reaches a maximum at an EO/Li⁺ mole ratio of 5 and a further increase

results in a decrease in the conductivity. This behavior is consistent with that reported in the literature.^{25,71} The dependence of the ionic conductivity on Li salt doping concentration can be adequately interpreted by two opposing effects. There is a buildup of charge carriers as the salt concentration is increased resulting in increased conductivity, but this is eventually offset by an increase in the viscosity of the polymer electrolyte which will impede the ion migration through the polymer matrix. Moreover, after a certain concentration, extra salt addition results in the formation of aggregates which do not act as charge carriers and lowers the ionic conductivity.

Table 5. Ionic Conductivity of PEO-35,000/LiTFSI Blend System

EO/Li ⁺	σ (S cm ⁻¹) at 25 °C	σ (S cm ⁻¹) at 40 °C	σ (S cm ⁻¹) at 55 °C	σ (S cm ⁻¹) at 70 °C
2	3.2×10^{-6}	7.8×10^{-6}	2.3×10^{-5}	5.5×10^{-5}
5	9.5×10^{-6}	3.8×10^{-6}	1.35×10^{-5}	4.6×10^{-5}
10	7.0×10^{-6}	1.9×10^{-6}	5.7×10^{-6}	4.1×10^{-5}
15	3.2×10^{-6}	2.5×10^{-6}	2.3×10^{-4}	1.8×10^{-5}
25	2.2×10^{-6}	4.3×10^{-6}	1.3×10^{-4}	3.4×10^{-4}

As seen in Figure 6, compared to 25 °C, the ionic conductivities were much higher at 70 °C, for the same doping level of EO/Li⁺. Thus, as the temperature of PEO-35,000/LiTFSI blend system is increased, the conductivity increases through an

enhancement in the segmental motion and thus the ion mobility rates are increased within the matrix. Moreover, at the higher temperature, larger ionic species may also become mobile and act as charge carriers. Figure 7 shows plots for log ionic conductivity vs. temperature for PEO-35,000/LiTFSI: As the blends are amorphous, a linear increase in ionic conductivity with increasing temperature is observed.

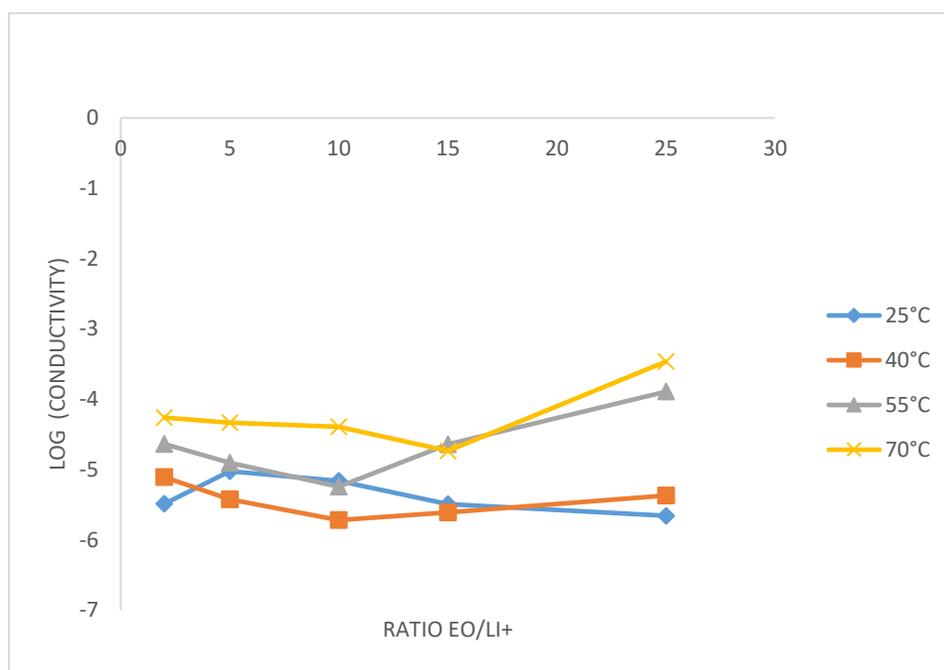


Figure 6. Log ionic conductivity vs. EO/Li⁺ mole ratio plots for PEO-35,000/LiTFSI.

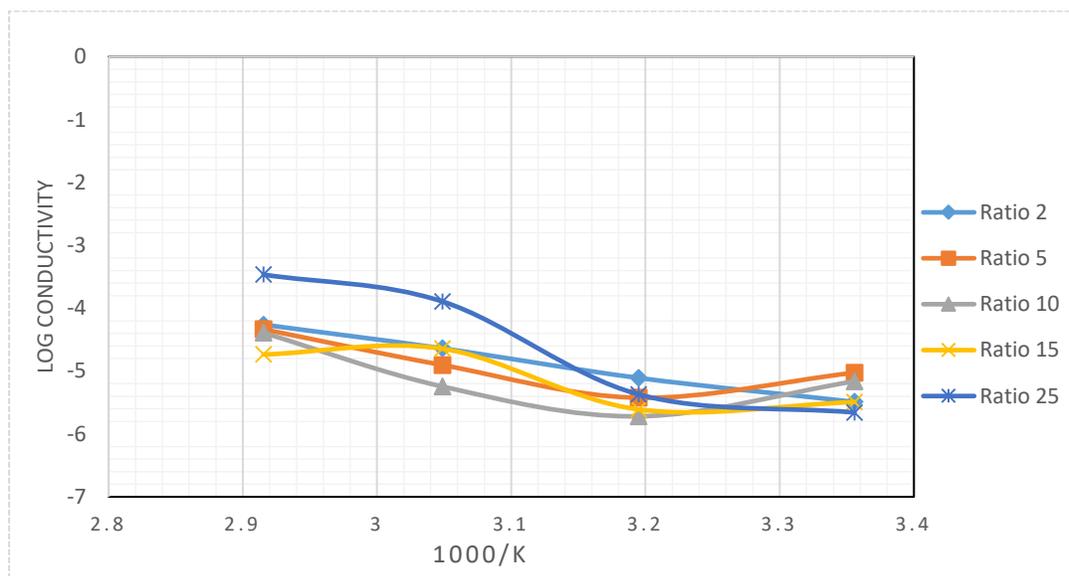


Figure 7. Log ionic conductivity vs. reciprocal temperature ($1/T$) for PEO-35,000/LiTFSI at various salt concentrations.

4.1.2 Ionic Conductivity of PEO (MW 100,000)/LiTFSI Blends

PEO 100,000/LiTFSI blends with different salt content are presented in Table 6. Analysis of the table indicates that the ionic conductivity increases as the salt content is increased; it reaches a maximum value at an EO/Li⁺ mole ratio of 5 and decreases as the salt content is further increased. Figure 8 shows the behavior of these blends. At first, increasing the salt leads to an increase in the number of charge carriers resulting in higher ionic conductivity. As temperature increases, the ionic conductivity increases and this behavior is consistent with that of literature reports.^{25,71} By increasing the temperature, the segmental motion is increased in the matrix resulting in increased rates of ion mobility. As seen in Figure 8, at 25°C, the maximum conductivity was observed at an

EO/Li⁺ ratio of 5 which is similar to the conductivity at 70 °C. At 70 °C, the degree of segmental motion of polymer chains will be the highest.

Table 6. Ionic Conductivity of PEO-100,000/LiTFSI Blend System

EO/Li ⁺	σ (S cm ⁻¹) at 25 °C	σ (S cm ⁻¹) at 40 °C	σ (S cm ⁻¹) at 55 °C	σ (S cm ⁻¹) at 70 °C
2	4.0×10^{-9}	9.6×10^{-9}	2.8×10^{-8}	7.8×10^{-8}
5	7.7×10^{-5}	6.1×10^{-5}	5.6×10^{-4}	7.7×10^{-4}
10	2.0×10^{-5}	$8. \times 10^{-5}$	3.8×10^{-5}	5.5×10^{-5}
15	2.9×10^{-6}	7.3×10^{-6}	2.2×10^{-5}	5.5×10^{-5}
25	2.5×10^{-6}	7.5×10^{-6}	2.1×10^{-5}	4.9×10^{-5}

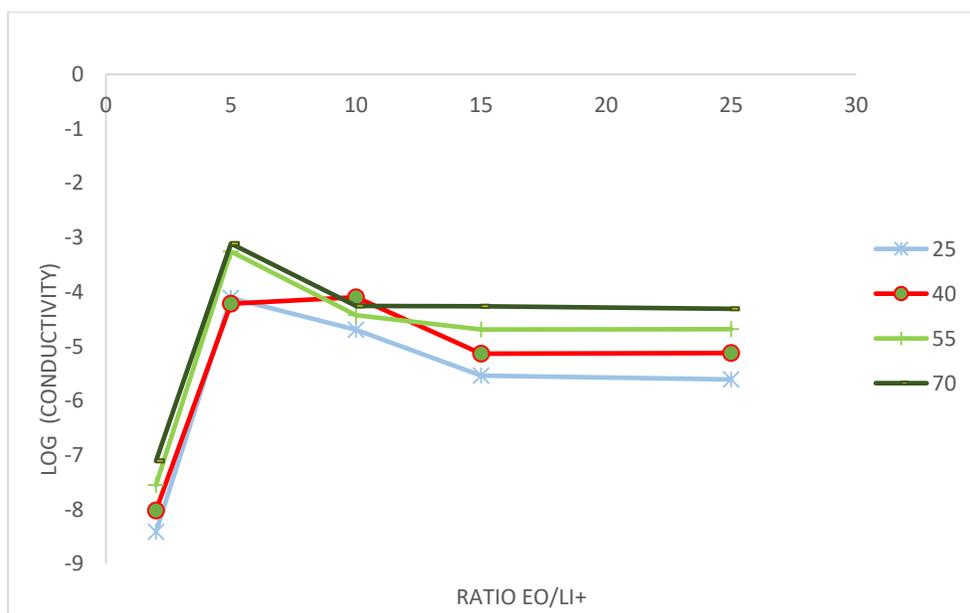


Figure 8. Log ionic conductivity vs. EO/Li⁺ mole ratio plots for PEO-100,000/LiTFSI.

Figure 9 shows the plots for log ionic conductivity vs. reciprocal ($1/T$) temperature for PEO-100,000/LiTFSI: As the blends are amorphous, a linear or nearly linear increase in ionic conductivity with increasing temperature is observed.

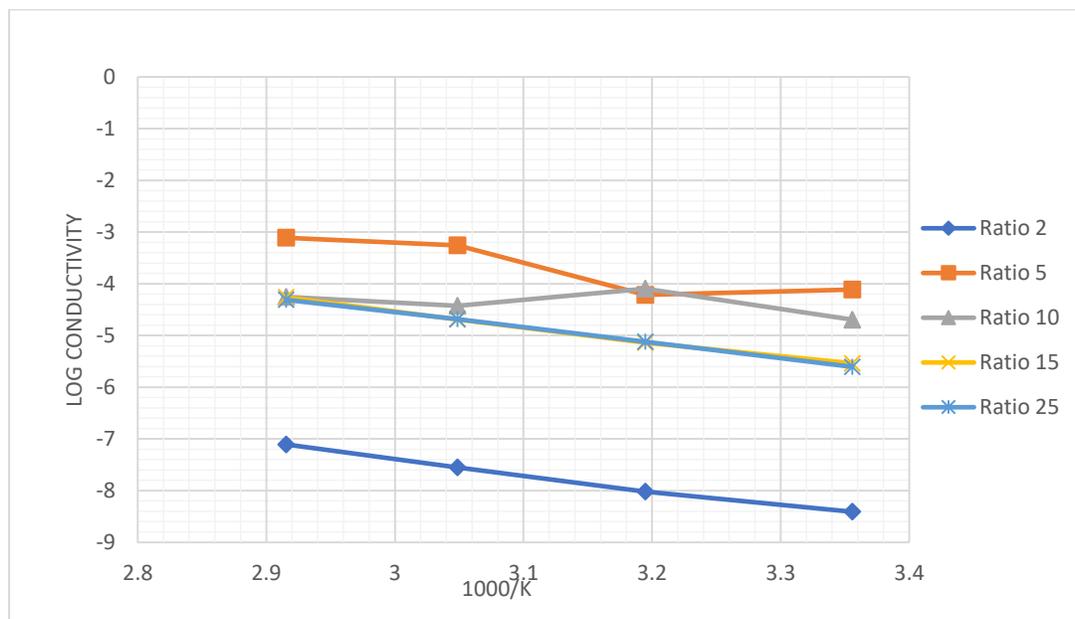


Figure 9. Log ionic conductivity vs. reciprocal temperature ($1/T$) for PEO-100,000/LiTFSI at different salt concentrations.

4.2 Addition of TFPFB to the PEO/LiTFSI System

To control ion-pairing behavior on the blends, TFPFB was added to the system. The addition of 10% by weight of TFPFB to the blend system showed higher ionic conductivities around $10^{-4} \text{ S cm}^{-1}$ and $10^{-5} \text{ S cm}^{-1}$ at 25°C on PEO-100,000 and PEO-35,000, respectively. Tables 7 and 8 show the effect of TFPFB on the ionic conductivities of the blends; it can be clearly noted that the addition of boron compound increases the ionic conductivity of the blends. The most interesting observation is that increase in conductivity with boron is not dependent on the salt content. Boron atom is a strong Lewis acid and interacts with anion of the Li salt and influences the transport number of

Li ions resulting in an increase of the conductivity (Figure 10). This is most likely taking place because the boron atom by interacting to the anion increases the inter-ionic radius and thus significantly decreases the formation of ion aggregates which in turn increases free ionic and solvent separated ion-pairs which are thought to be significantly more contributing to as charge carriers compared to higher aggregated structures. Therefore, addition of an anion receptor will improve the ionic conductivity of the blends.

Table 7. Ionic Conductivity of PEO-100,000/TPFPB/LiTFSI Blend System

Blend System TPFPB /LiTFSI	EO/Li ⁺	σ (S cm ⁻¹) at 25 °C	σ (S cm ⁻¹) at 40 °C	σ (S cm ⁻¹) at 55 °C	σ (S cm ⁻¹) at 70 °C
90%PEO-100,000/10%	5	2.5×10^{-4}	4.6×10^{-4}	1.2×10^{-3}	1.8×10^{-3}
90%PEO-100,000/10%	10	2.7×10^{-5}	1.8×10^{-4}	6.9×10^{-4}	9.7×10^{-4}

Table 8. Ionic Conductivity of PEO-35,000/TPFPB/LiTFSI Blend System

Blend System TPFPB /LiTFSI	EO/Li ⁺	σ (S cm ⁻¹) at 25 °C	σ (S cm ⁻¹) at 40 °C	σ (S cm ⁻¹) at 55 °C	σ (S cm ⁻¹) at 70 °C
90%PEO-35,000/10%	5	8.7×10^{-5}	2.4×10^{-4}	3.2×10^{-4}	6.1×10^{-4}
90%PEO-35,000/10%	10	1.8×10^{-4}	1.9×10^{-4}	5.2×10^{-4}	7.6×10^{-4}

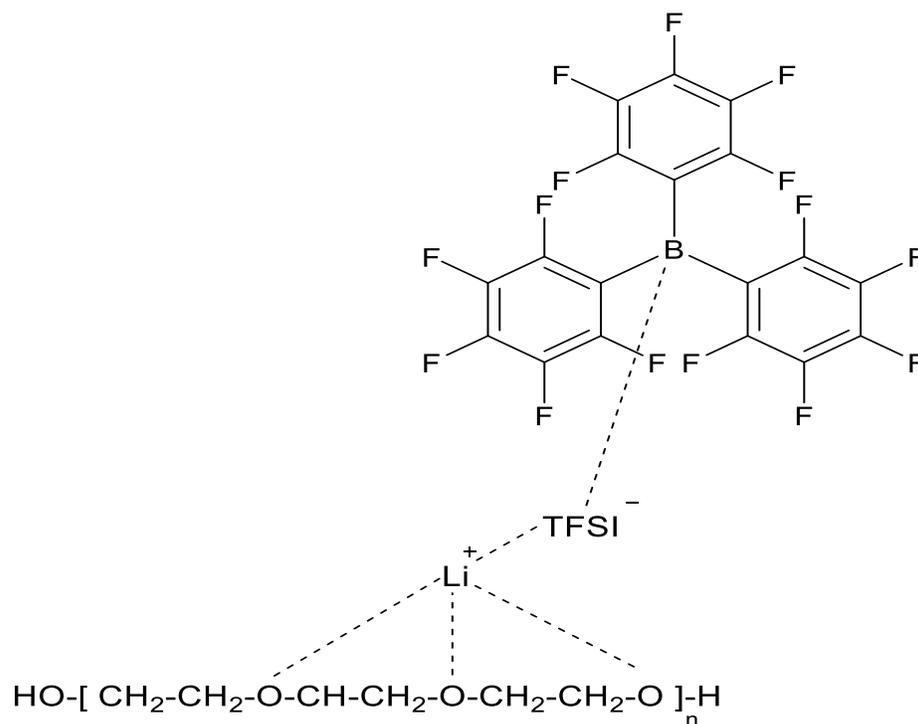


Figure 10. Interaction between TPFPB and PEO-100,000/LiTFSI blend system.

A second interesting observation (Figures 11 and 12) is that when 10% of the borane additive is present, the log conductivity vs. temperature plot shows a fairly sharp linear increase of the ionic conductivity with increasing temperature suggesting that ion motion take place by a free volume mechanism and is similar for both PEO-35,000/LiTFSI/10% TPFPB and PEO-100,000/LiTFSI/10% TPFPB. The fairly linear increase also suggests that the addition of the TPFPB affects the ion pairing quite significantly by decreasing ionic aggregation.

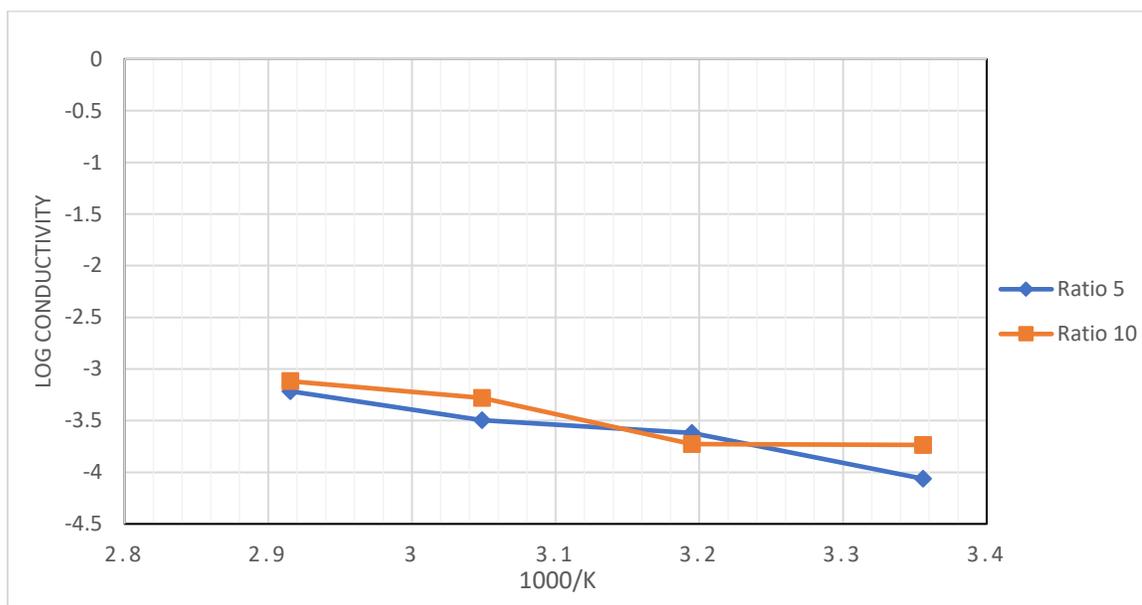


Figure 11. Log conductivity vs. temperature for PEO-35,000/LiTFSI/10% TFPFB (9:1).

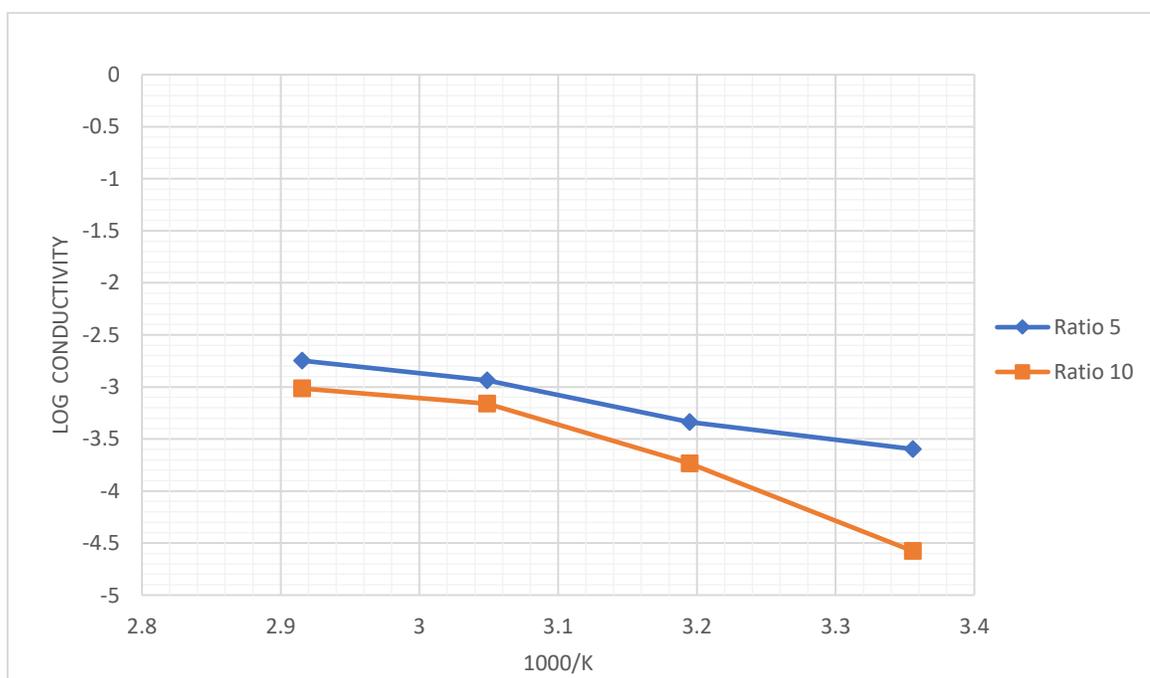


Figure 12. Log conductivity vs. temperature for PEO-100,000/LiTFSI/10% TFPFB (9:1).

4.3 DSC of the PEO 100,000/LiTFSI Blend System

To understand the thermal transitions of the pure polymer and effect of salt content on polymer blends, DSC studies were carried out. In Figures 13 and 14, the DSC thermograms of the pure PEO and the PEO 100,000/LiTFSI blend having an EO/Li⁺ ratio of 2 are shown, respectively. The DSC of the pure PEO thermogram shows a crystalline system with a sharp endothermic peak at 67 °C and does not show any glass transitions. In Figure 14, the thermogram of the PEO 100,000/LiTFSI blend system is shown. The thermogram shows two transitions: A glass transition at -55 °C which is indicative of the presence of an amorphous phase in the blend and a broad melting transition between 50 °C and 80 °C signifying that the crystalline phase of the blend consists of smaller crystals compared to the pure PEO polymer. Both of these observations suggest that the large TFSI is an effective plasticizer for the blend system. It should be noted that blends with smaller anions such as perchlorates have lower conductivities, because the smaller anions do not significantly have a plasticizing effect. These observations are consistent with reported data in the literature.²⁵ In Figures 15 and 16, the DSC thermograms of PEO 100,000/LiTFSI/TPFPB (10%) blend having an EO/Li⁺ ratio of 10 and 5 are shown, respectively. In Figure 15, the DSC thermogram shows a broad melting temperature with a fairly sharp melting point at 50 °C. It also shows a glass transition temperature at around -35 °C suggesting a matrix which has both amorphous and crystalline phases. In Figure 16, the thermogram of the blend with the higher salt content shows only a glass transition temperature at -55 °C indicating the formation of purely amorphous systems. The room temperature ionic conductivity of the system is also higher at $2.5 \times 10^{-4} \text{ S cm}^{-1}$

and thus a matrix solid electrolyte which is extremely suitable for solid state batteries is formed.

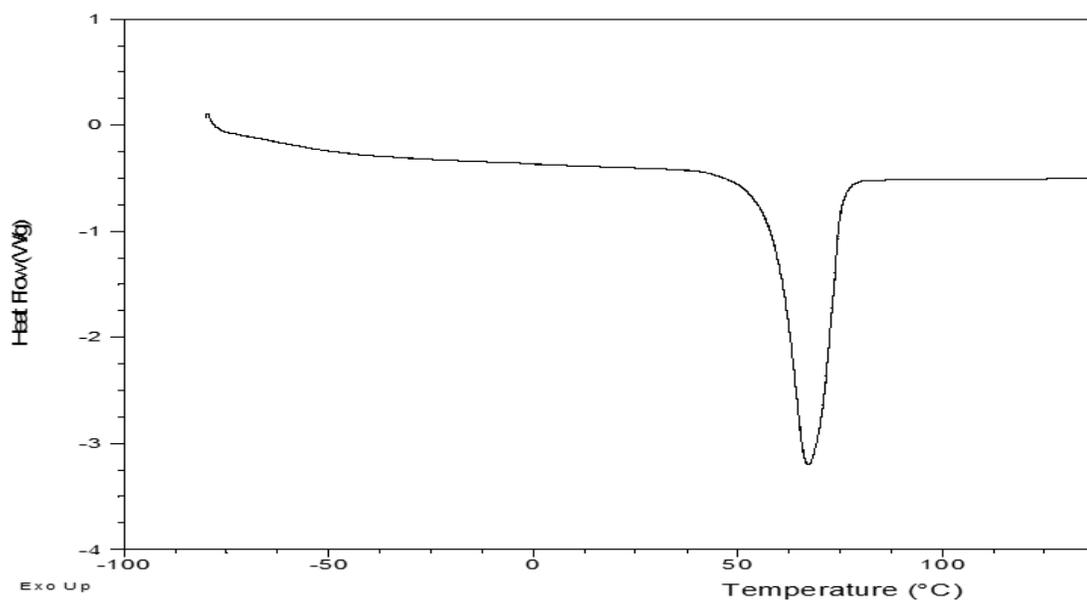


Figure 13. DSC of pure PEO-100,000.

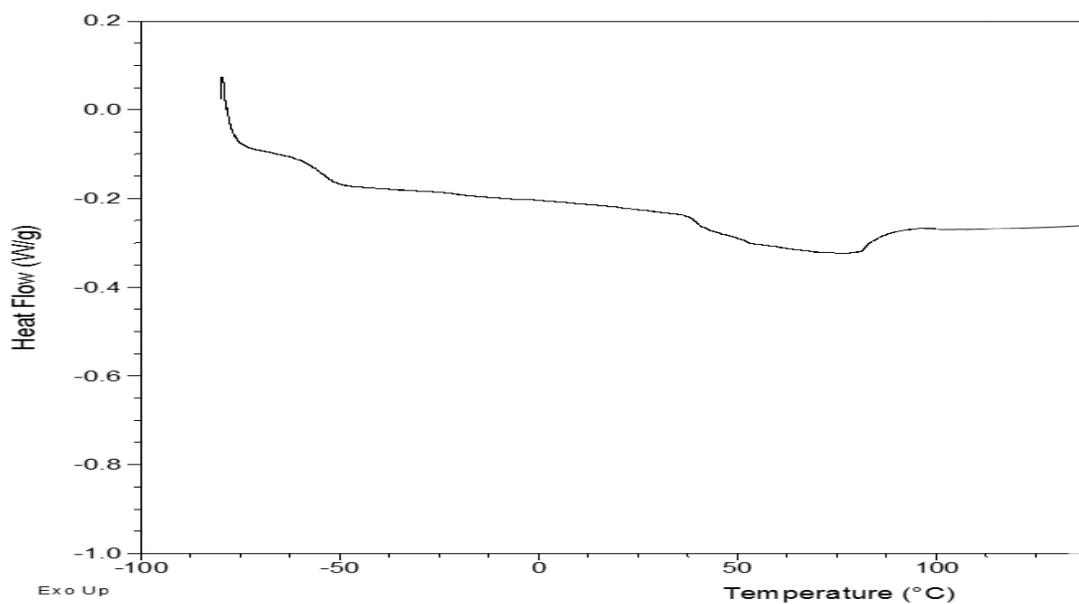


Figure 14. DSC of PEO-100,000/LiTFSI blend system.

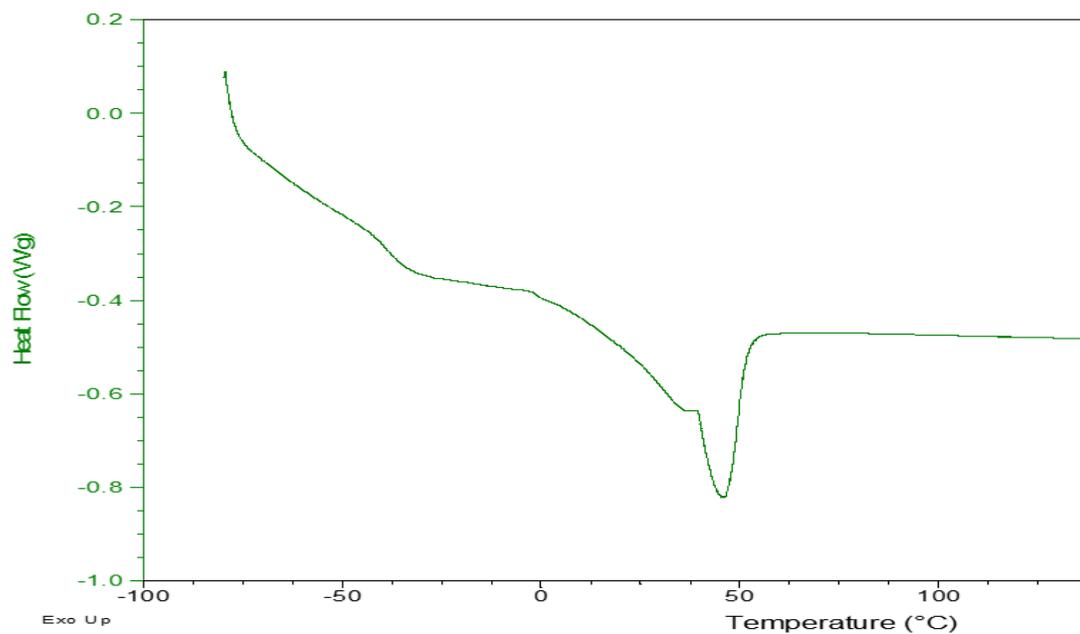


Figure 15. DSC of PEO-100,000/LiTFSI/TPFPB blend system (EO to Li⁺ ratio: 10).

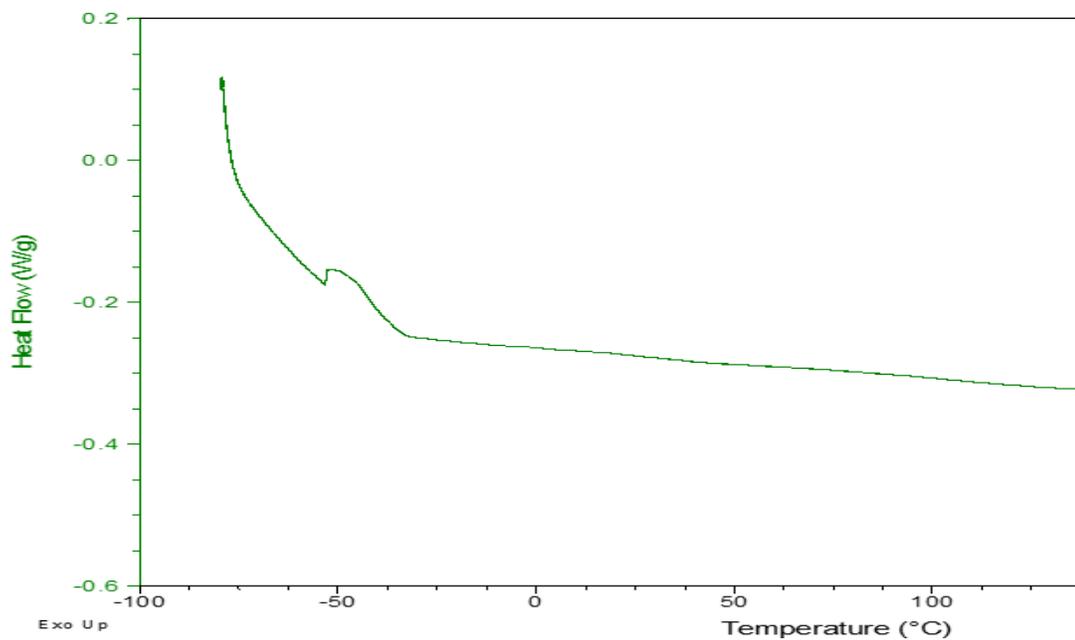


Figure 16. DSC of PEO-100,000/LiTFSI/TPFPB blend system (EO to Li⁺ ratio: 5).

CHAPTER V

CONCLUSION AND SUMMARY

Our studies reveal that a simple method like the solution blending of polymers such as PEG and PEO with LiTFSI and TPFPB is a practical technique to prepare economical solid polymer electrolytes with desired properties. The PEO-35,000/TPFPB/LiTFSI blend at an ethylene oxide/Li⁺ mole ratio of 5 exhibits ionic conductivity values of 9.45×10^{-6} at 25 °C, whereas PEO-100,000/TPFPB/LiTFSI blend at an ethylene oxide/Li⁺ mole ratio of 5 exhibits ionic conductivity values of 7.7×10^{-5} . The PEO-100,000/TPFPB/LiTFSI blend at an ethylene oxide/Li⁺ mole ratio of 2 exhibits ionic conductivity values of $2.5 \times 10^{-4} \text{ S cm}^{-1}$ is most suitable for use as electrolytes for application in high density energy storage devices. High room temperature ionic conductivities were observed (around $10^{-4} \text{ S cm}^{-1}$) for the system and from a conductivity aspect; these electrolytes are suitable for use in lithium-air batteries.

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