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Liquid Organic Electrolytes: Blends of Low Molecular Weight Methoxyoligooxyethylene (MPEGs)/LiTFSI Salt

Rasha Alshahrani
rasha.alshahrani@students.cau.edu

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ABSTRACT

CHEMISTRY

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<u>LIQUID ORGANIC ELECTROLYTES: BLENDS OF LOW MOLECULAR WEIGHT</u>

<u>METHOXYOLIGOOXYETHYLENEGLYCOL (MPEGs)/LiTFSI SALT</u>

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

Thesis dated December 2017

Blends containing methoxyoligooxyethyleneglycol (MPEGs) (MW 350 and 550) and bis(trifluoromethane)sulfonimide lithium (LiTFSI) salt were prepared by solution blending process using tetrahydrofuran (THF) as a solvent. The ionic conductivity of the blends of different compositions were determined at four temperatures i.e. 25°C, 40°C, 60°C and 70°C. A maximum ionic conductivity value of 3.9×10^{-3} S cm^{-1} at 25°C was obtained for the blends containing MPEG-350 at an ethylene oxide to lithium salt ratio of 1:10. The ionic conductivity increases with increasing temperature and shows that the ion transport is aided by the segmental motion of the MPEG chains. ^{7}Li NMR spectroscopy was used to study the nature and dynamics of the salt clusters in the blends.

LIQUID ORGANIC ELECTROLYTES: BLENDS OF LOW MOLECULAR WEIGHT

METHOXYOLIGOOXYETHYLENEGLYCOL (MPEGs)/LiTFSI SALT

A THESIS

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RASHA ALSHAHRANI

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LIST OF ABBREVIATIONS

B-MPEGs	Boron-Methoxyoligooxyethylene glycol
LITFSI	Bis(trifluoromethane)sulfonimide Lithium salt
σ	Conductivity
Ea	Energy of Activation
g	gram
LPEs	Liquid polymer electrolytes
^{7}Li-NMR	Lithium-Seven Nuclear Magnetic Resonance
MPEGs	Methoxyoligooxyethylene glycol
NMR	Nuclear Magnetic Resonance
PEO	Poly(ethylene oxide)
σ (S cm^{-1})	siemens per centimeter
THF	Tetrahydrofuran

CHAPTER I

INTRODUCTION

The ever growing electric transportation market, that is, hybrid electric vehicles (HEVs), as well as plugin hybrid electric vehicles (PHEVs) have provided major impetus to developing higher energy density storage devices.[1] Therefore, light weight i.e. high energy density solvent-free batteries have regained much attention. The research into solvent-free batteries have prompted research into the area of polymer based electrolytes.[2] The polymeric electrolyte films are safe and may be processed into thin films. The most common polymeric electrolyte contains ethylene oxide groups (CH_2CH_2O) (PEO) which may be present in either an amorphous phase or in a crystalline phase. The PEO is capable of solvating lithium cations through ion-dipole and Van der Waals interactions. However, it has been established that ion movement is faster within an amorphous PEO domain compared to crystalline domain. In the amorphous domains segmental motion facilities the ion transport.[2] The study reported in this thesis was to determine ion conductivity of lower molecular weight (MW 350 and MW 550) methoxyoligooxyethylene glycols, which are amorphous at room temperature, as a function of bis(trifluoromethane)sulfonimide lithium (LITFSI) content. The structure of MPEG-350 and MPEG-550 are shown in Figures 1 and 2. Furthermore, lithium-7 NMR spectroscopy has been carried out to understand the nature of ion aggregates in the electrolyte systems.[2,3]
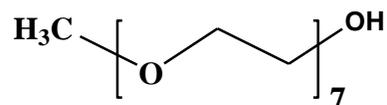
Figure 1. The chemical structure of methoxyoligooxyethylene glycol (MW 350).
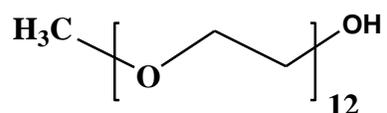
Figure 2. The chemical structure of methoxyoligooxyethylene glycol (MW 550).

1.1 Methoxypolyethylene glycol (MPEG) and Poly(ethylene oxide) (PEO)

The most common polymeric structures used to prepare liquid and solid polymer/salt electrolytes are PEG and PEO. Both are structurally similar in that the basic repeat unit is ethylene oxide but differ in molecular weight. MPEG is referred to lower molecular weight (< 10000) polymers and PEO to polymers which are higher molecular weight (> 10000).

According to Weston and Steele, the ionic conductivity of the PEO/LiCLO$_4$ blends increases sharply at about 65 °C which is the melting temperature of the crystalline domains of the polymers. Above this temperature, the polymer is amorphous with high segmental motion which enhances ion movement through the matrix resulting in increased ionic conductivity.[4] This study showed that ion mobility is better in amorphous oxyethylene domains and hence several research groups have developed high

molecular weight polymers and polymers blends which are amorphous at room temperature. Examples of totally amorphous polymers are shown in Figure 3.

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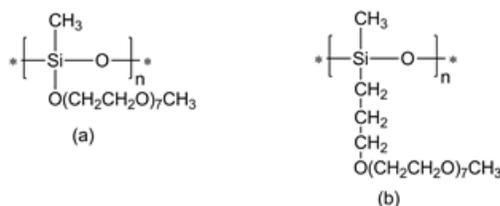
Figure 3. (a) Poly[ω-methoxyhepta(oxyethylene)ethoxy]methoxy-siloxane (PMMS)
(b) Poly[ω-methoxyoligo(oxyethylene)propyl]methyl-siloxane (PAGS).

Blends of poly[ω-methoxyhepta(oxyethylene)ethoxy]methoxy-siloxane (PMMS) and poly[ω-methoxyoligo(oxyethylene)propyl] methyl-siloxane (PAGS) with Lithium perchlorate show room temperature ionic conductivities of around 10^{-4} S cm^{-1} .[5,6,7] Blends of higher molecular weight poly(ethylene oxide), which has large crystalline domains, and lithium perchlorate show room temperature ionic conductivities lower than 10^{-7} S cm^{1}. The generally accepted lower ionic conductivity value required for use in a solid state energy storage device is 10^{-5} S cm^{-1} and thus it is necessary to use PEO based amorphous polymers such as the two shown in Figure 3.

Methoxyoligooxyethylene glycol (MW 350) and methoxyoligooxyethylene glycol (MW 550) are amorphous at room temperatures and it is expected that these two oligomeric materials may prove to be suitable for preparing highly conductive electrolytes.

1.2 Lithium-Air and Lithium-Ion Batteries

Lithium-air and lithium-ion batteries are high density energy storage devices. Lithium-ion battery is composed of a positive electrode, a negative electrode, and mostly a solid state organic electrolyte.[8,9] On the other hand, lithium-air battery is composed of an anode, a liquid electrolyte, as well as oxygen gas which act as a cathode as shown in Figure 4.
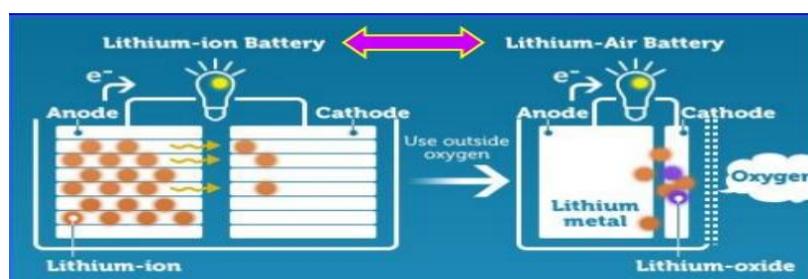
Figure 4. Image of lithium-ion compared to lithium-air batteries.

An electrolyte acts as the medium or pathway for conduction of lithium ions between the two electrodes. The difference between lithium ion battery and lithium air battery lies in the type of the electrolyte used and the cathode material. The lithium-air battery uses oxygen gas and lithium-ion battery uses intercalated lithium compound as the cathode. Both of these batteries can be recharged and are thus secondary batteries. The electrolyte medium in both batteries is normally organic materials which are good media for lithium ion movement and are electrical insulators (no electron movement).[10,11] Electrolytes should be non-volatile, perhaps possible for fabrication into thin films, non-flammable, and high safety. The cathode, anode, and electrolyte are used to convert chemical energy into electrical energy. The reaction is called oxidation-reduction. The reaction is reversible, especially when the voltage is exerted to the battery.[12,13]

An oxidation reaction in both batteries take place at the negative electrode during discharge of lithium batteries.[14,15] During charging, positively charged ions produced tend to move towards the positive electrode. Similarly, the electrons move towards the positive electrode via the external circuit. The positive electrode is the site where reduction takes place.[16,17] In contrast, the oxidation-reduction takes place in the reverse direction in the discharging process.

1.3 Comparison Between Low and High Molecular Weight MPEGs or PEOs

The molecular weight of the polymer is one of the factors affecting its ionic conductivity. This is because the ions in the polymer often hop between adjacent liquid-like surroundings.[18] The intensity of the hopping determines the conductivity. More vigorous hopping results into high conductivity unlike low hopping, which results in low conductivity. Studies have revealed that the polymer diffusion coefficients which can be correlated with polymer segmental motion are inversely proportional to its molecular weight.[18] This means that the diffusion coefficients tend to decrease with an increasing molecular weight. According to Yukio et al. the conductivity tends to increase 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 (600K) to create a 50/50 blend system and with 10% by weight lithium triflate content show a conductivity maximum value of 3×10^{-3} S cm^{-1} at 25 degrees Celsius.[19] On the other hand high molecular weight PEO (greater than 20K) show ionic conductivity only around 10^{-7} S-cm^{-1} at 25 degrees Celsius which is not suitable for either lithium-air or lithium-ion batteries. This is because high molecular weight PEO is crystalline and crystalline domain are not suitable for ion-transport as such domains do not possess significant

segmental motion. In a review of literature, we have noted that pure lower weight

MPEGS have not been studied with regards to their ionic conductivity behavior.

Therefore, this study focuses on the ionic conductivity of electrolytes based on pure

MPEGs-350 and 550.

CHAPTER II

LITERATURE REVIEW

Polymer based electrolytes is an interdisciplinary field of study that entails

disciplines of electrochemistry, inorganic chemistry, organic chemistry, as well as

polymer science. The study of polymer electrolytes has numerous applications not only in

electrolytes but also in solid-state, rechargeable lithium-ion and lithium-air batteries, as

well as supercapacitors. Abraham first reported on lithium-air battery in 1996 using a

nonaqueous electrolyte.[20] Pernot et al in the year 1973 launched the polymer electrolyte

field study; however, their discovery remained insignificant until Armand et al. carried

out significant research in the years that followed.[21] Riddick et al were able to

demonstrate the ionic conductivity in crystalline complexes of alkali metal salts, and

polyethylene oxides .[22]

2.1 Poly(ethylene oxide) Based Electrolytes: Effect of Using Plasticizers

Methoxypolyethylene glycol (MPEG) has been studied by Cabana et al. as a

plasticizer for high molecular weight PEO-LiCF$_3$SO$_3$ complexes .[23] According to

Cabana et al. the conductivity of the polymer increased from 3×10^{-7} to 3×10^{-4} S/cm at

40 ^{0}C when low molecular weight MPEG was added.[23] The conductivity was measured

when there was an addition of 65-mol % MPEG to the PEO-LiCF$_3$SO$_3$ system. The T$_g$

decreased due to softening of the polymer film by the addition of the MPEG. According

to Cabana et al. creeping was not serious in the highly diluted films for temperatures of up to 40°C.[23] Methoxypolyethylene glycol was an effective plasticizer and significantly increased the mobility of the ions. Yukio et al. studied polymer electrolytes which were prepared by blending high molecular weight PEO, poly(methylacrylate) and $LiClO_4$ as the salt.[19] Yukio et al. observed that the highest conductivity attained was only 1×10^{-8} S/cm. Garcia et al. studied the lithium NMR spectroscopy of polymer electrolytes.[24] According to Garcia et al., the Li NMR spectra line widths showed that ionic mobilities were influenced by segmental motion of the polymer chains and were extremely narrow above the glass transition temperature.[24] Narrower lines for the lithium signals can be correlated with higher ionic mobilities.

The conductivity of PEO-lithium salt complexes is suitable for use as electrolytes at temperatures higher than 100°C, which is too high for the operation of a battery. The conductivity tends to be poor below 60°C as the material is mostly crystalline. Therefore, the addition of plasticizers such dimethoxypoly(ethylene glycol) can decrease the crystallinity of the PEO and thus result in conductance which are acceptable for room temperature operation of batteries.[19]

2.2 LiTFSI Salt

LiTFSI stands for lithium bis-trifluoromethane sulfonimide. This lithium salt has excellent electrochemical properties, as well as high thermal and chemical stability. The stability enhances its safety, as well as performance during its applications in areas such as electrical vehicles, flat panel screens, power tools, laptop, e-bikes, and smartphones. This salt is a key component in liquid electrolyte for Li-ion battery. The salt can be easily obtained in the pure form i.e. purity of 99.99%.

It has a melting point of around 234-238°C.[15] Its color is white, and in most cases

it exists as a powder or as crystals. Use of LiTFSI has resulted in high battery

performance, high intrinsic safety, reduced battery cost, reduced battery filling time, and

has no aluminum corrosion. LiTFSI salt has a larger anion group i.e. a soft anion, that is,

TFSI- and this group greatly influences its ionic conductivity because the larger anion

results in decreased anion-cation interaction and thus possibly has more free ions and

solvent separated ion-pairs as opposed to triple anions, quadrupoles or higher aggregates.

The LiTFSI also acts as a *p*-dopant for purposes of enhancing conductivity for solar

cells.[15]

2.3 Conductivity of LiTFSI Mixture Combined with Boron Compound

Boron compounds' are anion receptors via acid-base interactions as shown in

Figure 5. The degree of ionic aggregation can be decreased using boron compounds.

Therefore, addition of boron compounds results in an increase in the ionic conductivity.[25]

Addition of equimolar amount of an organoboron to LiTFSI in a PEO matrix improves

the ionic conductivity up to 10^{-5} S cm^{-1} at 50°C.[25] Therefore, boron and low molecular

weight substances are incorporated into the electrolytes in lithium batteries.

$$B {-} \left[CH_2CH_2CH_2(O {-} CH_2CH_2)_n {-} OCH_3 \right]_3$$
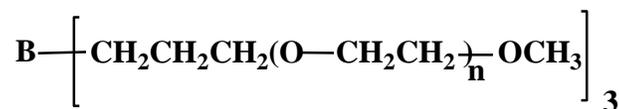
Figure 5. The chemical structure of boron allyl MPEGs 350 available in the Khan lab.

2.4 Advantage of Lithium-Air Battery Compared to Lithium-Ion Battery

For the automotive sector, the gasoline energy density is rated at 13 kwh/kg, and this corresponds to only 1.7 kwh/kg of energy that is provided to the wheels of the vehicle after losses.[3] However, the lithium air battery is capable of attaining 12 kwh/kg minus the oxygen mass. Similarly, when compared to lithium-ion battery, the lithium air battery has 5-15 times specific energy potential.[26] Other benefits of lithium air battery includes; complete discharge, and regeneration of lithium metal atoms.[27]

The application of such batteries has been restricted to just a couple charge–discharge cycles because of low stability of the electrolytes as by-products are formed during the cycling. However, by selecting a reasonable stable electrolyte and a solid cell design, lithium–air battery has been shown to be stable for several cycles. In any case, in spite of broad research endeavors, a few issues with respect to both the terminals and electrolytes have so far constrained the execution of the lithium–air battery to only a few charge–discharge cycles and a low rate capacity.[27] One disadvantage of the lithium air battery is the presence of reactive lithium metal, which is required to be in contact with an electrolyte, however, it should not react with that electrolyte. The second disadvantage is the presence of the porous cathode, which must only permit transport oxygen gas.

2.4.1 Lithium-Air Battery

The international community has garnered interest in lithium-air batteries because of its exceptional potential in the application of high energy density rechargeable batteries.[28] Research endeavors have been dedicated to the practical implementation of this technology, but there are major issues that hinder the performance of this battery.[13]

The battery (lithium air) is typically made up of anode (metal), organic electrolyte and a carbon-supported air electrode. Lithium peroxide is formed as a result of the oxygen reduction process via a series of intermediary steps that also result in an oxygen radical anion formation.[29] However, the lithium air battery cannot work effectively with currently available organic electrolyte because the electrolyte is decomposed in the general process.[4] Most of the currently available organic electrolyte has a carbonyl group which is attacked by the highly reactive radical anion. For that reason, many researchers are working to develop new organic electrolytes which can be suitable for use in lithium-air batteries.

Dimethoxy ethane (DME)-based ionic solutions is a good example of a suitable electrolyte. However, overpressure or volatility and cost in the DME case limit their use. The most commonly used polymer electrolytes used as media in lithium-air batteries are currently based on polyethylene oxide (PEO) and lithium salts.[30] The reasons for the use of these two, is because of their enhanced degree of ionic conduction. Other candidates for the lithium air batteries are the end-capped glymes including the tetra-ethylene glycol dimethyl ether.

2.4.2 Properties of Lithium-Air and Lithium-Ion Batteries

Lithium batteries have distinct features that enable them to be used in many electronic devices. Some of the properties of these batteries include high battery voltage. The nominal voltage of these batteries usually ranges from 3V-3.6V.[24] The voltage value is almost double that of manganese dry cell.[1] You just need one battery instead of two manganese dry cell to get the same power. Second, these batteries are lightweight with high energy density. The lithium-air batteries are preferred because they provide service

for a longer period unlike conventional batteries. Third, they can be used in extreme temperatures. These batteries utilize organic solvents that cannot decompose under extreme temperatures as compared to manganese dry cell.[31] Four, these batteries are very conservative. In this case, their performance remains better even after being used for a long period. Five, these batteries dissipates high power.[32]

CHAPTER III

MATERIAL AND METHODS

3.1 Materials

Methoxypolyethylene glycol or methoxoligooxyethylene glycol (MPEGs) (MW 350 and 550) was acquired from Sigma Aldrich Chemical Company and dried by freeze drying. Tetrahydrofuran (THF) was purchased from Sigma Aldrich Chemical Company and was purified by distillation from sodium and benzophenone just before use. Bis(trifluoromethane sulfonimide) lithium salt was acquired from Sigma Aldrich Chemical Company and dried in a vacuum oven just before used. 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 was used to measure the resistance of the samples. Resistance of the samples were determined by the two probe method under nitrogen gas at 25ºC, 40°C, 60 °C and 70°C. The measurements were carried out both during the heating and cooling cycles. Each resistance measurements were repeated seven times.194 MHz ^{7}Li NMR spectroscopy on the bulk samples was carried out using a Bruker AVANCE 500 MHz NMR spectrometer. The sample was place in a 5 mm NMR tube

and a second smaller tube containing LiCl in D_2O was placed into the 5 mm tube for

using an internal lock and an internal standard.

3.3 Methods

3.3.1 Preparation of Methoxyoligooxyethylene glycol (MPEG) (MW 350 and 550)/LiTFSI Blends

Blends of MPEG (MW 350& 550) and LiTFSI were prepared by dissolving the

components in 10 mL of THF with continuous stirring. After the mixture was stirred for 8

hours at room temperature, the solvent was removed under nitrogen gas. The blends were

dried in a vacuum oven for 2 days at 50°C. The conductivity was measured at 25ºC,

40°C, 60 °C and 70°C. The compositions of the blends prepared are listed in Table 1. The

salt content in the blends are indicated as a mole ratio of ethylene oxide repeat unit to

lithium salt.

Table 1. MPEG/LiTFSI Blend Compositions

Polymer	Salt	Mole ratio EO/ Salt
1 g of Methoxypolyethelene glycol (MW 350 and 550)	Bis(trifluoromethane)sulfonamide lithium salt.	2
1 g of Methoxypolyethelene glycol (MW 350 and 550)	Bis(trifluoromethane)sulfonamide lithium salt.	5
1 g of Methoxypolyethelene glycol (MW 350 and 550)	Bis(trifluoromethane)sulfonamide lithium salt.	10
1 g of Methoxypolyethelene glycol (MW 350 and 550)	Bis(trifluoromethane)sulfonamide lithium salt.	15
1 g of Methoxypolyethelene glycol (MW 350 and 550	Bis(trifluoromethane)sulfonamide lithium salt.	25

3.3.2 Preparation of Methoxypolyethylene glycol (MPEG) (MW 350 and 550)/LiTFSI/Triglymeboron Blends

MPEG/B-[CH$_2$CH$_2$CH$_2$(O-CH$_2$CH$_2$)$_7$-OCH$_3$ (Triglyme boron)/LiTFSI salt were prepared by dissolving the components in 10 mL of THF followed by stirring for 8 hours. The solvent was removed by evaporation under an N$_2$ stream. The blends were dried for two days at 50°C. After drying the blends, conductivity was measured at four different temperatures 25 °C, 40°C, 60°C and 70°C. Approximately one (1.0) grams of the blends were prepared and the composition of the blends are listed in Table 2.

Table 2. MPEG/B-[CH$_2$CH$_2$CH$_2$(O-CH$_2$CH$_2$)$_7$-OCH$_3$]$_3$ (Triglyme boron)/LiTFSI Salt Blends

Polymer	Boron compound	Weight ratio MPEG/Triglyme B	EO/Li$^+$
MPEGs (MW 350 & 550)	Triglymeboron	9:1	2
MPEGs (MW 350 & 550)	Triglymeboron	8:2	2
MPEGs (MW 350 & 550)	Triglymeboron	9:1	5
MPEGs (MW 350 & 550)	Triglymeboron	8:2	5
MPEGs (MW 350 & 550)	Triglymeboron	9:1	10
MPEGs (MW 350 & 550)	Triglymeboron	8:2	10

CHAPTER IV

RESULTS AND DISCUSSION

4.1 MPEGs/LITFSI Blends

The blends of MPEGs and LIFTSI were prepared by solution processing using tetrahydrofuran as the solvent. The molecular weights of the MPEGs used were 350 and 550. The compositions of the blends prepared are listed in Table 1. The LiTFSI salt in the blends is reported as ethylene oxide repeat unit to Li^+ mole ratio.

The resistance of the blends were measured using a two probe setup at 25^oC, $40°C$, $60 °C$ and $70°C$. In order to ensure reproducibility, the measurements were carried out both during the heating and cooling cycles. The conductivity, σ, was calculated using the following equation:

$$\sigma = 1/ RA \qquad\qquad \text{Equation 1}$$

where R and A are resistivity and thickness, respectively.

4.1.1 Ionic Conductivity of (MPEGs) (MW 350)/LiTFSI

In Table 3, the ionic conductivity values of the MPEG-350/LiTFSI as a function of salt content are listed. The conductivity increases as the salt content is increased and reaches a maximum at an ethylene oxide/Li^+ ratio of 10 and further increase results in a decrease in the conductivity. The behavior is also shown in Figure 6.

Table 3. Ionic Conductivity of MPEGs-350/LiTFSI Blend System

Ethylene Oxide/Li$^+$	σ (S cm^{-1}) at 25°C	σ (S cm^{-1}) at 40 °C	σ (S cm^{-1}) 60 °C	σ (S cm^{-1}) 70 °C
2	1.0×10^{-3}	2.5×10^{-3}	6.8×10^{-3}	7.9×10^{-3}
5	1.7×10^{-3}	3.7×10^{-3}	6.8×10^{-3}	8.0×10^{-2}
10	3.9×10^{-3}	3.8×10^{-3}	7.9×10^{-3}	1.3×10^{-2}
15	1.6×10^{-4}	8.5×10^{-4}	2.3×10^{-3}	3.0×10^{-3}
25	1.7×10^{-4}	5.4×10^{-4}	1.6×10^{-3}	2.0×10^{-2}

This behavior is consistent with reported literature data. Initially as the salt is increased, the number of charge carries increases resulting in higher ionic conductivity.[7,33] However, when the salt reaches a certain concentration, additional salt addition to the blend result in formation of aggregates which not only do not contribute as charge carriers but also the large aggregates results in formation of domains which are not conductive. The overall ionic movement regions are lowered within the matrix i.e. overall results in lower ionic conductivity. Additionally, as salt content in increased, the ion-dipole interaction between the lithium cation and the polymer segments decreases segmental motion which perhaps results in a lowering of the ion mobility in the matrix.

As the temperature is increased, the ionic conductivity increases and this observation is consistent with literature reports.[7] Increasing the temperature increases the segmental motion in the matrix and thus the ion mobility rates are increased. What is particularly interesting in these blend systems, see Figure 6, is that the maximum conductivity at 25°C is observed at an ethylene oxide/Li$^+$ ratio of 10; however, when the temperature is increased to 70°C, the maximum conductivity is observed at an ethylene

oxide/Li$^+$ ratio of 5. This observation suggests that the dynamics among the various ionic structures in the matrix are affected at 70ºC. At 70 ºC there should be greater degree of segmental motion of the polymer chains and also perhaps the equilibria among ion-pair, triple anions or cations, quadrupoles or higher aggregates changes and larger fraction of the salt act as charge carriers.
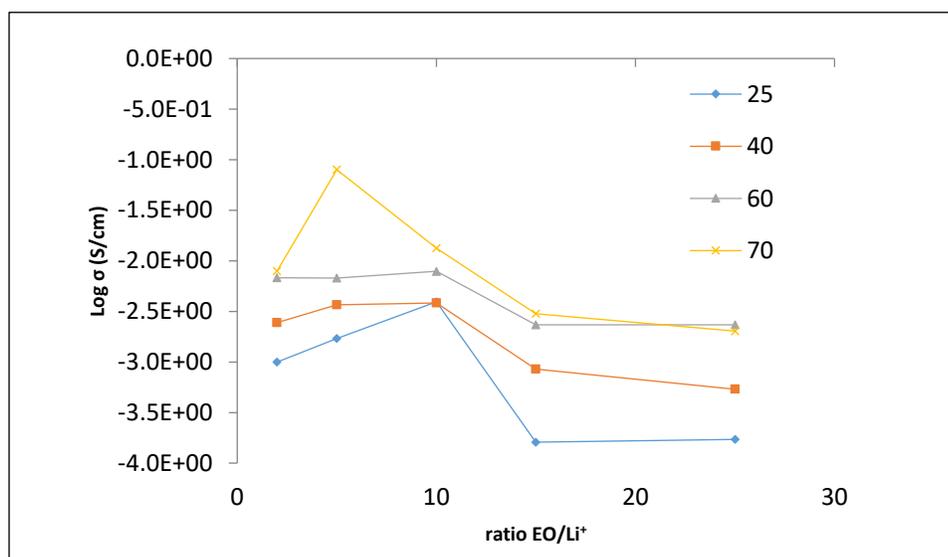
Figure 6. Log ionic conductivity vs. ethylene oxide/Li$^+$ mole ratio plots for MPEG350/ LiTFSI.

The LiTFSI dissolves in the matrix via ion-dipole or Lewis acid–base interactions. When the concentration of the LiTFSI is low, the salt most likely forms a polymer separated ion-pairs and free anions i.e. the Li$^+$ is surrounded by the oligooxyethylene and interacts with three or more oxygen atoms. In this situation the Li$^+$ is highly mobile and acts as a charge carrier. Further increase in the salt concentration most likely forms tight ion pairs because the solvating ability of the oligooxyethylene is saturated, i.e. sites are not available for interacting with the Li$^+$. At this stage of salt concentration, the system

possibly has polymer separated ion-pair (Li$^+$ $\|$A$^-$) and tight ion-pair (Li$^+$A$^-$). Further increase results in the formation of higher aggregates e.g. triple cations (Li$^+$A$^-$Li$^+$$\|A^-$) , ion quadrupoles (Li$^+A^-$)$_2$ and perhaps even higher aggregates (Li$^+$A$^-$)$_n$. Equation 2 shows the equilibrium that may be plausible in the matrix. Polymer separated ion-pairs and to a smaller extent triple cations may be considered to be charge carriers.

$$Li^+ \, \| \, A^- \, \leftrightarrow \, Li^+ A^- \leftrightarrow Li^+ A^- Li^+ \| A^- \, \leftrightarrow \, (Li^+ A^-)_2 \, \leftrightarrow \, (Li^+ A^-)_n \qquad \text{Equation 2}$$

Figure 7 shows plots for log σ vs temperature. As the blends are amorphous, one would expect a linear or nearly linear increase in ionic conductivity with increasing temperature. This is observed for the MPEG (350)/LiTFSI blend system.

Figure 7. Log ionic conductivity vs. reciprocal temperature (1/T) at different ratios of (MW 350)EO/Li$^+$.

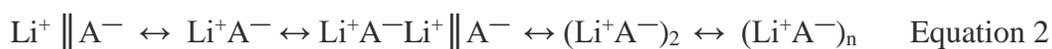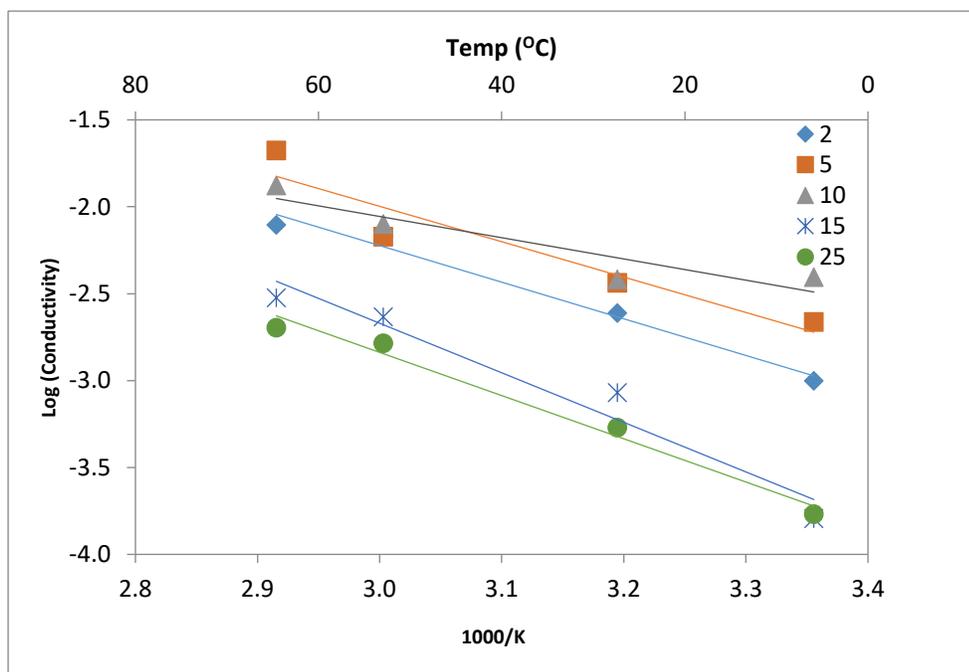Also the energies activation are shown in Table 4. Lower energy of activation results in

higher conductivity.

Table 4. Energy of Activation (kJ/mol) for MPEGs-350/LiTFSI Blend

Ratio	Ea
2	2.1088
5	2.0363
10	1.2218
15	2.8522
25	2.4859

4.1.2 Ionic Conductivity of (MPEGs) (MW 550)/LiTFSI

Table 5 lists the ionic conductivity values for the MPEG-550/LiTFSI blend

systems. The conductivity behavior at 25°C is somewhat similar to the behavior for the

MPEG-350/LiTFSI system. A maximum conductivity at 25°C is observed at an ethylene

oxide/Li$^+$ mole ratio of 10 and at 70°C the maximum is observed at ethylene oxide/Li$^+$

(Figures 8 and 9) mole ratio of 5. Therefore, it is quite plausible that at the higher

temperature the triple cation may be acting as charge carriers (see Eqn. 2).

Table 5. Ionic Conductivity of MPEGs-550/LiTFSI Blend System

Ethylene Oxide/Li$^+$	σ (S cm^{-1}) at 25°C	σ (S cm^{-1}) at 40 °C	σ (S cm^{-1}) 60 °C	σ (S cm^{-1}) 70 °C
2	7.2×10^{-4}	1.7×10^{-4}	5.3×10^{-3}	8.8×10^{-3}
5	1.0×10^{-3}	3.1×10^{-3}	5.9×10^{-3}	7.1×10^{-2}
10	2.8×10^{-3}	1.8×10^{-2}	3.5×10^{-2}	4.6×10^{-2}
15	1.1×10^{-4}	2.1×10^{-3}	2.4×10^{-3}	2.6×10^{-3}
25	7.8×10^{-4}	2.2×10^{-3}	3.0×10^{-3}	1.9×10^{-2}

The conductivity observed for the LiTFSI should be higher than salts with smaller anions, which have higher lattice energies. LiTFSI has large anions and low lattice energies, which promote high conductivity.[34] Li salt dissolves in a polymer when the solvation energy of the polymer with Li^+ is large enough to overcome the lattice energy of the salt. In LiTFSI the anions are large and leads to reduced ion-ion interactions.[34]

Figure 8. Log ionic conductivity vs. ethylene oxide/Li^+ mole ratio plots for MPEGs 550/LiTFSI.

Figure 9. Log σ vs. temperature for MPEGs 550/LiTFSI at different salt contents.

As the temperature of MPEG-550/LiTFSI blend system is increased, the conductivity in general increases. The system with an ethylene oxide to Li$^+$ mole ratios of 2, 5 and 10 increases with the most significant increase observed for the ethylene oxide to Li$^+$ mole ratio of 5. The conductivity of the ethylene oxide to Li$^+$ mole ratios of 15 and 25 initially increases but decreases as the temperature goes over 60°C. This behavior is not completely understood at this time. The equilibria among the different species present in the system possibly have an effect (see Eqn 2).

4.2 Addition of Triglyme Borane to (MPEGs) (MW 350 and 550)/LiTFSI System

A triglyme borane was added to the two blend systems to control the ion-pairing behavior as shown in Figure 10.

$$B \left[CH_2CH_2CH_2(O-CH_2CH_2)_n OCH_3 \right]_3$$
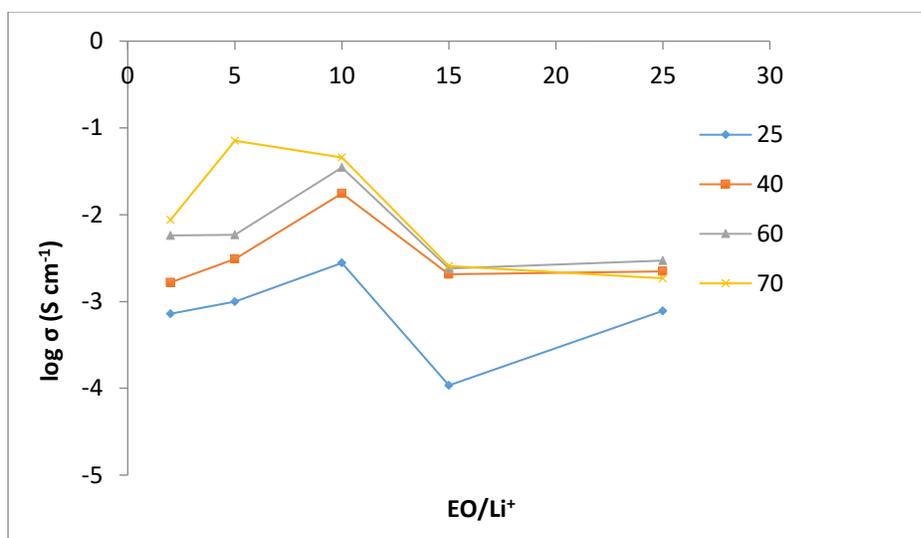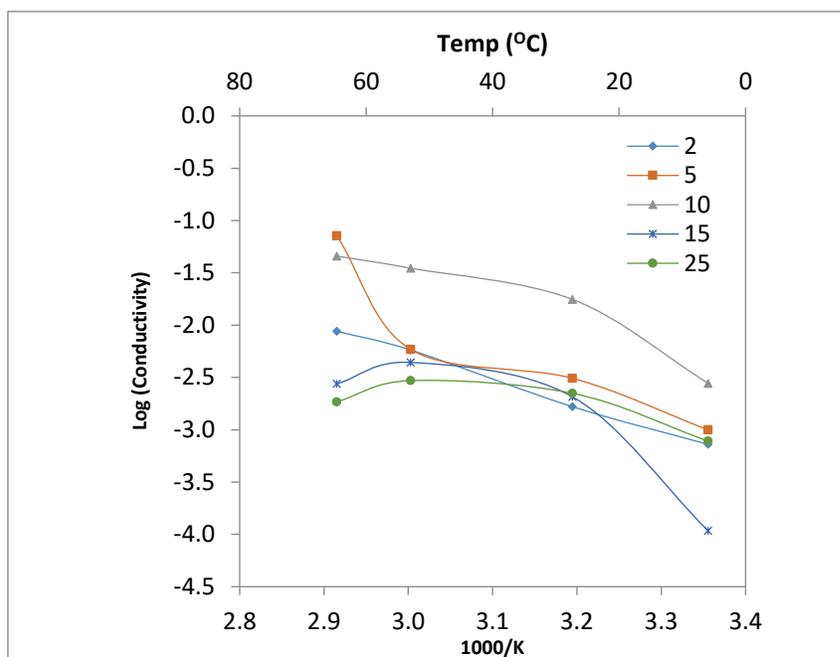
TFSI⁻   Li⁺

Figure 10. Depiction of triglyme borane interaction with LiTFSI.

The triglyme borane was added at either 10% or 20 % by weight to the blend system. Addition of the borane additive show high ionic conductivity around 10^{-3} S cm^{-1} at 25 $^{\circ}$C. Tables 6 and 7 show the effect of addition of the additive to the blend system. It is particularly interesting to note that the ionic conductivity of the blend with the borane molecule is not significantly dependent 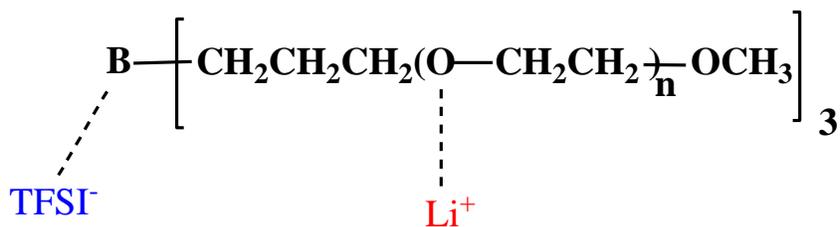on the salt content within the range that was studied. Without borane the conductivity increases initially with salt content, reached a maximum and decreased past the maximum, which has been explained because of the complex nature of the structures of the salt in the matrix. We believe that the borane additive affects the behavior because the boron atom, a strong Lewis acid, interacts with the anion and increases the interionic distance between the anion and the cation. This perhaps results in greater number of free or polymer separated cations and thus increased mobility or conductance is observed at lower salt content.

Addition of a Triglyme borane additive results in several interesting observations but two of the observations are quite unique. Addition of 10% or 20% borane additive to either the MPEG (350) or MPEG (550), the ionic conductance seems to be independent of the salt content and quite high (around 10^{-3} S cm^{-1}). Therefore, these blend systems

display high ionic conductivity over a large window of salt content and thus slight

precipitation of salt will not effect the overall battery performance which is a problem

for most PEO based systems.

Table 6. Ionic Conductivity at 25°C of MPEGs-350/Triglyme-B/LiTFSI Blend System

Blend System Triglyme-B /LiTFSI	Ethylene Oxide/Li$^+$	σ (S cm^{-1})
90% PEO-350/10%	2	2.2x10^{-3}
80% PEO-350/20%	2	1.1x10^{-3}
90% PEO-350/10%	5	1.9X10^{-3}
80% PEO-350/20%	5	2.1X10^{-3}
90% PEO-350/10%	10	1.7x10^{-3}
80% PEO-350/20%	10	3.4x10^{-3}

Table 7. Ionic Conductivity at 25°C of MPEGs-550/Triglyme-B/LiTFSI Blend System

Blend System Triglyme-B /LiTFSI	Ethylene Oxide/Li$^+$	σ (S cm^{-1})
90% MPEG-550/10%	2	2.4x10^{-3}
80% MPEG-550/20%	2	1.8x10^{-3}
90% MPEG-550/10%	5	1.8X10^{-3}
80% MPEG-550/20%	5	2.3X10^{-3}
90% MPEG-550/10%	10	1.2x10^{-3}
80% MPEG-550/20%	10	1.6x10^{-3}

A second interesting observation is that when 10% of the borane additive is

present, the log σ vs temperature plot (Figures 11 and 12) shows a fairly sharp linear

increase of the ionic conductivity with increasing temperature suggesting that ion

movements are taking place by a free volume mechanism and is similar to the behavior of

most PEO based electrolyte system. However, when the additive content is increased

20%, the increase is not significant with increasing temperature (Figures 13 and 14).The

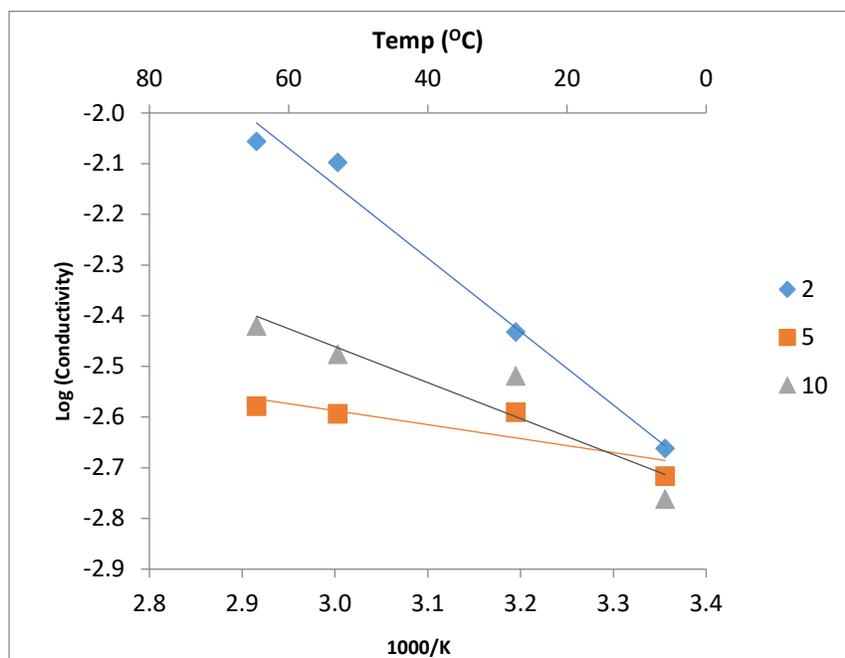exact reason for this observation is not currently understood.

Figure 11. Log σ vs. temperature for MPEG-350/LiTFSI/10% Triglyme-B.
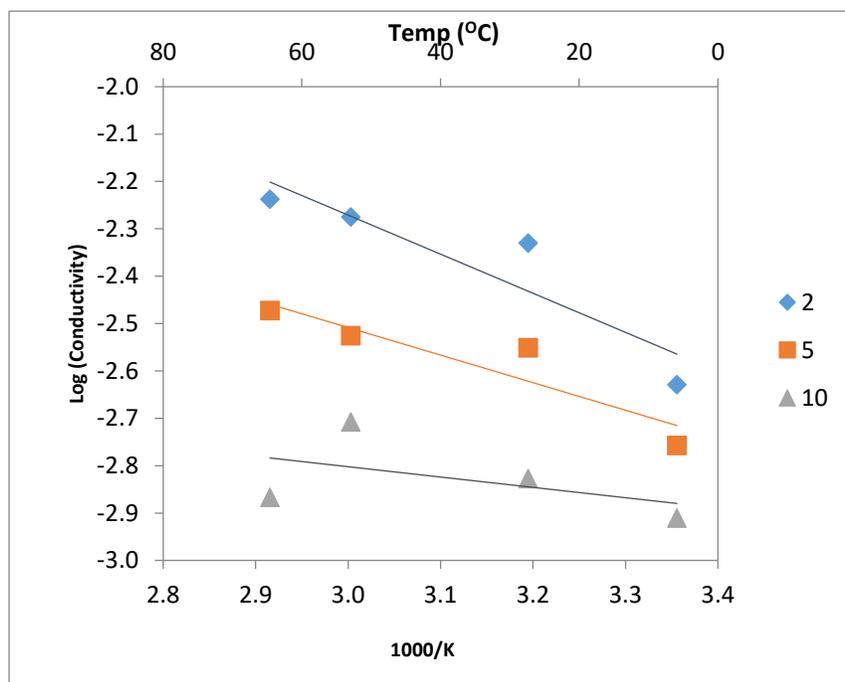

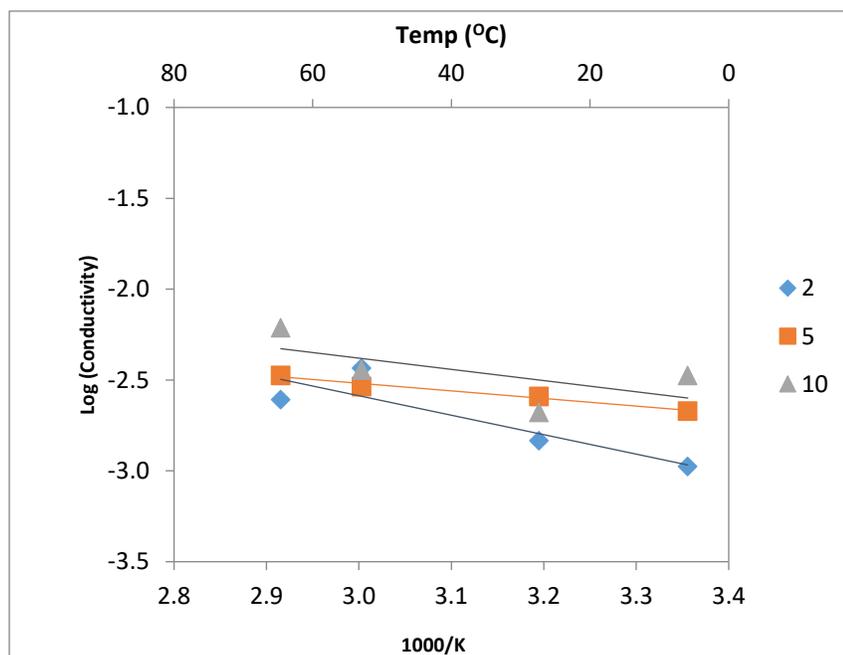**Figure 12.** Log σ vs. temperature for MPEG-550/LiTFSI/10% Triglyme-B.

Figure 13. Log σ vs. temperature for MPEG-350/LiTFSI/20% Triglyme-B.
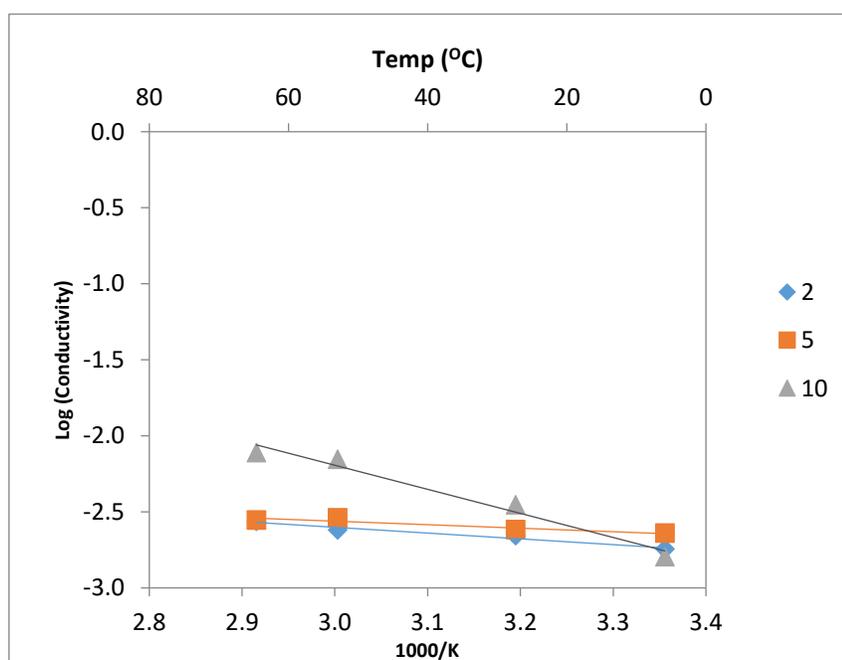
Figure 14. Log σ vs. temperature for MPEG-550/LiTFSI/20% Triglyme-B.

The energy activiation for Triglyme-B with MPEG/LiTFSI blend clarifys that adding

Triglyme-B with blends gives high and stable conductivity as listed in Table 8.

Table 8. Energy of Activation (kJ/mol) for Triglyme-B with MPEGs/LiTFSI Blends

Triglyme-B 10%- MPEG (350) 90%		B 20%-MPEG (350) 80%	
Ratio	Ea	Ratio	Ea
2	1.4471	2	1.0704
5	0.2757	5	0.4182
15	0.709	15	0.6169

Triglyme-B 10 %- MPEG (550) 90%		B 20%- MPEG (550) 80%	
Ratio	Ea	Ratio	Ea
2	0.8251	2	0.38
5	0.5819	5	0.2311
15	0.2182	15	1.5836

4.3 ^{7}Li NMR Spectroscopy of MPEG (350 or 550)/LiTFSI Blend

Equation 2 as previously disscused shows equilibria depicting possible structures

of the LiTFSI in the electrolyte. In order to understand the nature of the equilibria and the

effect of the salt content in the blends, ^{7}Li NMR spectroscopy has been carried out.

Lithium seven NMR spectra can provide insight into the type of ionic structures

present.[35] Figures 15 to 20 show 194 MHz ^{7}Li NMR spectra of MPEG/LiTFSI blends in

the bulk state. The NMR spectra were locked using D_2O and LiCl in D_2O was used as an

internal reference. The bulk NMR spectra were run using a 5 mm NMR tube into which a

2nd narrower tube containing the LiCl/D_2O solution was inserted.

Figure 15. 194 MHz ^{7}Li-NMR spectrum of bulk MPEGs-350 at ethylene oxide to lithium mole ratio of 2.

Figure 16. 194 MHz ^{7}Li-NMR spectrum of bulk MPEGs-350 at ethylene oxide to lithium mole ratio of 10.

Figure 17. 194 MHz ^{7}Li-NMR spectrum of bulk MPEGs-350 at ethylene oxide to lithium mole ratio of 15.

Figures 18, 19 and 20 show the[7]Li-NMR spectra of MPEGs-550/LiTFSI. They are similar to the MPEGs-350. The broader peak is at a ratio of 10:1 which gives high conductivity and this is contrary with the concept and is not entirely understood.
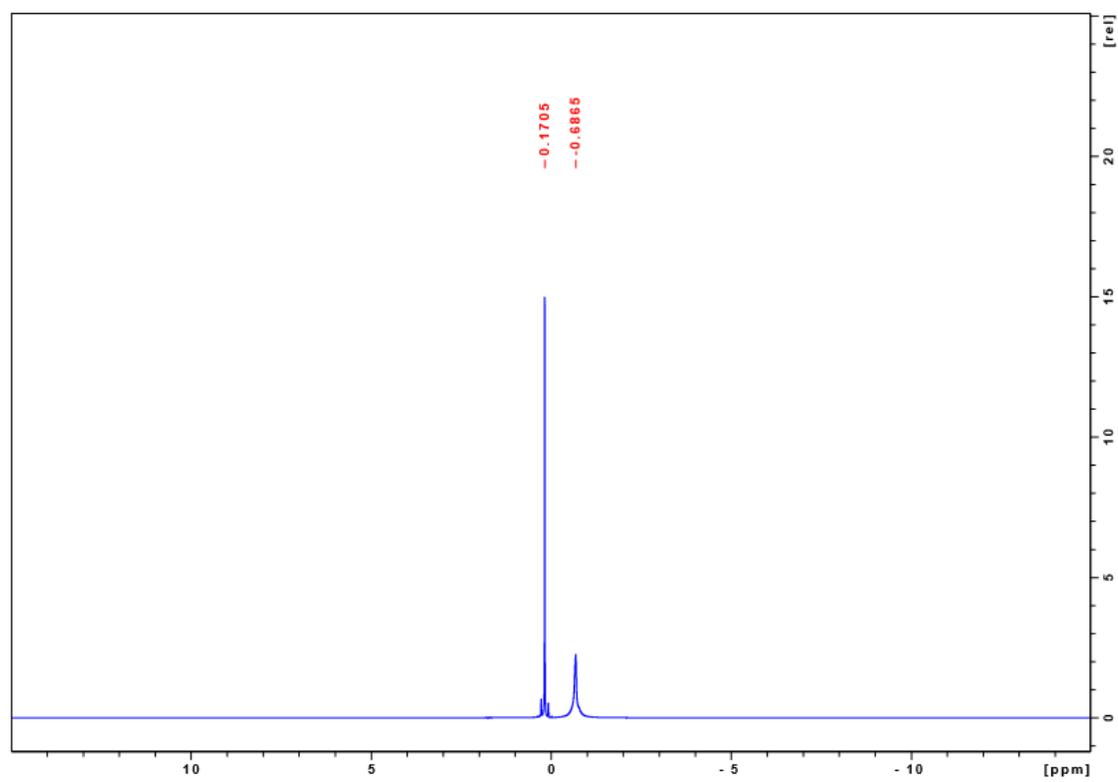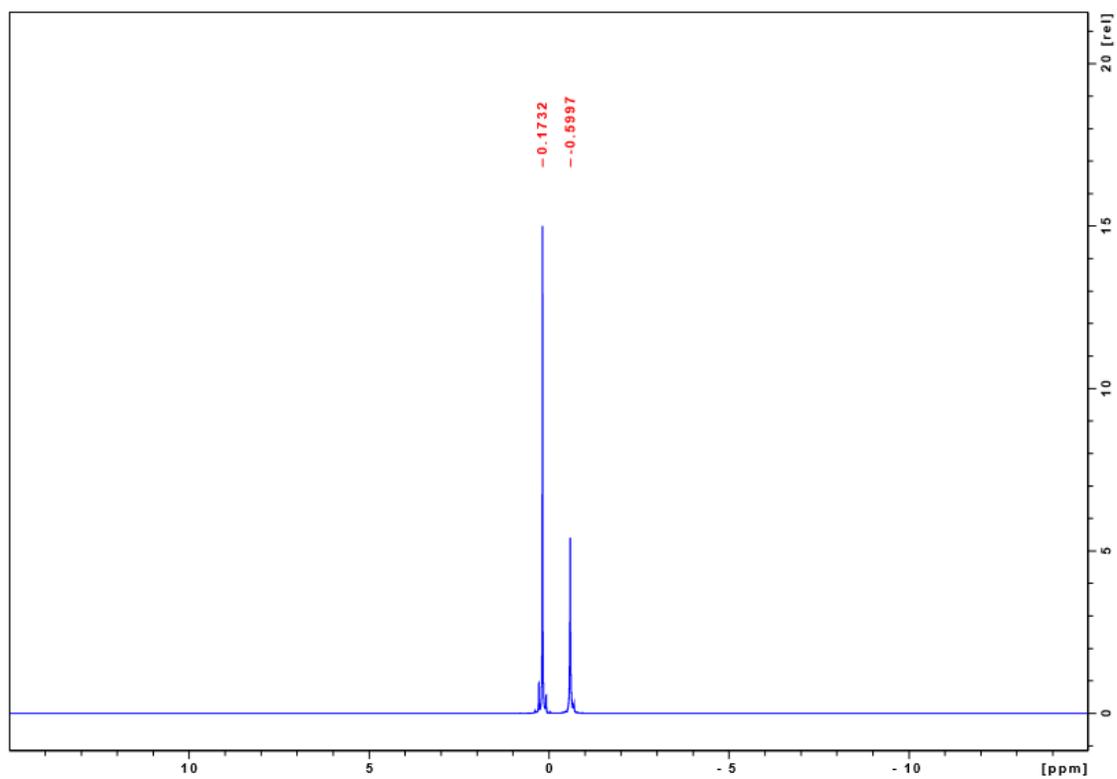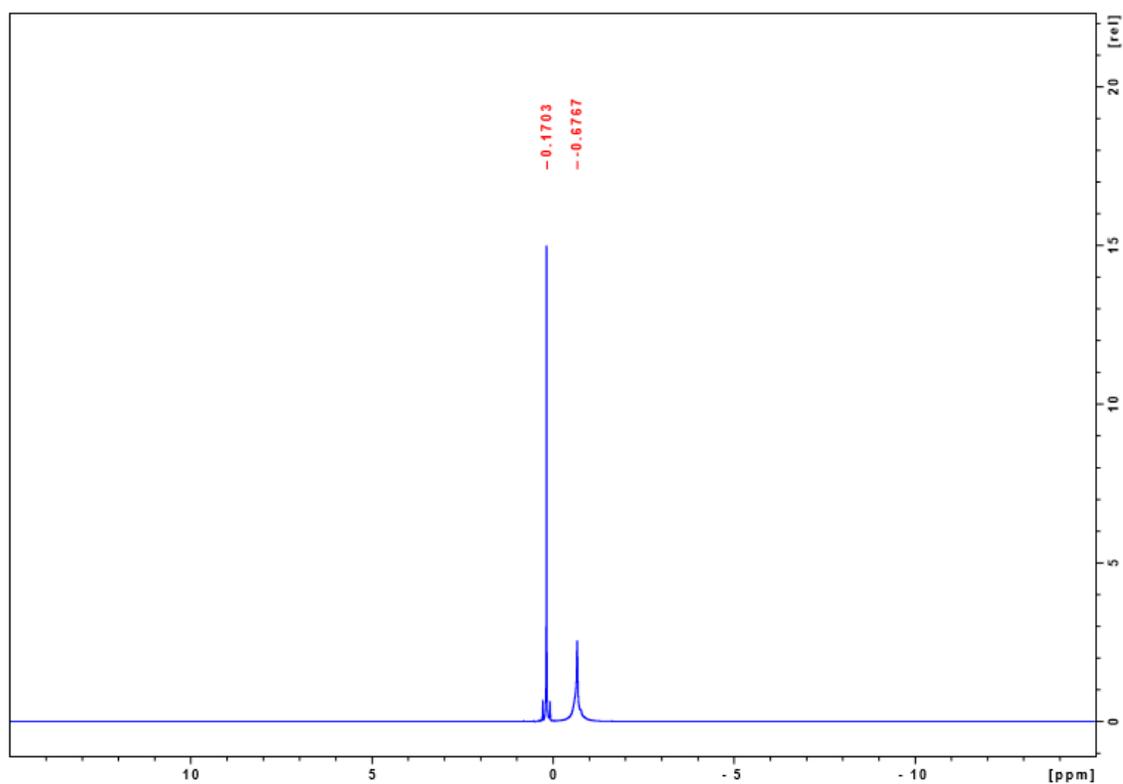

Figure 18. 194 MHz ^{7}Li-NMR spectrum of bulk MPEGs-550/LiTFSI at ethylene oxide to lithium mole ratio of 2.
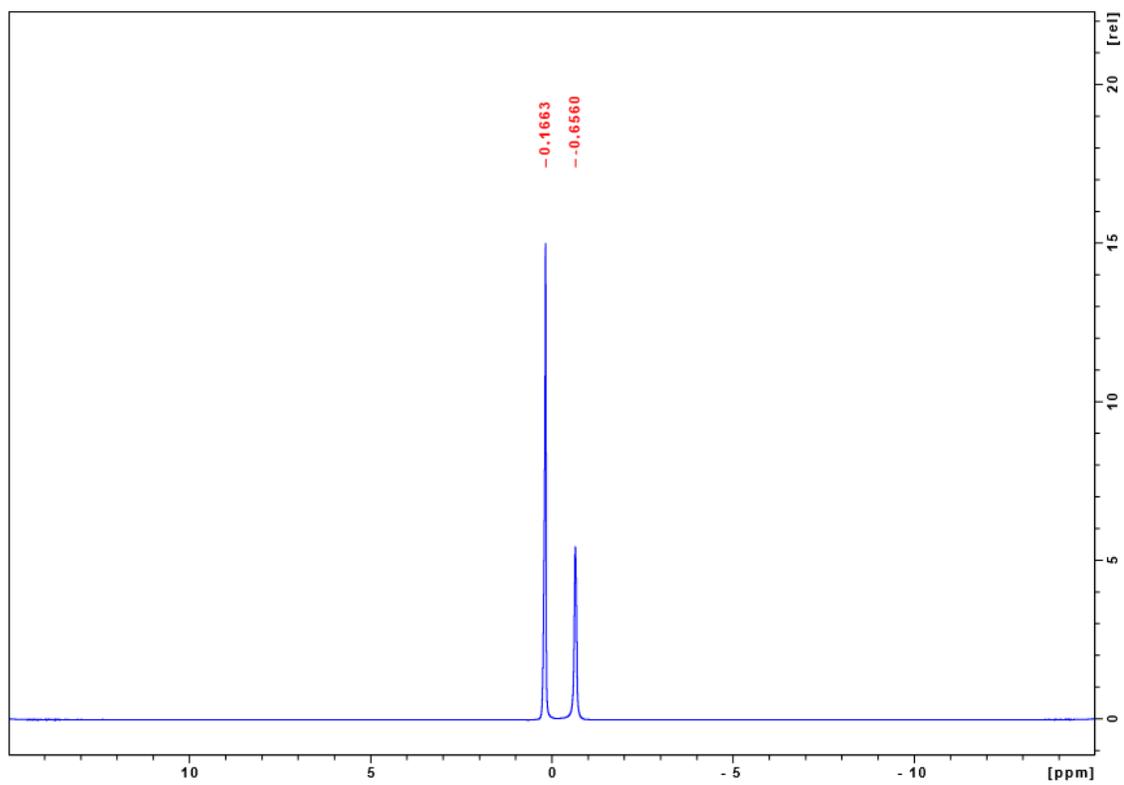
Figure 19. 194 MHz ^{7}Li-NMR spectrum of bulk MPEGs-550/LiTFSI at ethylene oxide to lithium mole ratio of 10.
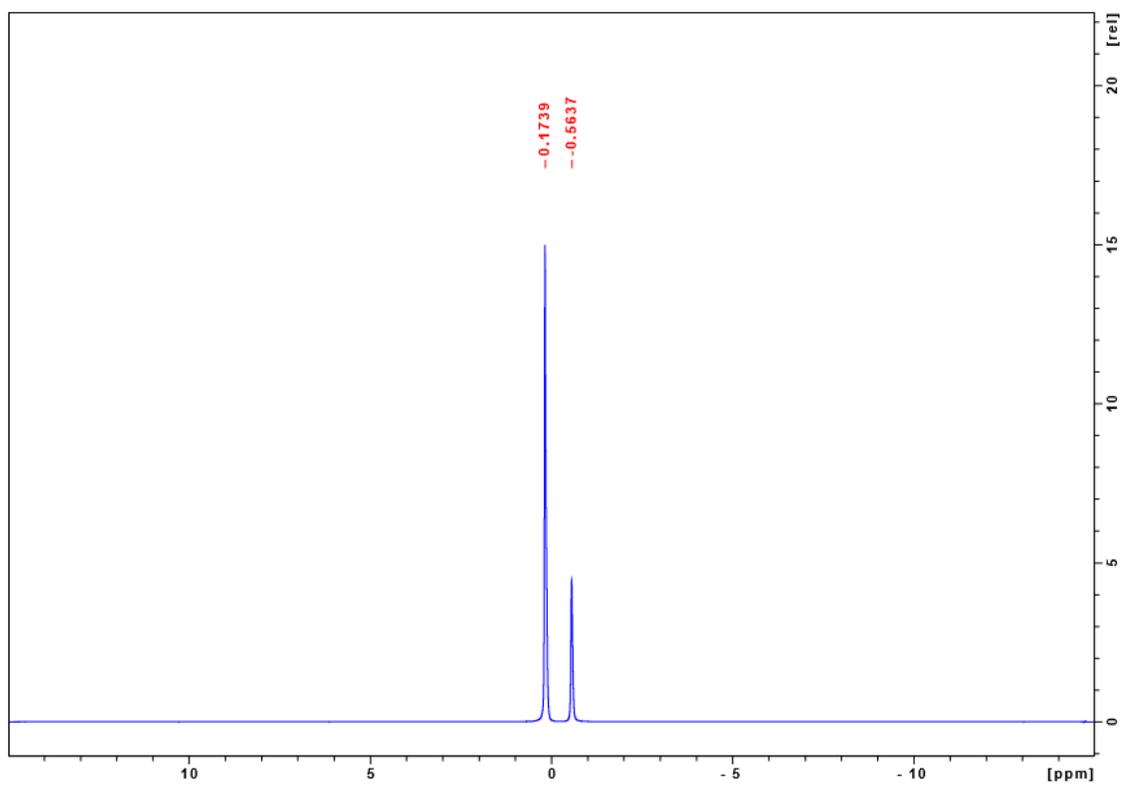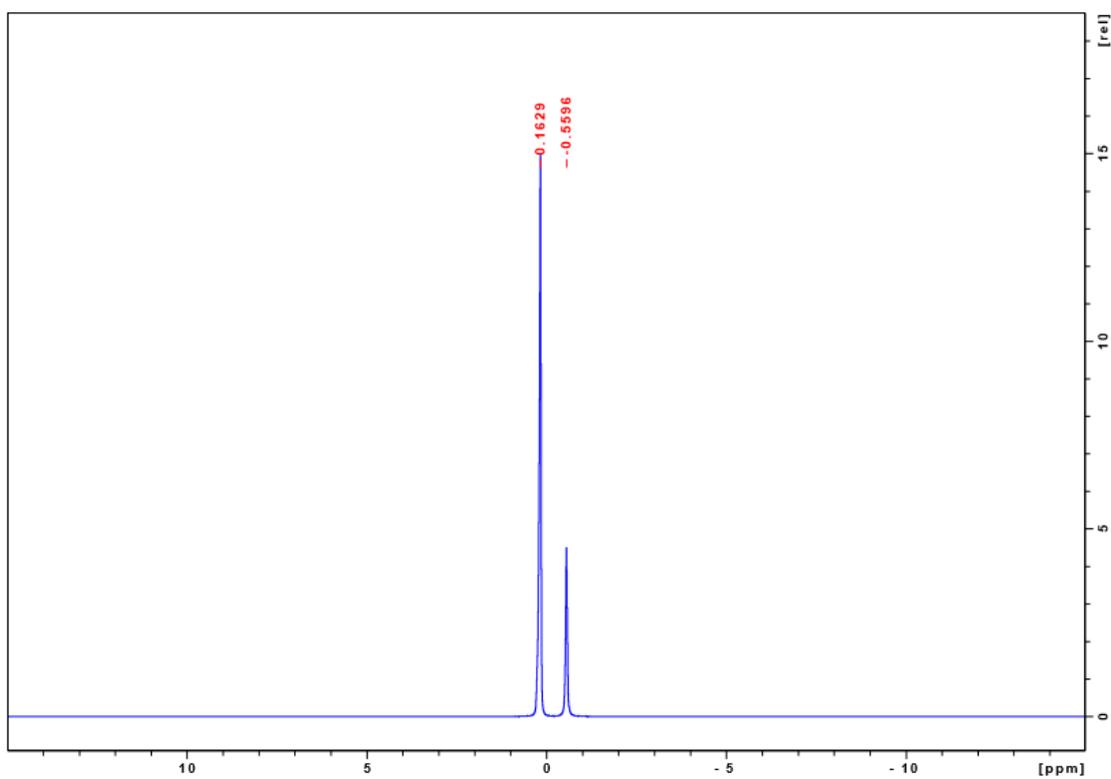
Figure 20. 194 MHz ^{7}Li-NMR spectrum of bulk MPEGs-550/LiTFSI at ethylene oxide to lithium mole ratio of 15.

The data from the NMR spectra is tabulated in Table 9. The ^{7}Li NMR peaks for the samples are observed upfield from the LiCl standard. As the salt content is increased, the chemical shift moves further upfield for both the blend system. In the MPEG-350/LiTFSI blend the lithium chemical shift at an ethylene oxide/Li^{+} mole ratio of 15 is observed at 0.39 ppm upfield from the LiCl standard, increasing to a mole ratio of 2, the peak appears at 0.52 ppm upfield suggesting that increasing salt content results in increased aggregation. Because the exchange between the different types of ionic structure is most likely fast on the NMR timescale, only one peak is observed. The linewidth of the lithium signal is relatively narrow also suggesting fast exchange. It is generally accepted that as higher aggregates are formed, the lithium signal shifts further up field, which is observed in these systems.[6,35]

Table 9. ^{7}Li NMR Chemical Shifts and Linewidths

MPEGs/LITFSI	Ratio	PPM-Up Field *	Half width
(MW 350)	2	0.5160	13 Hz
	10	0.4265	5 Hz
	15	0.3898	10 Hz
(MW 550)	2	0.5064	10 Hz
	10	0.4897	17 Hz
	15	0.3967	14 Hz

Reference is 5.0 M LiCl.

*Internal standard LiCl (5.0 M)/D$_2$O.

CHAPTER V

CONCLUSION AND SUMMARY

The study reported in this thesis is the first report on the ionic conductivity of pure MPEG (350 and 550)/LiTFSI blends. The study was carried out to evaluate whether these types of liquid organic electrolytes will be suitable for use in lithium-air batteries that require liquid electrolytes. High room temperature ionic conductivities were observed (around 10^{-3} S cm^{-1}) for the system and from a conductivity aspect, these electrolytes are suitable for use in lithium-air batteries. The conductivity increases as the salt content is increased and reaches a maximum at an ethylene oxide/Li$^+$ mole ratio of 10 and further increase results in a decrease in the conductivity. This behavior is consistent with literature reports. What is particularly interesting in these blend systems, see Figure 6, is that the maximum conductivity at 25°C is observed at an ethylene oxide/Li$^+$ mole ratio of 10; however, when the temperature is increased to 70°C, the maximum conductivity is observed at an ethylene oxide/Li$^+$ mole ratio of 5. This observation suggests that the dynamics among the various ionic structures in the matrix is affected at 70°C. At 70 ^{o}C greater degree of segmental motion of the polymer chains effects the equilibria among ion-pair, triple anions or cations, quadrupoles or higher aggregates changes and larger fraction of the salt act as charge carriers. In the MPEG-

350/LiTFSI blend the lithium chemical shift at an ethylene oxide/Li^+ mole ratio of 15 is observed at 0.39 ppm upfield from the LiCl standard, increasing to a mole ratio of 2, the peak appears at 0.52 ppm upfield suggesting that increasing salt content results in increased aggregation. Because the exchange between the different types of ionic structure is most likely fast on the NMR timescale, only one peak is observed. The linewidth of the lithium signal is relatively narrow suggesting fast exchange. It is generally accepted that as higher aggregates are formed, the lithium signal shifts further upfield, which is observed in these systems. Overall the system shows high ionic conductivity and also the ionic-transport through the matrix is by a free volume mechanism.

APPENDIX A

Ionic Conductivity of MPEG-350 /Triglyme-B/LiTFSI System

Blend System	Ethylene Oxide/Li$^+$	σ (S cm^{-1}) at 40°C	σ (S cm^{-1}) at 60°C	σ (S cm^{-1}) at 70°C
90%MPEG350/10% Triglyme-B /LiTFSI	2	3.7×10^{-3}	8.0×10^{-3}	8.8×10^{-3}
80%MPEG350/20% Triglyme-B /LiTFSI	2	1.5×10^{-3}	3.7×10^{-3}	2.5×10^{-3}
90%MPEG350/10% Triglyme-B /LiTFSI	5	2.6×10^{-3}	2.6×10^{-3}	2.6×10^{-3}
80%MPEG350/20% Triglyme-B /LiTFSI	5	2.6×10^{-3}	2.9×10^{-3}	3.4×10^{-3}
90%MPEG350/10% Triglyme-B /LiTFSI	10	3.0×10^{-3}	3.3×10^{-3}	3.8×10^{-3}
80%MPEG350/20% Triglyme-B /LiTFSI	10	2.1×10^{-3}	3.6×10^{-3}	6.1×10^{-3}

APPENDIX B

Ionic Conductivity of MPEG-550 /Triglyme-B/LiTFSI System

Blend System	Ethylene Oxide/Li$^+$	σ (S cm^{-1}) at 40°C	σ (S cm^{-1}) at 60°C	σ (S cm^{-1}) at 70°C
90%MPEG550/10% Triglyme-B /LiTFSI	2	4.7×10^{-3}	5.3×10^{-3}	5.8×10^{-3}
80%MPEG550/20% Triglyme-B /LiTFSI	2	2.2×10^{-3}	2.4×10^{-3}	2.7×10^{-3}
90%MPEG550/10% Triglyme-B /LiTFSI	5	2.8×10^{-3}	3.0×10^{-3}	3.4×10^{-3}
80%MPEG550/20% Triglyme-B /LiTFSI	5	2.4×10^{-3}	2.9×10^{-3}	2.8×10^{-3}
90%MPEG550/10% Triglyme-B /LiTFSI	10	1.5×10^{-3}	2.0×10^{-3}	1.4×10^{-3}
80%MPEG550/20% Triglyme-B /LiTFSI	10	3.5×10^{-3}	7.0×10^{-3}	7.7×10^{-3}

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