

## ABSTRACT

Title of Document:                   NANOSTRUCTURED THIN FILM POLYMER  
  ELECTROLYTES FOR FLEXIBLE BATTERY  
  APPLICATIONS

Ayan Ghosh, Doctor of Philosophy, 2009

Directed By:                       Professor Peter Kofinas  
  Fischell Department of Bioengineering

In recent years, the interest in polymeric batteries has increased dramatically. With the advent of lithium ion batteries being used in cell phones and laptop computers, the search for an all solid state battery has continued. Current configurations have a liquid or gel electrolyte along with a separator between the anode and cathode. This leads to problems with electrolyte loss and decreased performance over time. The highly reactive nature of these electrolytes necessitates the use of protective enclosures which add to the size and bulk of the battery. Polymer electrolytes are more compliant than conventional inorganic glass or ceramic electrolytes. The goal of this work was to design and investigate novel nanoscale polymer electrolyte flexible thin films based on the self-assembly of block copolymers.

Block copolymers were synthesized, consisting of a larger PEO block and a smaller block consisting of random copolymer of methyl methacrylate (MMA) and the lithium salt of methacrylic acid (MAALi). The diblock copolymer [PEO-*b*-(PMMA-*ran*-PMAALi)] with added lithium bis(oxalato)borate, LiBC<sub>4</sub>O<sub>8</sub> (LiBOB) salt (in the molar ratio ethylene oxide:LiBOB = 3:1) was used to form flexible translucent films which exhibited nearly two orders of magnitude greater conductivity than that shown by traditional high molecular weight PEO homopolymer electrolytes, in the absence of ceramic fillers and similar additives. The presence of the smaller second block and the plasticizing effect of the bulky lithium salt were shown to effectively reduce the crystallinity of the solid electrolyte, resulting in improved ion transporting behavior. The tailored solid self-assembled diblock copolymer electrolyte matrix also exhibits an exceptionally high lithium-ion transference number of 0.9, compared to a value between 0.2 and 0.5, shown by typical polymer-lithium salt materials. The electrolyte material also has a wide electrochemical stability window and excellent interfacial behavior with lithium metal electrode. The combination of these properties make electrolyte membranes composed of the diblock copolymer PEO-*b*-(PMMA-*ran*-PMAALi) and LiBOB salt, viable electrolyte candidates for flexible lithium ion based energy conversion/storage devices.



NANOSTRUCTURED THIN FILM POLYMER ELECTROLYTES FOR  
FLEXIBLE BATTERY APPLICATIONS

By

Ayan Ghosh

Dissertation submitted to the Faculty of the Graduate School of the  
University of Maryland, College Park, in partial fulfillment  
of the requirements for the degree of  
Doctor of Philosophy  
2009

Advisory Committee:  
Professor Peter Kofinas, Chair/Advisor  
Professor Robert M. Briber  
Professor Chunsheng Wang  
Professor Sheryl H. Ehrman  
Professor Ganesh Sriram

© Copyright by

Ayan Ghosh

2009

## DEDICATION

To my Mom and Dad, for their endless support and encouragement.

## ACKNOWLEDGEMENTS

First and foremost, I thank my advisor, Professor Peter Kofinas, for his steadfast support and guidance through the duration of my Ph.D. research. I have always considered myself to be very lucky to have him as a mentor and for the freedom and independence I have received in pursuing my research interests. He has been a source of encouragement even through the downs of this journey. In my future endeavors, I shall try to achieve the standards of dedication and discipline that I have seen in him over the years.

I would like to thank Professor Robert Briber for all that I have learnt from him during our group meeting discussions. His comments and explanations helped me understand things that were often missed upon casual inspection. In spite of his busy schedule and commitments he was always available with his suggestions and thoughts. I am grateful to Dr. Briber's research group as well, for all the help I have received from them over the years.

I would also like to thank Professor Chunsheng Wang for always being available whenever I sought his advice. His insights have been invaluable in helping me get a better grasp of the electrochemical aspect of my research.

This work would not have been complete without the presence of my friends and family. Words cannot express the experience I have had at Maryland, thanks to an excellent lab group and an exceptional circle of friends. To Arthur von Cresce,

Linden Bolisay, Daniel Janiak, Brendan Casey and Joshua Silverstein for the friends they are, and making this graduate chapter truly memorable. To Ta-I Yang and Pinar Akcora, for entertaining my endless stream of questions. To Sanem Argin, Angela Fu, Angela Mariani, Irene Bacalocostantis and Aaron Fisher, for all the good times whenever they were around. To Erin Falco, Aimee & Matt Ketner, Patricia Castellanos, Vivek & Vikansha Dwivedi, Vinod Lakshminarayan and Rakesh Kumar for the great friends they are. I am at a loss for words to convey my gratitude to my parents and brother for all their sacrifices and for always being around. Finally to my uncle, Dr. Amit Biswas who has been a role model for me over the years. To him and to my Dad, for being the motivation for me to pursue graduate studies.

# TABLE OF CONTENTS

List of Tables .....	vii
List of Figures .....	viii
1. Introduction.....	1
1.1    Significance.....	1
1.2    Background .....	4
1.3    Polymer Selection and Design .....	13
1.4    Salt Selection .....	17
2. Nanostructured Block Copolymer Dry Electrolyte.....	20
2.1    Introduction.....	20
2.2    Experimental .....	22
2.3    Results and Discussion .....	25
2.4    Conclusions.....	32
3. Block Copolymer Solid Electrolyte with high Li-ion Transference Number .....	35
3.1    Introduction.....	35
3.2    Experimental .....	37

3.3	Results and Discussion .....	40
3.4	Conclusions .....	51
4.	Conclusions and Future Work .....	53
	Bibliography .....	58

## LIST OF TABLES

Table 3.1: Lithium-ion transference number data of electrolyte films made from diblock copolymer PEO- <i>b</i> -(PMMA- <i>ran</i> -PMAALi) and the LiBOB salt. Li/Electrolyte/Li cell under a constant d.c. potential bias of 10 mV.....	41
---	----



## LIST OF FIGURES

Figure 1.1: Wireless capsule endoscope: (a) External View; (b) Layout; (c) Schematic cross-section: 1 - optical dome, 2 - short focal aspheric lens, 3 - white LEDs, 4 - CMOS imager, 5 - standard button watch batteries, 6 -ASIC transmitter, 7 - antenna [3].	3
Figure 1.2: Discharge process in a lithium ion battery.	6
Figure 1.3: Equivalent circuit representation of the electrolyte.	11
Figure 1.4: Determination of resistance from a typical impedance scan.	12
Figure 1.5: Chemical structure of block copolymer.	13
Figure 1.6: Self-assembled polymer electrolyte morphology.	14
Figure 1.7: Chemical structure of lithium-bis-(oxalato) borate.	18
Figure 2.1: Chemical structure of self-assembled diblock copolymer	21
Figure 2.3: Salt optimization of PEO- <i>b</i> -(PMMA- <i>ran</i> -PMAALi) diblock copolymer at room temperature (21°C).	29
Figure 2.4: Temperature studies of PEO- <i>b</i> -(PMMA- <i>ran</i> -PMAALi) diblock copolymer in the temperature range 0–70°C.	31
Figure 2.5: DSC scans of PEO- <i>b</i> -(PMMA- <i>ran</i> -PMAALi) diblock copolymer with different added compositions of LiBOB compared to native PEO.	33

Figure 3.1: Electrolyte membrane constructed from the diblock copolymer PEO- <i>b</i> -(PMMA- <i>ran</i> -PMAALi) and the LiBOB salt (picture taken shortly after removal from an Argon glovebox). .....	38
Figure 3.2 (a): Impedance scans from two electrolyte samples taken before and after potentiostatic measurements at room temperature (21–23°C). .....	42
Figure 3.2 (b): Current <i>vs.</i> time profile of the polymer films, obtained at room temperature (21–23°C), under a 10 mV d.c. bias. ....	43
Figure 3.3: Linear sweep voltammetry of electrolyte films made from the diblock copolymer PEO- <i>b</i> -(PMMA- <i>ran</i> -PMAALi) and LiBOB (molar composition EO:LiBOB = 3:1) at (a) room temperature (21– 23°C) and (b) 60°C. A scan rate of 1 mV s <sup>-1</sup> was used with a stainless steel working electrode and a lithium metal counter electrode. ....	45
Figure 3.4: Overvoltage profiles of certain cycles during the Li plating/stripping tests of Li/ PEO- <i>b</i> -(PMMA- <i>ran</i> -PMAALi) + LiBOB (EO:LiBOB = 3:1)/Li cell at room temperature (21–23°C). ....	47
Figure 3.5: Overvoltage <i>vs.</i> time profile of Li/ PEO- <i>b</i> -(PMMA- <i>ran</i> -PMAALi) + LiBOB (EO:LiBOB = 3:1)/Li cell at room temperature (21–23°C). A current flux of 0.1mA/cm <sup>2</sup> was applied on the film with the polarity being reversed every hour. ....	48
Figure 3.6: Impedance responses of the Li/ PEO- <i>b</i> -(PMMA- <i>ran</i> -PMAALi) + LiBOB (EO:LiBOB = 3:1)/Li cell at room temperature (21–23°C)	

obtained at the end of different cycles. The solid lines represent the  
corresponding data fitting of the impedance scans. ....49

Figure 3.7: Overvoltage studies of Li/ PEO-*b*-(PMMA-*ran*-PMAALi) + LiBOB  
(EO:LiBOB = 3:1)/Li cell at room temperature (21–23°C): (a)  
interfacial resistance profile of the cell from impedance scans and  
galvanostatic cycling, (b) resistance values obtained from data  
fitting of the impedance profiles to an equivalent circuit (see *insert*). .....50

Figure 4.1: Environmental degradation of an electrolyte membrane constructed  
from the diblock copolymer PEO-*b*-(PMMA-*ran*-PMAALi) and the  
LiBOB salt upon exposure to normal atmospheric conditions.....56

# Chapter 1

## Introduction

### 1.1 Significance

The goal of this research is to investigate the use of novel thin film battery electrolytes based on the self-assembly of block copolymers. The developed all-solid state nanoscale polymeric electrolyte could result in a light-weight shape conforming battery that employs an electrolyte without the risk of leakage of toxic and corrosive liquid electrolytes. Such a solid electrolyte would also effectively perform the role of a separator, suppressing dendritic growth through the electrolyte. Solid polymer electrolytes are generally more electrode compliant than conventional inorganic or ceramic electrolytes and gel-type electrolytes. The ease of processing of solid polymers would allow for the production of thin film nanoscale batteries that could be wound into coils or processed as sheets or coatings. The self-assembly of block copolymers has been used as templates to create this unique nanoarchitecture. One of the distinct advantages of block copolymers is the controllability of the size and morphology of their self-assembled periodic nanostructures by altering the volume fraction of each polymer block. Depending on the volume fraction of each respective

block, morphologies like lamellae, hexagonal closed packed cylinders, bicontinuous gyroids and body centered cubic spheres can be obtained. A polymeric electrolyte based on nanoscale self-assembly will provide for devices with integrated electronics and can be distributed over a large substrate area as freestanding flexible films or coatings. In the design of miniature devices, the shape and weight of the energy source is a major constraint. The risks of electrolyte leakage and flammable components give rise to safety concerns, which have been a key deterrent in the use of batteries for implantable systems. The inherent reactivity of the electrolyte imposes the need for bulky containment layers. A polymer electrolyte based battery system would require a laminating layer, for example Mylar, to shield it from external elements. Such a battery system will provide for a lighter and flexible energy source that would be intrinsically safe and biocompatible. Stand alone sensors and medical devices like pacemakers, implantable pumps and treatment probes would benefit greatly from the conformal and safe nature of all-solid polymer electrolyte based energy sources.

Applications can be found in devices like BIONs™, that are implanted under a patient's skin with the function of tissue simulation, parameter monitoring and data communication [1]. Endoscopy, a minimally invasive medical diagnostic procedure, has been a popular tool for visual inspection of affected sites inside the body. This technique was further revolutionized by the advent of wireless capsule endoscopy [2]. It is interesting to note that the main constraint to the size and shape of this untethered diagnostic probe is the battery [3], which forms the largest component of the capsule (Figure 1.1).

Advances in science have envisioned the creation of mobile manipulators that would transport sensors, drug delivery devices, and cell harvesting tools to the desired locations in the body and possess the essential degrees of freedom to perform the necessary diagnostic and treatment tasks. Such a manipulator would need to (1) operate in-vivo without causing any damages to the surrounding organs/tissues, (2) carry the necessary payloads, (3) provide power to the payloads, and (4) send the information to the external instruments. One of the fundamental limitations that make it very challenging to realize the desired manipulators is the lack of adequate power sources. The untethered mobile manipulator would need to carry onboard batteries for this purpose. Traditional batteries add weight to the platform and impose size constraints.

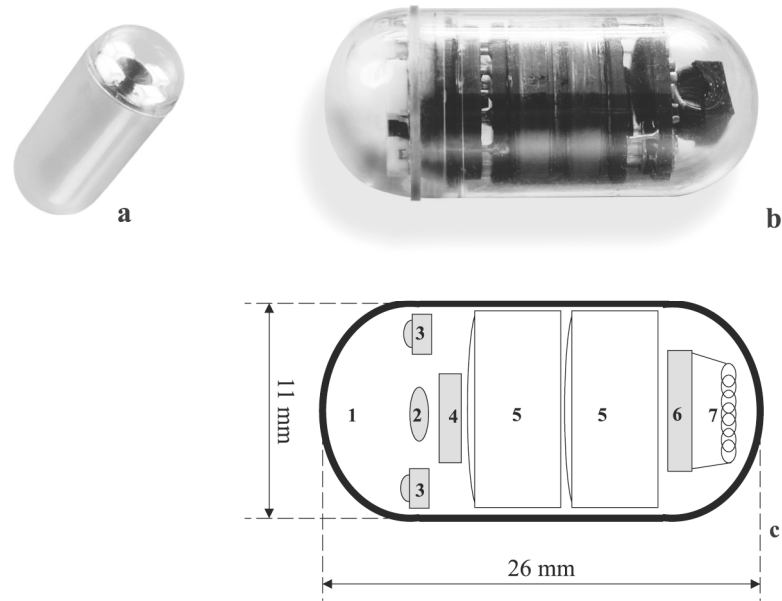


Figure 1.1: Wireless capsule endoscope: (a) External View; (b) Layout; (c) Schematic cross-section: 1 - optical dome, 2 - short focal aspheric lens, 3 - white LEDs, 4 - CMOS imager, 5 - standard button watch batteries, 6 -ASIC transmitter, 7 - antenna [3].

ints. Realizing the envisioned mobile manipulators would require the development of conformal batteries that can be integrated in multi-functional structures. In addition to storing energy, these conformal batteries would also have to play a structural role and should not pose any size restrictions. Developing such conformal batteries will require creation of chemical formulations that should be compatible with the materials and manufacturing processes used to realize the manipulators.

## 1.2 Background

Laptop computers and mobile phones have become smaller and faster, but with increased demands on energy. Current portable battery configurations have a liquid or gel electrolyte between the anode and cathode. This leads to problems with electrolyte loss and decreased performance over time. The highly reactive nature of these electrolytes necessitates the use of protective enclosures which add to the size and bulk of the battery. As portable battery-operated devices decrease in size and efficiency, there is a greater requirement for batteries to have high charge densities and current capacities along with the versatility of size, shape and weight. Lithium is one of the most electropositive elements ( $-3.04$  Volts versus standard hydrogen electrode) in the electrochemical series. Also, its low density ( $0.53 \text{ g cm}^{-3}$ ), makes it the most potent of charge carriers. It possesses the largest electrical density per unit weight among all solid elements of the periodic table. All these benefits are however offset by its extreme reactive nature, limiting the full use of these benefits.

Safety is the ever-growing concern in energy storage systems with the possibility of leaks, production of flammable reaction products and internal shorting existing in liquid electrolyte battery systems. These disadvantages can be considerably offset by the use of a shape-conforming solid polymer electrolyte. Polymers offer the advantages of being robust, light-weight, non-combustible and can be molded in various sizes and shapes to suit the requirements of the application. Due to their solid-like nature, polymer electrolytes are expected to be less reactive than their liquid counterparts and thus more stable towards lithium. For polymer electrolytes to be useful in practical applications, it is necessary that they exhibit appreciable room temperature conductivities and also play the role of separator, which is often an additional component in liquid electrolyte systems. In addition to low temperature performance it is also important that the polymer should have good cycle life and sufficient mechanical and thermal strengths to endure internal pressure and temperature variations during battery performance.

The discharge of batteries depends solely on the conduction of ions from the anode to the cathode. The electrodes must possess the dual capability of transferring ions to and from the electrolyte and at the same time being electrically conductive with respect to the external circuit, while the electrolyte should be ionically conductive (Figure 1.2). The goal of the developed polymer nanostructured electrolyte is to transmit ions, in this case  $\text{Li}^+$ , in the solid state. A solid state electrolyte has some attractive advantages [4]. First, there is no leakage of toxic liquid electrolyte for a consumer to come into contact with, as for example in lead-acid batteries used in automobiles. Secondly, the ease of processing a polymer electrolyte



would allow for the production of a thin film shape-conforming battery that could be wound into coils or processed as sheets.

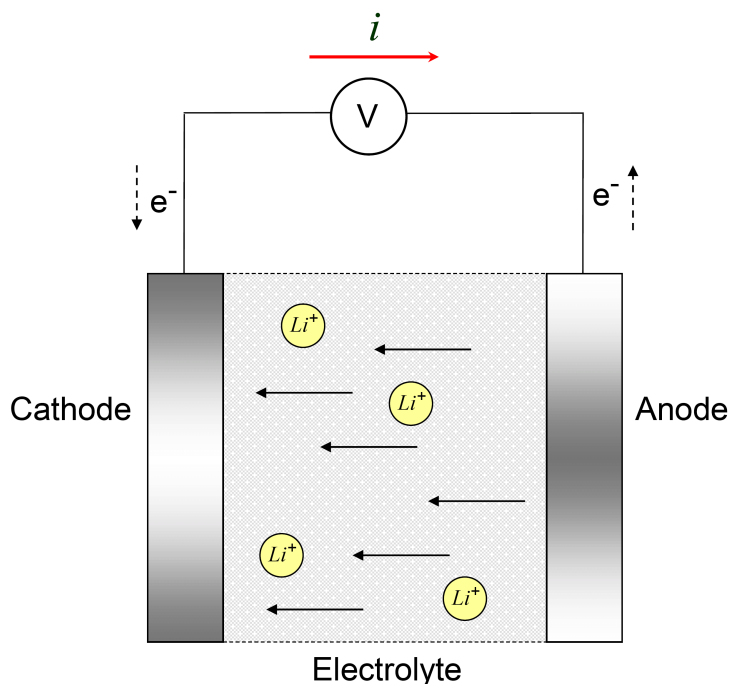


Figure 1.2: Discharge process in a lithium ion battery.

In the selection of a polymer electrolyte for secondary batteries, both ionic conductivity and transference number are important parameters of consideration. A secondary or rechargeable battery is one which can be subjected to multiple charge-discharge cycles as opposed to the single irreversible discharge of a primary battery. Ionic conductivity is any conduction mechanism where the current is sustained by the flow of ions as opposed to electrons within the medium [5]. The transference number of a given ion is the fraction of the total charge carried by that particular ion across a fixed reference plane. Ions may carry significantly different portions of the total current if their mobilities are different. A large transference number can reduce concentration polarization of electrolytes during charge-discharge steps, and thus

sustain the electrolyte's power density. Hence, the conductivity of the electrolyte is linked to the maximum power obtainable, whereas, the maximum limiting current that can be drawn from the cell and number of cycles it can be subjected to, is related to the transference number. In an ideal situation it is desirable that in addition to a high ionic conductivity, the transference number of lithium ions approaches unity. Compatibility with the electrodes is another issue of consideration. The reactivity of lithium metal limits the use of most electrolytes which often result in passivation of the electrode surface.

There is an abundance of published work on polymer electrolytes for use in batteries. In 1973, Fenton introduced the complex forming capability of poly(ethylene oxide) (PEO) with alkali metal salts [6]. The use of PEO as a solid solvent for lithium salts was then proposed by Armand in 1979 [7]. Later work done by Bruno Scrosati and co-workers has been one of the major contributions to this field over the years [8-11]. Significant research was done by his group into gel electrolytic systems using poly(acrylonitrile) (PAN) and poly(methylmethacrylate) (PMMA) along with the more popular poly(vinylidene fluoride) (PVDF) matrices [12-17]. The use of ceramic fillers like Titanium Dioxide ( $\text{TiO}_2$ ), Aluminum Oxide ( $\text{Al}_2\text{O}_3$ ), Lithium Aluminum Oxide ( $\text{LiAlO}_2$ ) and fumed Silica ( $\text{SiO}_2$ ) in composite polymer electrolytes has been successfully shown to increase conductivity by preventing the crystallization of polymer chains [8, 10, 18, 19]. Nanometer-scale ceramic powders may also improve the mechanical strength and interfacial properties of the polymer films. However, the mechanisms with which these fillers induce such enhancements are not yet fully understood. Composite electrolytes have been shown to demonstrate better stability

towards the lithium electrode by reducing the electrolyte-electrode interfacial resistance [20, 21].

Research done by Peter Bruce indicates the possibility of enhanced lithium transport in the crystalline domains of poly(ethylene oxide) (PEO). Here polymer chains are considered to fold into cylindrical tunnels in which the  $\text{Li}^+$  ions are said to be located [22-24]. It has been suggested that lithium ions are transported through the tunnels coordinated by the oxygen atoms of PEO, whereas, the anions exist in the inter-chain space outside the polymeric chain tunnels. This is contradictory to the widely accepted view that the conduction of ions in polymer electrolytes occur almost predominantly in the amorphous phase. Work published by Henderson and Passerini indicate that the ionic conductivity of the amorphous material is indeed significantly greater than its crystalline counterpart [25]. Irrespective of the results shown by Bruce, motion of ions through crystalline domains does open up an interesting avenue of deliberation. The challenge, however, lies in gaining control over the orientation of these crystalline pathways to form the shortest possible route between the two electrodes, rather than a pathway akin to a random walk. If such a goal were to be achieved, crystalline polymers may yet prove to be a solution for polymer electrolytes, where room temperature conductivity of amorphous polymer matrices is still limited to  $10^{-4} \text{ S cm}^{-1}$ .

Besides the use of ceramic fillers, another school of thought incorporates room temperature ionic liquids (RTILs), which dissolve lithium salts and improve the ionic conductivity of the polymer matrix. These RTILs possess additional desirable properties like negligible vapor pressure and low room temperature viscosity. These

advantages are offset by poor stability towards lithium metal. The use of imidazolium cation based RTILs has been studied by Watanabe and co-workers [26-28]. Henderson and Passerini have reported the successful use of RTILs consisting of N-alkyl-N-methylpyrrolidinium cations and bis(trifluoromethanesulfonyl) imide anions (PYR<sub>1R</sub>TFSI) in PEO, with room temperature conductivities greater than 10<sup>-4</sup> S cm<sup>-1</sup> [29-33]. The assembled cells incorporating these ionic liquids, however, did show some capacity fade with increasing number of cycles [27, 32].

The Mayes [34-37] and Kanamura [38-40] groups have extensively researched block and graft copolymer systems as polymer matrices for electrolytes. The MIT group primarily used poly(oligo-oxyethylene methacrylate) (POEM) as one of the blocks. They also published work on single ion conducting electrolytes where the anion is a part of the polymeric backbone. These polymers were however reported as having lower than conventional conductivities, which was attributed to problems with lithium ion dissociation [37]. The Kanamura and later Balsara [41] groups used poly(styrene) (PS) blocks to enhance the mechanical properties of the solid polymer electrolyte.

In the work from the Kofinas group published in *Journal of Power Sources* [42], an ionically conducting A/B diblock copolymer was used as a template for the synthesis and confinement of lithium manganese oxide nanoparticles. The diblock copolymer functions as a composite anode in a lithium battery system. Impedance spectroscopy, galvanostatic testing, x-ray diffraction and transmission electron microscopy were used to characterize the anode and polymer electrolyte. Galvanostatic testing indicated that 300 or more cycles were possible with 90%

retention of capacity [42]. These results show that the nanostructured block copolymer has potential as a lithium battery material in both electrolyte and cathode areas. In the work published in *Macromolecules* [43], an A/B/C triblock copolymer was synthesized having potential applications as a self-contained nanoscale battery. The anode block contained an organocobalt block. The electrolyte block of the copolymer was a poly (ethylene oxide) analogue. The last block acted as the template to form metal oxide nanoparticles to function as the cathode. The triblock copolymer was synthesized by Ring Opening Metathesis Polymerization (ROMP) using Grubbs' catalyst.  $^1\text{H}$  and  $^{13}\text{C}$  NMR, FTIR, UV-Vis, GPC with light scattering and XPS were used to characterize the self-assembled nanoscale polymer battery material.

Electrical characterization of polymer electrolytes can be carried out using both d.c. and a.c. measurements. Between the two, alternating current methods have been the most popular method in determining the electrical properties of polymer materials. This method provides information not only on the long range migration of ions but also gives insight into the polarization occurring within the electrolyte [5]. In general, two idealized polymer electrolyte types are considered:

- *Type I*, where only one of the ionic species is mobile.
- *Type II*, where both the ions of the dissolved salt are mobile.

The block copolymer nanostructured electrolyte is predicted to be a Type I electrolyte, with the mobility of the anion greatly hindered due to its much larger size in comparison with  $\text{Li}^+$ . Impedance spectroscopy is used to determine the ionic conductivity of the material by measuring the impedance of the cell over a frequency range from 1 Hz to 1 MHz. Two parameters are used to relate the current flowing

through the sample to the potential applied across it: the opposition to the flow of charge given by the resistance  $R = V/I$  and the phase difference between the current and the voltage represented by phase angle  $\theta$ . The electrolyte is represented by a simple equivalent circuit (Figure 1.3) of a parallel resistor and capacitor in series with another resistor.

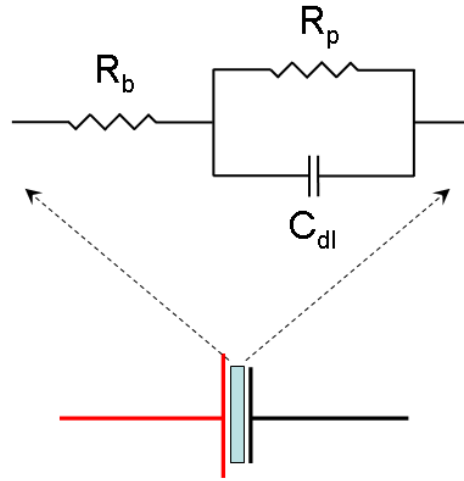


Figure 1.3: Equivalent circuit representation of the electrolyte.

Where,

- $R_b$  is the bulk or electrolyte resistance
- $R_p$  is the polarization or charge transfer resistance
- $C_{dl}$  is the double layer capacitance

The simulation of such a circuit over the frequency range results in a semicircle governed by the equation:

$$Z = R_b + \frac{R_p}{1 + \omega^2 C_{dl}^2 R_p^2} - j \frac{\omega C_{dl} R_p^2}{1 + \omega^2 C_{dl}^2 R_p^2} \quad (1.1)$$

Where, the frequency is represented by  $\omega$ . We obtain  $R_b$  from the high frequency intercept of the semicircle, whereas the total resistance ( $R_b + R_p$ ) of the electrolyte is given by the low frequency intercept (Figure 1.4). The conductivity is obtained from the resistance using the following relationship:

$$\sigma = \frac{t}{R_l A} \quad (1.2)$$

Where,

- $\sigma$  is the conductivity
- $R_l$  is the ionic resistance of the material
- $t$  is sample thickness
- $A$  is the surface area of the sample

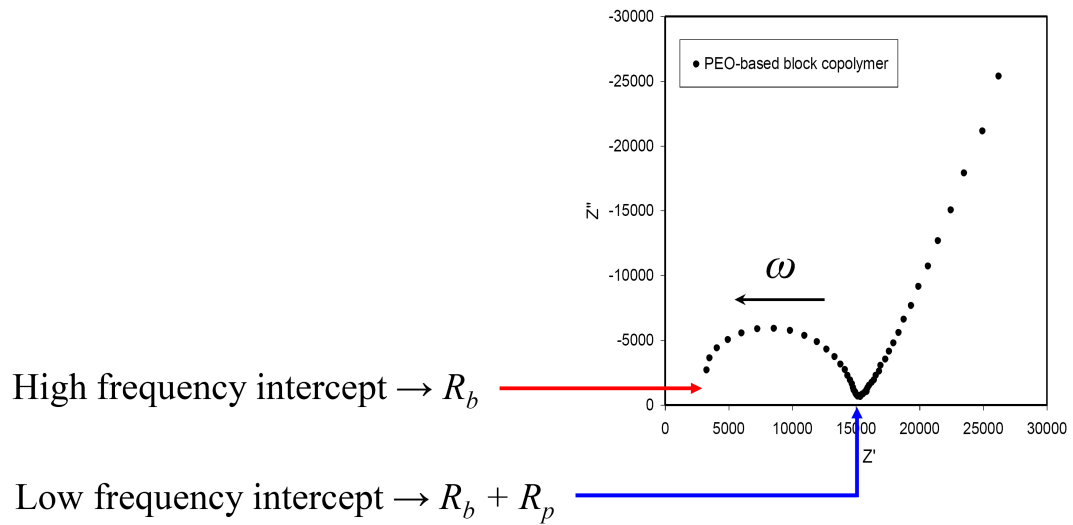


Figure 1.4: Determination of resistance from a typical impedance scan.

### 1.3 Polymer Selection and Design

Poly (ethylene oxide) (PEO), the first reported solvent-free polymer electrolyte, has been a popular material in solid electrolyte research for many years now because of its ability to form complexes with lithium salts and its compatibility with battery electrodes. However, its room temperature conductivity is far lower than that desired for any practical battery application. It is generally perceived that the motion of ions across the electrolyte arises due to the segmental motion of polymer chains [44]. Hence, in order to increase the conductivity, amorphous polymer electrolytes with a low glass transition temperature are more desirable. The use of poly (methyl methacrylate) (PMMA) as a gelatinization agent in electrolytes was first introduced two decades ago by Iijima [45]. In later work by Appetecchi [12], it was found that the transference numbers for PMMA based systems was considerably higher than that of conventional PEO based systems.

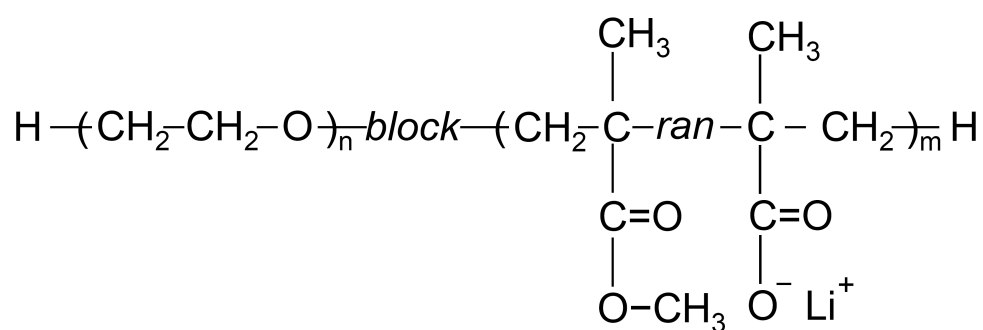


Figure 1.5: Chemical structure of block copolymer.

To attain appreciable levels of conductivity, it is important to carefully tailor the electrolyte matrix. This research was aimed at the development of a nanostructured



thin film battery electrolyte based on a partially hydrolyzed block copolymer of poly(ethylene oxide) and poly(methyl methacrylate) (Figure 1.5). PEO is chosen because of its ability to form stable complexes with lithium salts and its possession of a higher conductivity than any other group of solvating polymers in the absence of organic solvents. The second block is chosen so that it can be functionalized to form lithium domains within the PEO matrix. A 6:1 block ratio of PEO:PMMA is chosen so that the minority of the block copolymer (PMMA) microphase separates into spherical domains. The methacrylate block was partially hydrolyzed with methanolic lithium hydroxide in 1,4-Dioxane medium to create lithium salt of methacrylic acid (MAALi) segments. In doing so, another lithium source was created within the spherical self-assembled microdomains of the diblock copolymer (Figure 1.6) where the anion is a part of the matrix and hence immobile. Due to the weak acidic nature of methacrylic acid, the ionic interactions between the lithium ion and the carboxylic acid will not strongly affect its conductivity through the polymer block.

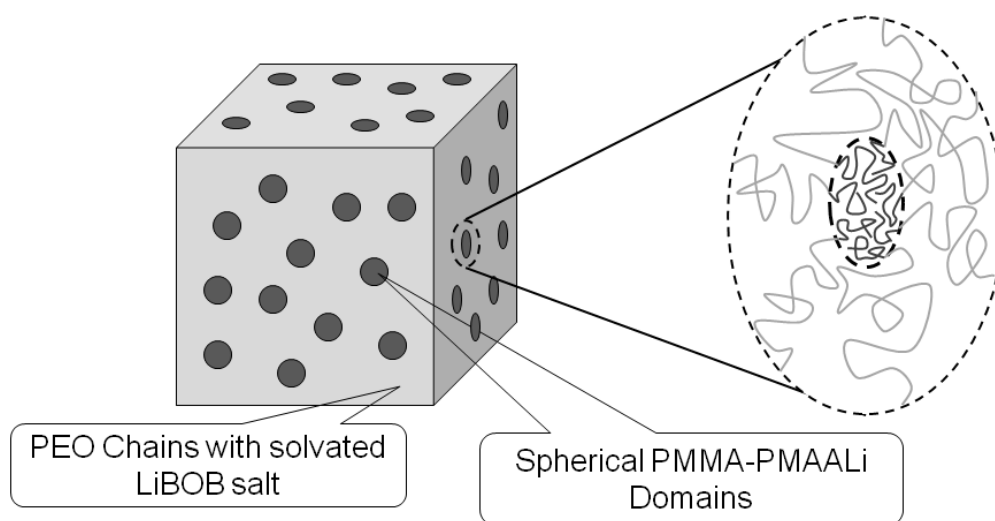


Figure 1.6: Self-assembled polymer electrolyte morphology.

Previous work by Kannan [46] reports the use of polymeric blends of PEO and PMMA with different plasticizers. The electrolyte system of this research is a self-assembled block copolymer, which will provide better lithium ion conductive and mechanical properties than the blend of homopolymers. It consists of poly(ethylene oxide) (PEO) as the first block, and a random copolymer of methyl methacrylate and lithium salt of methacrylic acid (PMMA-*ran*-PMAALi) as the second block (Figure 1.5). The block copolymer system in this research shows better promise than previously published systems in the following ways:

1. The polymer matrix does not involve major portions of non-conducting blocks which are usually used to enhance the mechanical properties of the material, but do not contribute in any way to the ion-transport of the conducting segments.
2. PMMA was selected because it can be functionalized to incorporate lithium into the polymeric backbone.
3. The electrolyte system uses PMMA ( $-\text{CO}_2\text{CH}_3$ ) in comparison to the MIT group, which synthesized a diblock copolymer system containing lauryl ester ( $-\text{CO}_2\text{C}_{12}\text{H}_{25}$ ) groups [36]. The longer non-oxygenated side chain of the polymer produced by the MIT group, we hypothesize, would work better as a means to provide more free volume if used in a *gel* electrolyte system. For a *dry* electrolyte system as the one in this work, the larger side chain which contains only carbon and hydrogen atoms does not aid in providing any conductive pathways for  $\text{Li}^+$

transport. It is the oxygen on the PEO block that contributes to the ionic conductivity by coordinating with the lithium ions.

4. The length of the PMMA block has been kept short so that PEO, which is the conducting block, forms the majority of the block copolymer matrix. The degree of hydrolysis will be low enough that the block copolymer's microphase separation is not disrupted. The proposed hydrolyzed polymer will act as a *polymer electrolyte*, rather than a *polyelectrolyte* with ionomer like ion cluster morphologies.
5. The PMMA block of the block copolymer system will be modified via partial hydrolysis in order to act as a lithium source in the material itself. The use of gel electrolytes based on PMMA with a gelling solvent has been reported by Appetecchi [12] to exhibit a better transference number. The aim of this research is to create a dry conductive electrolyte, whose ionic conductivity is intimately associated with the local segmental motions of the polymer. In comparison to a gel, whose conductivity is often that of the trapped liquid inside the polymer matrix and is not indicative of the ion-transport properties of the polymer.
6. Since a low molecular weight polymer has been chosen, which is also a diblock copolymer; this further suppresses the tendency of PEO to form crystalline regions by reducing the free volume available to the PEO chains, thus enhancing its ionic conductivity.
7. The Hikichi group [47] has reported NMR studies which indicate complexation of methacrylic acid with PEO. The polymer material of this research will avoid such complexation, because only a very small fraction of the polymer contains the

lithium salt of carboxylic acid groups. It is expected that the presence of ions from the added lithium salt will act as an effective screening barrier to further subdue such complexation.

A polymer electrolyte's ionic conductivity can also be enhanced by addition of small amounts of plasticizer, namely low molecular weight poly(ethylene glycol) (PEG) to PEO, which have shown to increase the amorphous regions responsible for ionic conductivity. The amount of plasticizer used is usually low enough to not disrupt the block copolymer microphase separation [48-50] or substantially affect the film's mechanical properties. In addition to reducing the crystalline content and increasing the polymer segmental mobility, the PEG plasticizer can result in greater ion dissociation which allows higher number of charge carriers for ionic transport. In our system, however, the effect of plasticizers was expected to be limited as the block copolymer itself is of low molecular weight.

## 1.4 Salt Selection

Lithium bis(oxalato)borate (LiBOB) (Figure 1.7) is used as the salt of choice in place of the popular lithium hexafluorophosphate ( $\text{LiPF}_6$ ), which poses major safety concerns in its susceptibility to hydrolysis and low thermal stability. This borate based salt introduced by Lischka [51], is readily solvated by our block copolymer. The advantages of using LiBOB are fourfold:

1. LiBOB slowly decomposes by hydrolysis into lithium metaborate ( $\text{LiBO}_2$ ) and monolithium salt of oxalic acid ( $\text{LiOOC-COOH}$ ). Both these decomposition products are benign, as compared to hydrofluoric acid ( $\text{HF}$ ) resulting from the hydrolysis of  $\text{LiPF}_6$  [52].
2. The bulky anion is expected to restrict its movement across the polymer electrolyte and thereby boosting the cation ( $\text{Li}^+$ ) transference number.

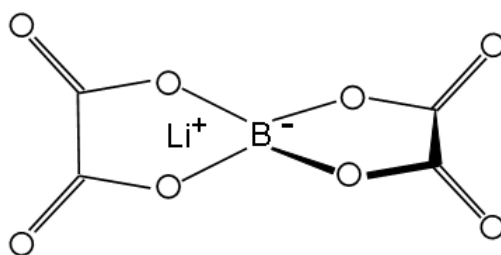


Figure 1.7: Chemical structure of lithium-bis-(oxalato) borate.

3. LiBOB possesses better thermal stability for above room temperature applications. It is stable up to 302 °C, where it decomposes instead of melting [53]. In contrast, pure  $\text{LiPF}_6$  is thermally stable up to 107 °C, dissociating into  $\text{LiF}$  and  $\text{PF}_5$  upon decomposition [54].
4. LiBOB-based electrolytes have also been shown to exhibit good conduction retention at elevated temperatures [53, 55].

It should be noted that the conductivity of  $\text{LiPF}_6$  is higher than LiBOB in non-aqueous solvents and that in low temperature applications, systems based on  $\text{LiPF}_6$  exhibit better capacity utilization [56]. However taking into account the focus of this

research on room and higher temperature performance of the solid electrolyte, LiBOB is preferred for its superior thermal and electrochemical performance. The safety limitations of  $\text{LiPF}_6$  also make a strong case for the selection of LiBOB.

## Chapter 2

### Nanostructured Block Copolymer Dry Electrolyte

#### 2.1 Introduction

In this study, the synthesis and characterization of a solid state polymer electrolyte with enhanced lithium transport based on a self-assembled block copolymer is described. In recent years, interest in polymeric batteries has increased dramatically. Current configurations have a liquid or gel electrolyte along with a separator between the anode and cathode. This leads to problems with electrolyte loss and decreased performance over time. The highly reactive nature of such electrolytes necessitates the use of protective enclosures, which add to the size and bulk of the battery. Polymer electrolytes are more compliant than conventional inorganic glass or ceramic electrolytes. Lightweight, shape conforming, polymer electrolyte-based battery systems could find widespread application as energy sources in miniature medical devices, such as pacemakers, wireless endoscopes, implantable pumps, treatment probes, and untethered robotic mobile manipulators.

The complex forming capability of poly (ethylene oxide) (PEO) with alkali metal salts, introduced by Fenton *et al.*[6] has been the starting point for an abundance of

published work on polymer electrolytes for use in batteries. A semi-crystalline polymer, PEO, has been a focal component in the design of numerous dry solvent-free electrolytes involving: blends [46], block copolymers [37, 41, 57, 58], branched networks [59], ceramic fillers [10, 19, 60, 61], room-temperature ionic liquids (RTILs) [26, 28, 30, 31], and specialized salts [62, 63], to name a few. It is important to carefully tailor the polymer electrolyte matrix to attain appreciable levels of conductivity in a solid-state medium. In this work, we have investigated a nanostructured thin-film battery electrolyte based on a diblock copolymer composed of a PEO block and a random copolymer of methyl methacrylate (MMA) and lithium salt of methacrylic acid (MAALi). The diblock copolymer [PEO-*b*-(PMMA-*ran*-PMAALi)] (Figure 2.1) with lithium bis(oxalate)borate, LiBC<sub>4</sub>O<sub>8</sub> (LiBOB) as the added lithium salt was used to create the dry, solid-state electrolyte films.

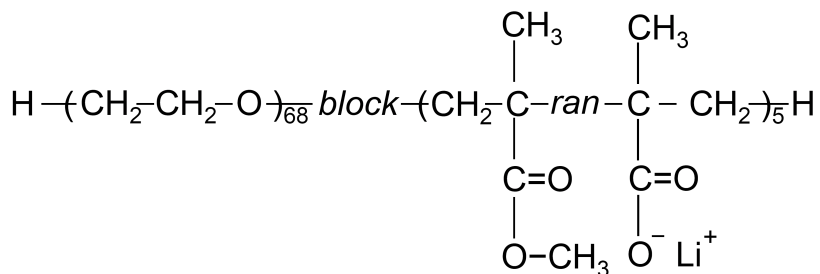


Figure 2.1: Chemical structure of self-assembled diblock copolymer

We selected a PEO-based diblock copolymer because of its ability to solvate alkali metal salts. The second block, which consists of a random copolymer of methyl methacrylate (MMA) and lithium salt of methacrylic acid (MAALi), was chosen for its ability to incorporate lithium ions within the microphase separated spherical



domains of the diblock copolymer [PEO-*b*-(PMMA-*ran*-PMAALi)] (Figure 1.4), creating a secondary lithium source. The primary focus of this work is the electrolyte performance at room temperature, and the experimental results display the role of polymer and salt selection toward this objective.

## 2.2 Experimental

The PEO-*b*-PMMA block copolymer with an average molecular weight 3000:500 of PEO to PMMA and polydispersity index of 1.16 was purchased from Polymer Source Inc. (Canada). LiBOB was obtained from Chemetall GmbH (Germany). All other chemicals and solvents were purchased from Aldrich and used as received.

Hydrolysis was carried out using lithium hydroxide monohydrate (LiOH·H<sub>2</sub>O) as the base. The block copolymer (PEO-*b*-PMMA) and LiOH·H<sub>2</sub>O were dissolved in a solvent mixture with a molar ratio of 2:1 between LiOH·H<sub>2</sub>O and the MMA units of the diblock copolymer. The solvent used was a 2:1 mixture of anhydrous 1,4-dioxane and anhydrous methanol. The hydrolysis process was carried out at 85°C for 20 h. As a result of the process, the PMMA block was hydrolyzed into a random copolymer of methyl methacrylate (MMA) and lithium salt of methacrylic acid (MAALi). This procedure was adapted from previous work reported by Mikes and Pecka [64]. After the hydrolysis step, the solvent was removed under vacuum using a Schlenk line setup with a liquid nitrogen solvent vapor trap. This dried diblock copolymer [PEO-*b*-(PMMA-*ran*-PMAALi)] was then stored in an Mbraun Labmaster 100 argon glove box for further use.

Solutions were prepared by adding varying concentrations of LiBOB salt to the diblock copolymer [PEO-*b*-(PMMA-*ran*-PMAALi)]. The solvent used was anhydrous tetrahydrofuran (THF), which was degassed using multiple cycles of a freeze-pump-thaw method. These polymer solutions were then cast into Petri dishes containing molds of fluorinated ethylene propylene coated aluminum sheets. The drying process extended over several days, resulting in 200–250  $\mu\text{m}$  thick films. Circular sections of the polymer electrolyte films were cut for conductivity measurements and mounted between two 316 stainless steel blocking electrodes. A poly (tetra fluoroethylene)-based O-ring was placed between the two electrodes to secure the sample thickness and surface area. The test cell assembly was sealed, protecting it from oxygen and humidity, before removal from the glove box for impedance analysis. The ionic conductivity ( $\sigma$ ) of the synthesized block copolymer electrolytes was determined from:

$$\sigma = \frac{t}{RA} \quad (2.1)$$

where  $t$ ,  $A$ , and  $R$  represent the thickness, surface area, and ionic resistance, respectively, of the electrolyte sample. Our assembled cell samples had a value of  $t/A$  of  $\sim 0.242 \text{ cm}^{-1}$ . The ionic resistance of the dry polymer electrolytes was obtained from impedance studies of the test cells using a Solartron 1287A/55B electrochemical system. The testing parameters were controlled by the associated CorrWare and ZPlot softwares, while the resulting data was analyzed by ZView.

The performance of the electrolyte was studied in the temperature range 0–70°C to characterize its temperature-dependent behavior. During the working life of a battery, it is often subjected to a wide spectrum of temperature changes. These

variations can be due to both external and internal factors. External sources are predominantly the surrounding environs which are region specific. Internal sources are mainly heat generation from electrochemical reactions taking place within. Also improper dissipation of energy from prolonged use often results in raising the internal temperature of the cell. Test cells were placed in a waterproof setup, immersed in a temperature-controlled water bath, and allowed 3–4 hours to equilibrate at every temperature stage before data collection.

Differential scanning calorimetry (DSC) measurements were performed using a TA Instruments Q100 calorimeter. Samples (~10 to 14 mg) of PEO and electrolyte films of diblock copolymer [PEO-*b*-(PMMA-*ran*-PMAALi)] with added LiBOB salt were sealed in hermetic aluminum pans inside the argon-filled glove box. The PEO homopolymer samples studied were of molecular weights 3.5 k, similar to that of the block copolymer. The measurements were carried out under nitrogen flow at a heating rate of 2.00°C/min and modulation of  $\pm 1.27^\circ\text{C}$  every 60 s, in the temperature range 40–120°C. Glass transition temperature ( $T_g$ ) studies were carried out by melting the samples sealed within the hermetic aluminum pans at 130°C followed by quenching them in liquid nitrogen. The measurements were carried out under nitrogen flow at a heating rate of 5.00°C/min.

0.1% solutions of the diblock copolymer [PEO-*b*-(PMMA-*ran*-PMAALi)] were prepared in THF and cast on transmission electron microscopy (TEM) grids. The grids were placed in a THF saturated dessicator to prolong the casting over a period of three days. No form of staining was used, with the image contrast coming from

lithium. TEM was performed with a JEOL 2100F field emission scanning electron microscope operating at 100 kV.

## 2.3 Results and Discussion

Polymer selection and design is a critical consideration in the development of a solvent-free conductive electrolyte matrix. PEO has been the material of choice because of its ability to form stable complexes with lithium salts and due to its possession of a higher conductivity than any other group of solvating polymers in the absence of organic solvents. In order to suppress PEO crystallinity and to enhance its conductivity, a low-molecular-weight block copolymer was chosen, consisting of PEO as the first block and a random copolymer of poly(methyl methacrylate) and lithium salt of poly(methacrylic acid) (PMMA-*ran*-PMAALi) as the second block. The nanostructured thin-film battery electrolyte does not contain major proportions of non-conducting blocks that are frequently used to enhance the mechanical properties of the material, but do not contribute in any way to the ion transport of the conducting segments. This was also the rationale behind the selection of PMMA ( $-\text{CO}_2\text{CH}_3$ ) in comparison to a diblock copolymer system containing lauryl ester ( $-\text{CO}_2\text{C}_{12}\text{H}_{25}$ ) groups [34]. The longer non-oxygenated side chain of the lauryl ester would work better as a means to provide more free volume if used in a gel electrolyte system. For a dry electrolyte system as the one in this work, the larger side chain, which contains only carbon and hydrogen atoms, would not aid in providing any additional conductive pathways for  $\text{Li}^+$  transport.

It has been shown that PEO undergoes complexation with carboxylic acid groups [47]. This complexation is driven by the proton-donating nature of poly(methacrylic acid) with PEO being a proton acceptor. The complexation of PEO chains is a concern, as it would restrict the segmental motion that drives ion transport. In tailoring the electrolyte matrix, a very small fraction of the polymer contains lithium salt of carboxylic acid groups. In addition, the presence of ions from the added lithium salt, acts as an effective screening barrier to subdue the complexation. The low carboxylic acid group content ensures that the block copolymer's microphase separation is not disrupted, as confirmed by the TEM (Figure 2.2). The images show lithium domains of approximate size 2 nm, templated by the diblock copolymer [PEO-*b*-(PMMA-*ran*-PMAALi)] morphology. Thus, the diblock copolymer acts as a polymer electrolyte, rather than a polyelectrolyte with ionomer-like ion cluster morphologies.

It is important to use the appropriate lithium salt concentration in order to obtain an optimum performance from the electrolyte. An ideal electrolyte is a medium that is rich in charge carriers and provides for a rapid transport of charge carriers through it. Too little salt results in poor conductivity. Too much salt not only severely affects the mechanical properties of the polymer, thus negating its inherent advantages, but also results in decreased conductivity [44]. We observed the same behavior with our LiBOB-doped diblock copolymer. Samples were prepared with different salt contents by varying the molar ratio between ethylene oxide (EO) units and LiBOB. Data were taken from a minimum of three different electrolyte test cells with polymers from different hydrolysis batches. A very similar trend in conductivity was observed across

the batches, although statistical analysis shows no significant statistical difference between electrolytes containing EO:LiBOB = 3:1 and 4:1 because of their close compositional proximity. Results show that the salt concentration was optimized at EO:LiBOB = 3:1 (Figure 2.3) for the best performance based on average conductivity obtained. This diblock copolymer electrolyte exhibited an average ionic conductivity value of  $1.26 \times 10^{-5} \text{ S cm}^{-1}$  at room temperature (21°C) as compared to  $2.6 \times 10^{-6} \text{ S cm}^{-1}$  measured for a PEO homopolymer of similar molecular weight (3.5 k) and molar composition of LiBOB. The value obtained for the diblock copolymer electrolyte is nearly two orders of magnitude greater than that shown by traditional high molecular weight PEO homopolymer electrolytes, in the absence of ceramic fillers and similar additives [11, 19].

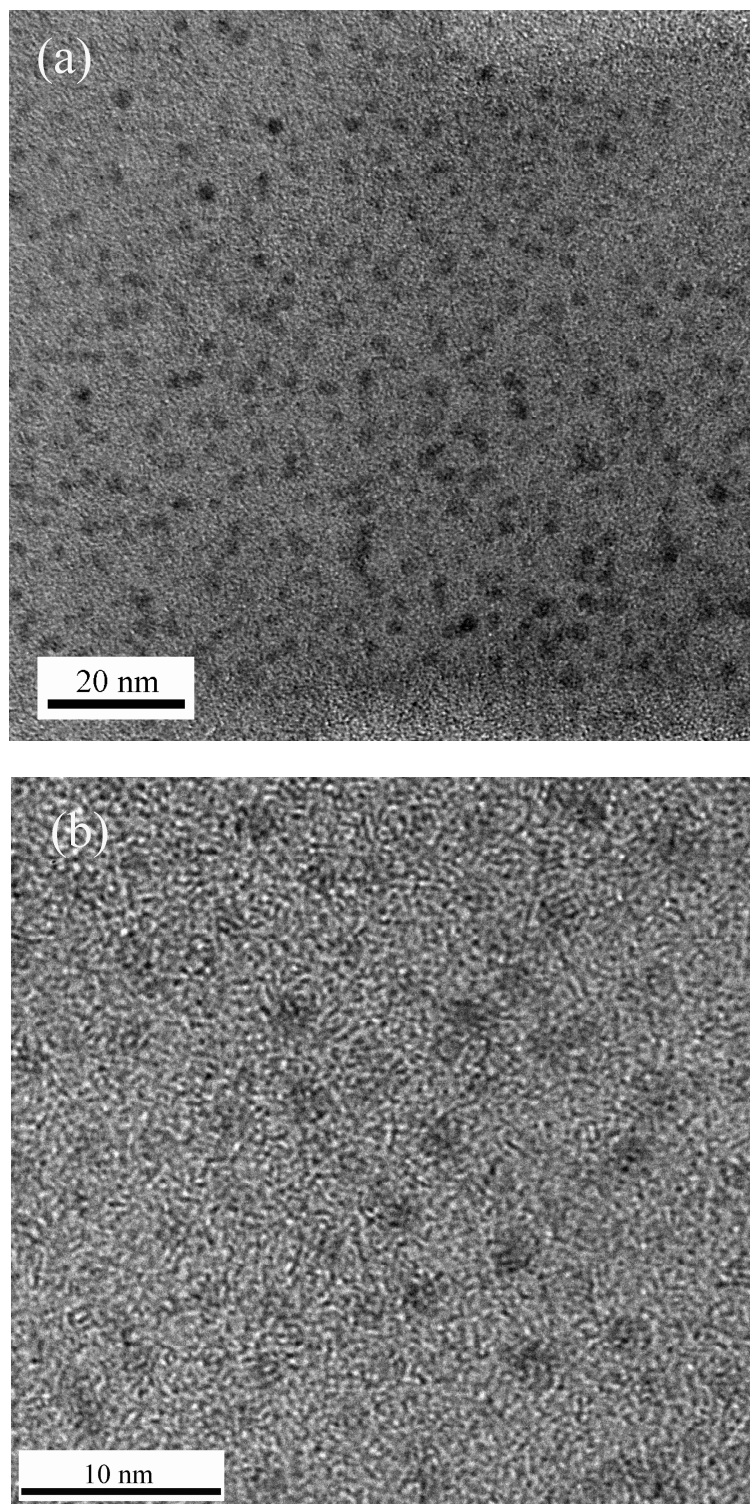


Figure 2.2: (a) TEM micrograph of PEO-*b*-(PMMA-*ran*-PMAALi) diblock copolymer and (b) higher magnification image showing lithium domains of  $\sim 2$  nm in size.

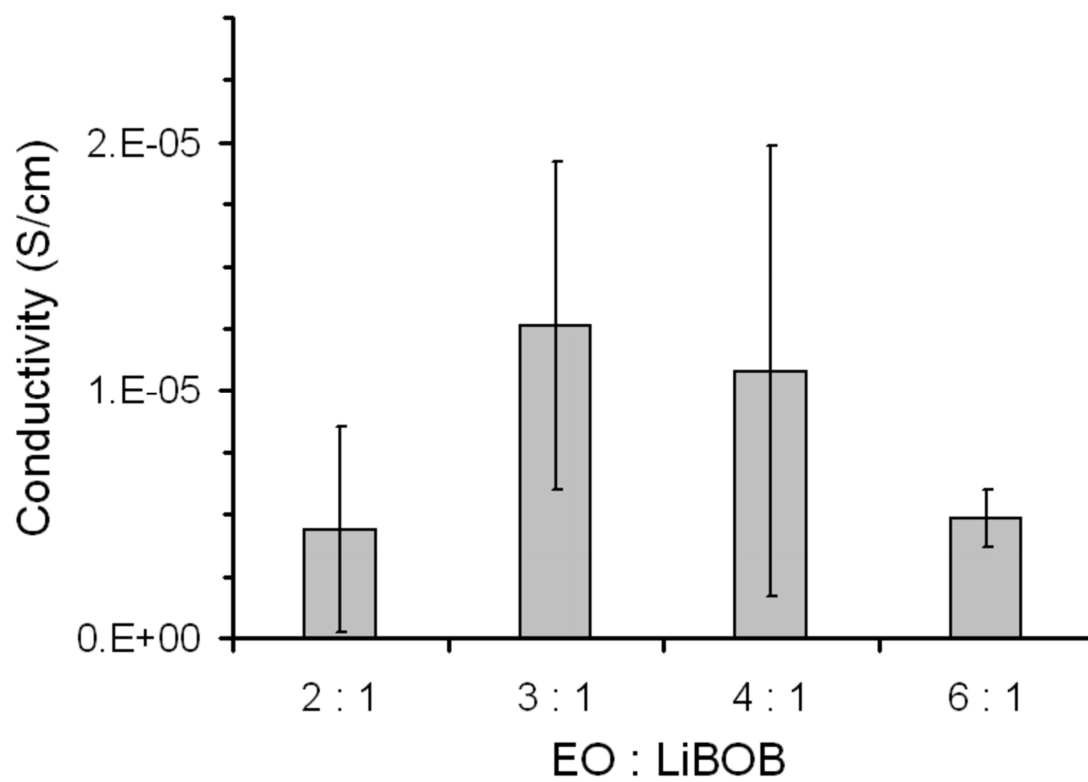


Figure 2.3: Salt optimization of PEO-b-(PMMA-ran-PMAALi) diblock copolymer at room temperature (21°C).



The electrolyte membranes showed the expected rise in conductivity with temperature (Figure 2.4). This is attributed to the increased segmental motion of the chains as PEO approaches its melting point. The optimized electrolyte sample achieved a conductivity of  $10^{-4} \text{ S cm}^{-1}$  as the sample temperature crossed  $40^{\circ}\text{C}$ . The temperature characterization was halted at  $70^{\circ}\text{C}$ , which is above the melting point of PEO. The physical appearance of the diblock copolymer electrolyte [PEO-*b*-(PMMA-*ran*-PMAALi)] also differed with varying salt content. Polymer electrolyte films with high salt loading (EO:LiBOB = 2:1) and low salt loading (EO:LiBOB  $\geq$  10:1) were brittle and opaque, whereas intermediate salt content films were flexible and translucent. The widely accepted view is that conduction of ions in polymer electrolytes occur almost predominantly in the amorphous phase due to the segmental motion of the polymer chain [44]. The flexibility of polymer films is related to the segmental motion of the chains and hence is a characteristic that can be associated with the conductivity potential of the electrolyte.

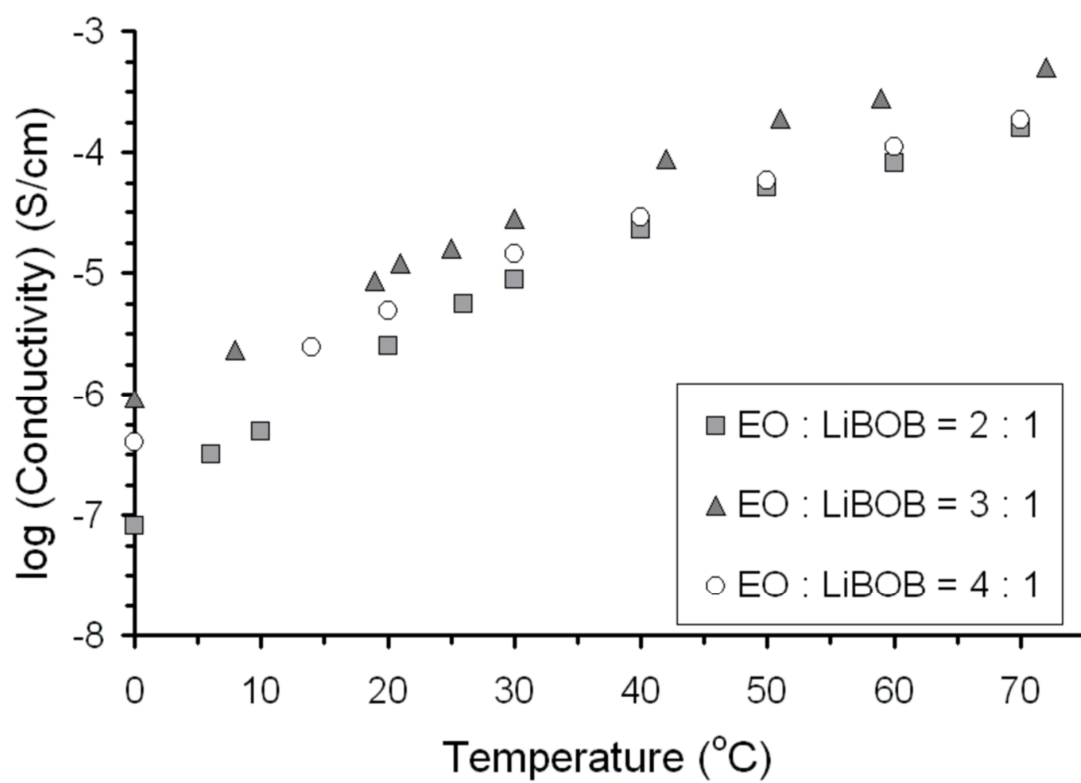


Figure 2.4: Temperature studies of PEO-b-(PMMA-ran-PMAALi) diblock copolymer in the temperature range 0–70°C.

DSC was performed to compare the initial crystallinity content in the polymer electrolytes. Scans of normalized heat flow (in watts per gram) against temperature (in °C) were obtained (Figure 2.5). The pure block copolymer showed reduced crystallinity as compared to PEO of similar molecular weight. The plasticizing effect of LiBOB salt aided in suppressing the crystallinity of the polymer electrolyte. These materials exhibited a suppressed melting over a broad temperature range. Crystalline domains were again shown to appear in low salt content (EO:LiBOB > 20:1) samples, as the plasticizing presence of LiBOB was reduced.  $T_g$  studies were carried out for the diblock copolymer electrolyte [PEO-*b*-(PMMA-*ran*-PMAALi)] with (EO:LiBOB = 3:1) and without salt content and PEO homopolymer of similar molecular weight (3.5 k). No significant shift in  $T_g$  was observed between the samples with PEO and PMMA-*ran*-PMAALi blocks showing glass transition temperatures at  $-25.9 \pm 1.5^\circ\text{C}$  and  $103.5 \pm 1.4^\circ\text{C}$ , respectively.

## 2.4 Conclusions

We have designed a self-assembled diblock copolymer electrolyte that exhibits higher ion transport at room temperature compared to traditional solid polymer electrolytes. TEM showed structured domains of lithium templated by the microphase separation of the block copolymer. The improved conductivity was attributed to reduction of crystallinity and introduction of secondary lithium domains in the conductive polymer matrix. The room-temperature conductivity was improved by an order of magnitude compared to similar molecular weight PEO homopolymers. The

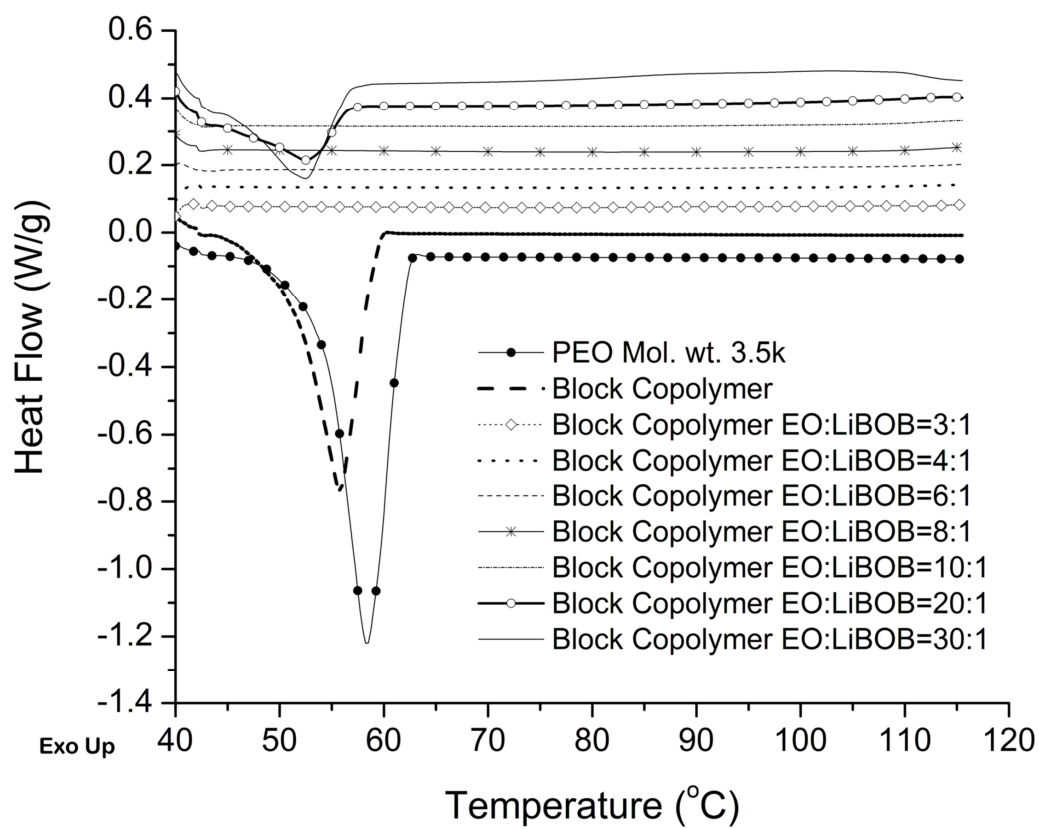


Figure 2.5: DSC scans of PEO-*b*-(PMMA-*ran*-PMAALi) diblock copolymer with different added compositions of LiBOB compared to native PEO.

diblock copolymer electrolyte [PEO-*b*-(PMMA-*ran*-PMAALi)] with added LiBOB salt (in the molar ratio ethylene oxide:LiBOB = 3:1) was used to form flexible translucent films which exhibited nearly two orders of magnitude greater conductivity than that shown by traditional high molecular weight PEO homopolymer electrolytes, in the absence of ceramic fillers and similar additives.

## Chapter 3

# Block Copolymer Solid Electrolyte with high Li-ion Transference Number

### 3.1 Introduction

The widespread use of high-energy density lithium-ion based batteries has been constrained by the safety concerns of its reactive components. Thus, the need to design, synthesize and optimize polymer structures for improved energy storage is of critical importance. Also, advances in lithium electrode chemistries have led to the development of batteries that are capable of delivering a high discharge potential ( $> 4.5\text{V}$ ) [65-67], driving the need for materials that are capable of withstanding such high voltage conditions. Unlike traditional liquid electrolytes, solid-state polymer electrolytes possess the high electrochemical stability window required for application in high voltage battery setups. Electrolyte membranes incorporating poly(ethylene oxide) (PEO) with a lithium salt have long been proposed as a viable candidate [6, 7, 10]. However, such materials have poor room temperature ionic-conductivity due to the semi-crystalline nature of PEO. In addition, PEO based electrolytes have the intrinsic disadvantage of possessing a low lithium-ion

transference number ( $T_{Li+}$ ), exhibiting a value between 0.2 and 0.5 [8, 68-70]. These polymer-lithium salt systems behave more like an anion transporting medium, resulting in a charge gradient across the medium. This increases the polarization across the polymer film, leading to loss of power drawn from the battery [71-73]. Studies done by Doyle *et al.* have shown that better performance is exhibited by polymer materials with  $T_{Li+} = 1.0$ , than those possessing an order of magnitude greater conductivity but a poorer  $T_{Li+}$  value [71]. Hence, the interest is to develop a conductive polymer with high ionic conductivity as well as high lithium ion transference.

Numerous electrolytes have been reported that possess single-ion transport properties and have a lithium ion transference numbers approaching 1.0. Single-ion polyelectrolyte systems have been successfully developed where the anion or the counter ion is effectively tethered to the polymer matrix [37, 74, 75]. Further, the use of various anion trappers has been shown to effectively boost the cation transference number [76-79]. These approaches, however, sometimes adversely affect the ionic conductivity of the electrolyte. The use of a lithium salt with a bulky counter ion remains one of the few viable options available to obtain moderately enhanced transference numbers without significantly sacrificing the ionic mobility of the electrolyte. Here we explore a polymer-lithium salt matrix containing a bulky anion and a partially charged polymer backbone.

We have previously discussed in Chapter 2, a diblock copolymer, which exhibits nearly two orders of magnitude greater ionic conductivity than that shown by traditional PEO homopolymer electrolytes, in the absence of ceramic fillers and

similar additives [80]. The polymer was composed of a larger PEO block and a smaller block consisting of a random copolymer of methyl methacrylate (MMA) and the lithium salt of methacrylic acid (MAALi). Transmission electron microscopy (TEM) showed the polymer microphase separate into spherical structures. Along with salt optimization studies of the diblock copolymer PEO-*b*-(PMMA-*ran*-PMAALi) with Lithium bis(oxalato)borate, LiBC<sub>4</sub>O<sub>8</sub> (LiBOB) salt, we also carried out thermal studies of the electrolyte material. The presence of the smaller second block and the plasticizing effect of the bulky lithium salt effectively reduced the crystallinity of the solid electrolyte resulting in its improved ion transporting behavior. In this study we discuss the electrochemical properties of the polymer electrolyte and report upon its unique transference behavior.

## 3.2 Experimental

The PEO-*b*-PMMA block copolymer (Molecular weight, 3000:500 for PEO:PMMA, polydispersity index of 1.16) was purchased from Polymer Source Inc. LiBOB was obtained from Chemetall GmbH and lithium foil was purchased from Aldrich. The diblock copolymer PEO-*b*-(PMMA-*ran*-PMAALi) was synthesized as described in our previous work [80]. The electrolyte films with different compositions of the diblock copolymer PEO-*b*-(PMMA-*ran*-PMAALi) and the LiBOB salt were solution cast onto Bytac<sup>®</sup> molds inside a Mbraun Labmaster 100 argon glove box. The resultant translucent polymer films (Figure 3.1) were dried for several days under an argon atmosphere, followed by at least 48 hours of drying under vacuum. For the



various tests, CR2032 coin cell enclosures were used to protect the moisture sensitive electrolyte materials.



Figure 3.1: Electrolyte membrane constructed from the diblock copolymer PEO-*b*-(PMMA-*ran*-PMAALi) and the LiBOB salt (picture taken shortly after removal from an Argon glovebox).

The electrolyte samples were mounted between two non-blocking lithium electrodes to determine the lithium-ion transference number of the solid electrolyte. The transference number ( $T_{Li+}$ ) was evaluated by d.c. potentiostatic measurements in conjunction with a.c. impedance spectroscopy according to the procedure described by Evans *et al.* [69]. Potentiostatic measurements were carried out to determine the initial ( $I_o$ ) and final steady state ( $I_s$ ) currents by applying a d.c. polarization voltage of

10 mV across the samples. Impedance spectroscopy (frequency range 1 MHz to 1Hz) was used to determine the film resistances before ( $R_o$ ) and after ( $R_s$ ) the potentiationstatic measurements. Transference numbers ( $T_{Li+}$ ) of the electrolyte samples were calculated from the following equation

$$T_{Li+} = \frac{I_s(\Delta V - I_o R_o)}{I_o(\Delta V - I_s R_s)} \quad (3.1)$$

where,  $\Delta V$  is the d.c. polarization voltage applied across the electrolyte film. A Solartron 1287A/1255B electrochemical testing platform was used to carry out the experiments. The testing parameters were controlled by the associated CorrWare and ZPlot softwares, while the resulting data was analyzed using CorrView and ZView. All elevated temperature measurements were carried out after equilibrating the cells in a Fisher Scientific Isotemp Model 281A vacuum oven.

Linear sweep voltammetry was used to determine the electrochemical stability window of the electrolyte material in a two electrode cell setup. A 316 stainless steel disc was used as the working electrode while a lithium disc served as the counter electrode. A voltage sweep was carried out on the material between 2.5 and 7 V at a constant scan rate of  $1 \text{ mV s}^{-1}$ .

Lithium stripping-plating experiments were performed to investigate the stability and reversibility behavior of the electrolyte material with the lithium metal electrode interface. The salt optimized electrolyte film was mounted between non-blocking lithium electrodes and a current flux of  $0.1 \text{ mA/cm}^2$  was applied on the film with the direction of the current being reversed every hour. Impedance spectroscopy was carried out at various intervals of the galvanostatic cycling.

### 3.3 Results and Discussion

The transference number of an ion is the fraction of the total current that is carried by the respective ion across a given medium. Different ions have dissimilar mobilities and hence may carry drastically different portions of the total current. After conductivity, in solid state materials, the transference number is significant particularly in secondary and rechargeable energy storage systems. The transference number is indicative of the polarity of the material and thus the number of cycles the cell can be put through. A large transference number can reduce concentration polarization of electrolytes during charge-discharge steps, and thus sustain the electrolyte's power density [71, 73].

Under a constant potential bias, if the final steady state and initial currents are given by ( $I_s$ ) and ( $I_o$ ), respectively, then the transference number can be very simply evaluated from  $T_{Li+} = I_s / I_o$ . This holds true for ideal electrolytes under a negligible polarization voltage. In real systems, however, a change in interfacial resistance occurs during potentiostatic studies. We used the methodology suggested by Evans *et al.* [69], to take into account the increase in the electrolyte-electrode interfacial resistance as the potentiostatic current decay is measured. We studied electrolyte samples having the molar composition EO:LiBOB = 3:1 and 4:1 based on the salt optimization, previously reported [80]. Figure 3.2(a) shows the impedance profile of two samples before and after the potentiostatic tests. The expected increase in interfacial resistance can be clearly observed between the initial and final impedance

responses of the sample with the 4:1 molar composition. The current-time profiles of the same two samples under a constant d.c. potential bias of 10 mV is shown in Figure 3.2(b). Using equation (3.1), average transference number values of  $\approx 0.89$  were obtained for the salt-optimized polymer electrolyte materials at room temperatures (21–23°C). Table 3.1 lists the transference numbers calculated for the two compositions with and without the interfacial resistance correction. At 60°C, average transference number values of  $\approx 0.75$  were obtained for electrolyte material having the molar composition EO:LiBOB = 4:1.

Table 3.1: Lithium-ion transference number data of electrolyte films made from diblock copolymer PEO-*b*-(PMMA-*ran*-PMAALi) and the LiBOB salt.  
Li/Electrolyte/Li cell under a constant d.c. potential bias of 10 mV.

Molar Composition (EO : LiBOB)	Temperature (°C)	$T_{Li^+} = \frac{I_s (\Delta V - I_o R_o)}{I_o (\Delta V - I_s R_s)}$	$T_{Li^+} = \frac{I_s}{I_o}$
3 : 1	21–23	$0.89 \pm 0.07$	$0.90 \pm 0.07$
4 : 1	21–23	$0.83 \pm 0.08$	$0.88 \pm 0.05$
3 : 1	60	$0.78 \pm 0.11$	$0.79 \pm 0.05$
4 : 1	60	$0.75 \pm 0.05$	$0.78 \pm 0.03$

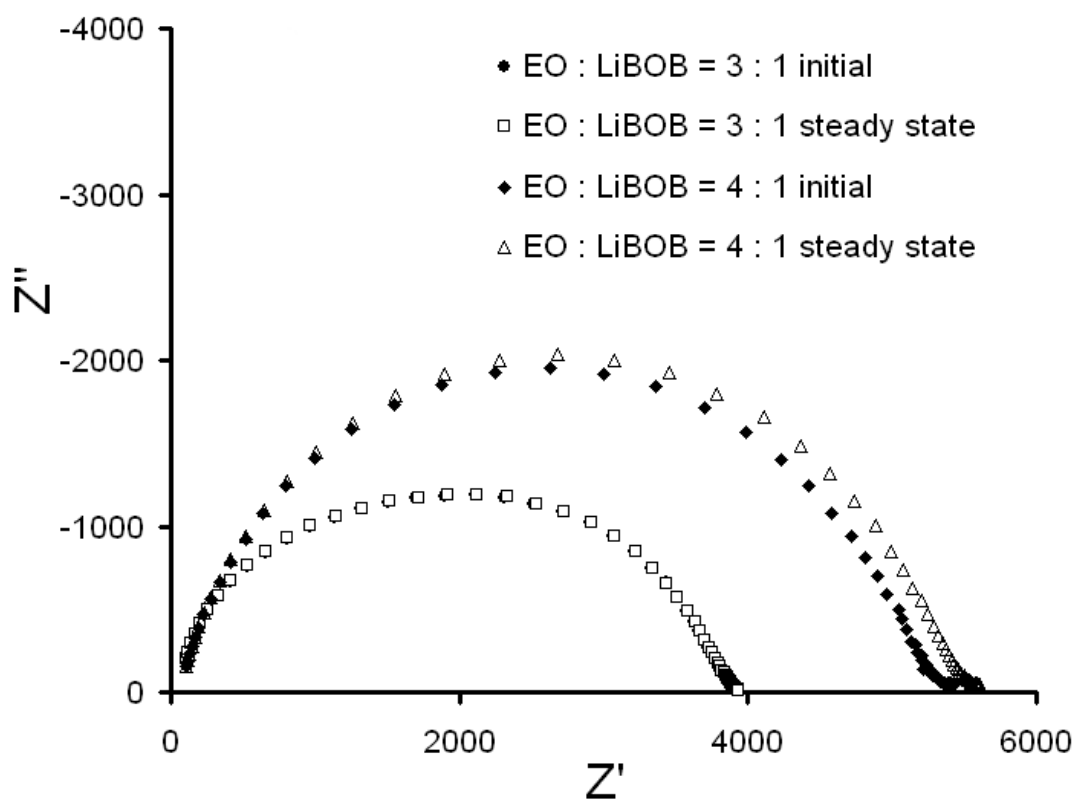


Figure 3.2 (a): Impedance scans from two electrolyte samples taken before and after potentiostatic measurements at room temperature (21–23°C).

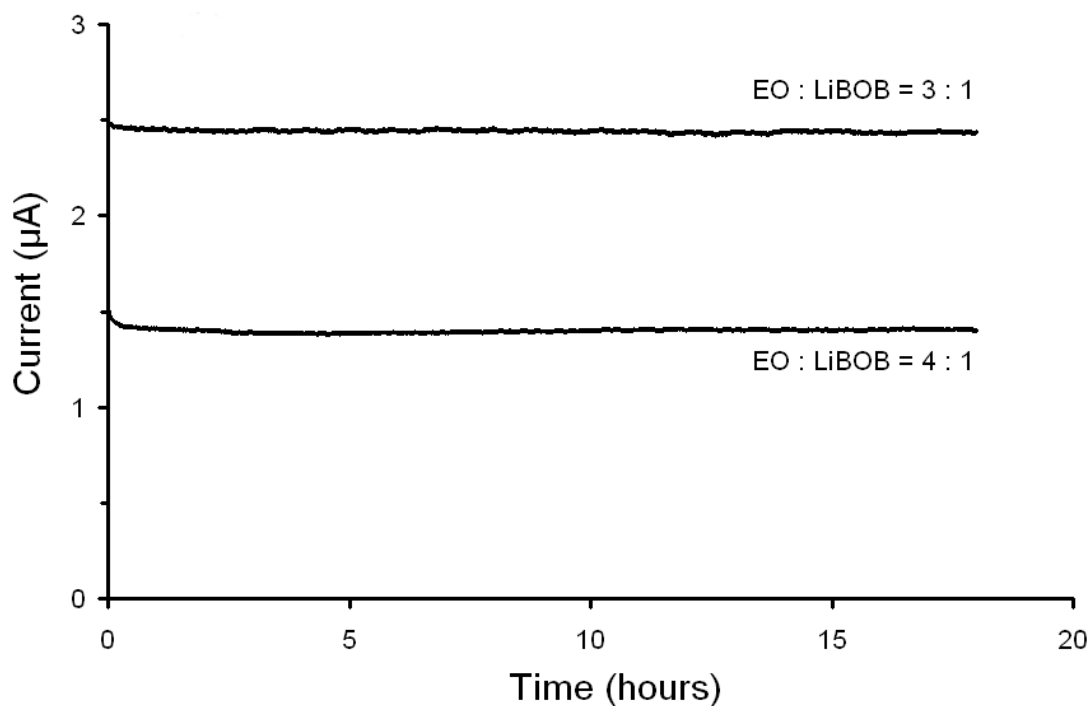


Figure 3.2 (b): Current vs. time profile of the polymer films, obtained at room temperature (21–23°C), under a 10 mV d.c. bias.

The large molecular size of the bis-oxalato borate (BOB) anion was expected to have an effect on the transference number of the lithium ion. However, obtaining such a high transference value in the absence of any anion trapper additives was not anticipated. Previous work done by Appetecchi *et al.* on LiBOB and PEO of higher molecular weight ( $1 \times 10^5$ ) reported transference numbers ranging from 0.25 to 0.30 at elevated temperatures (60 °C and 100 °C) [68]. In our system, we suspect that interactions between the bis-oxalato borate anion and the secondary part (PMMA-*ran*-PMAALi) of the block copolymer may be the determining reason behind this behavior. The exact mechanism behind the enhanced transference performance is not fully understood and merits further investigation. Determination of the exact basis

behind achieving a high cation ( $\text{Li}^+$ ) transference number while avoiding the use of anion trappers and tethered polyanions will greatly aid the design of future electrolyte matrices.

Considering the high voltage range in which most lithium based electrode chemistries operate, the electrochemical stability of the electrolyte material and its interfacial interactions with the electrodes have a significant bearing on the long term performance of the battery. In order for the energy storage/conversion cells to effectively perform, it is pertinent that the electrolyte materials employed also have a wide electrochemical stability window well beyond the operating potential of the electrodes. Linear sweep voltammetry experiments have shown that the salt-optimized electrolyte films exhibit an electrochemical stability greater than 5.0 Volts (Figure 3.3(a)) at room temperature (21–23°C), making them excellent candidates for high potential lithium based battery cells. We further tested the electrolyte material at a higher temperature (60°C) for comparison. Once again the polymer electrolyte showed very good electrochemical stability (Figure 3.3(b)) with material degradation taking place only above 5.0 Volts.

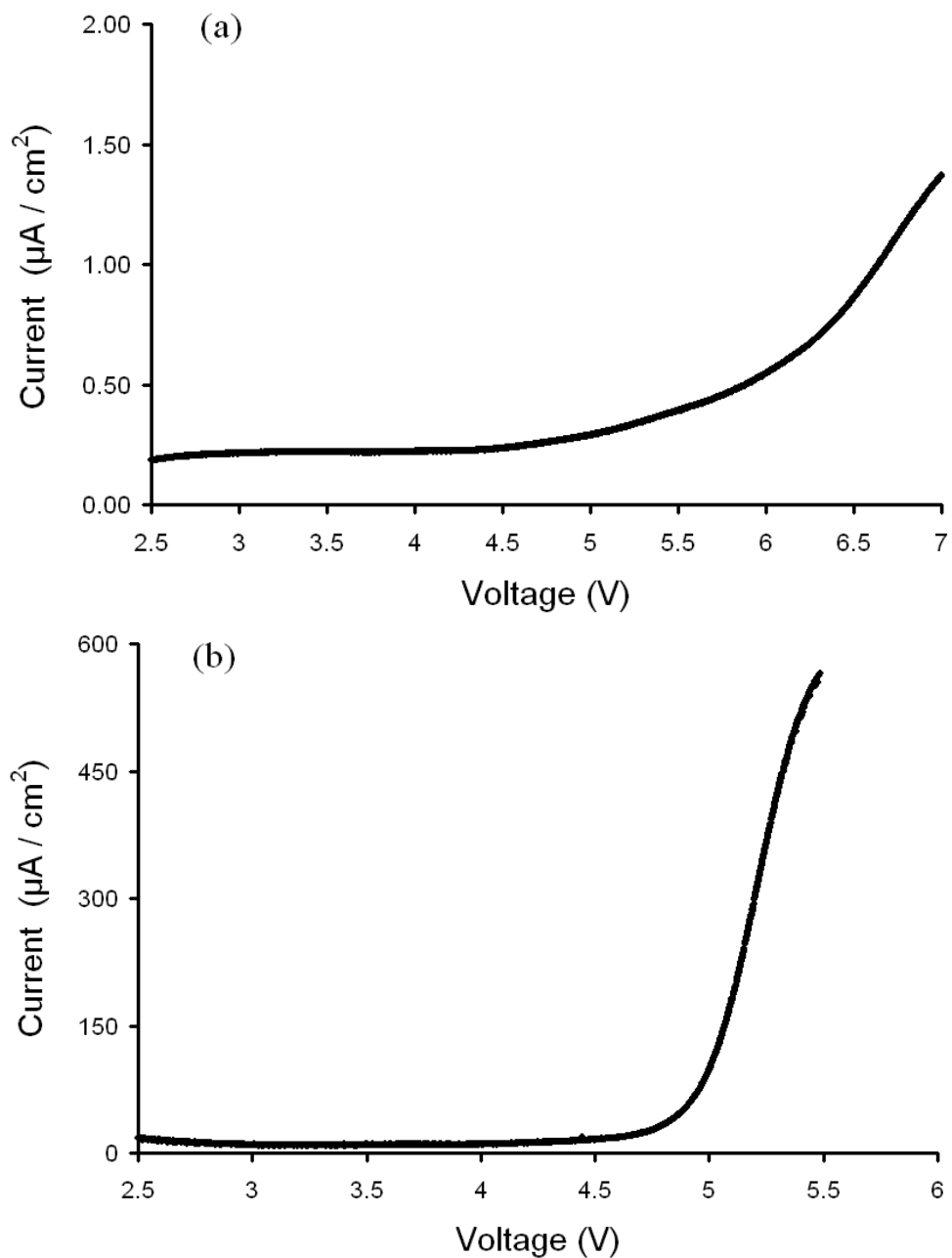


Figure 3.3: Linear sweep voltammetry of electrolyte films made from the diblock copolymer PEO-*b*-(PMMA-*ran*-PMAALi) and LiBOB (molar composition EO:LiBOB = 3:1) at (a) room temperature (21–23°C) and (b) 60°C. A scan rate of 1  $\text{mV s}^{-1}$  was used with a stainless steel working electrode and a lithium metal counter electrode.



The stability of the solid state polymer electrolyte material towards the lithium anode was evaluated by monitoring the change in overvoltage during the lithium plating/stripping tests at room temperature (21–23°C). For this study, the electrolyte film (molar composition EO:LiBOB = 3:1) was sandwiched between symmetrical lithium electrodes; a current flux of  $0.1\text{mA}/\text{cm}^2$  was run through the electrolyte material for an hour before reversing the polarity. Galvanostatic cycling was performed for 100 cycles. At different cycle intervals, impedance scans were carried out to compare the interfacial resistances evaluated from the d.c. and a.c. methods. Typical voltage profiles during the Li plating/stripping cycling are shown in Figure 3.4. The overvoltage profile and impedance responses at different cycles were used to evaluate stability of polymer electrolyte during the lithium plating/stripping cycles. The overvoltage profile (Figure 3.5) of the material shows a voltage increase in the initial cycles (every cycle representing 2 hours on the overvoltage-time plot). The subsequent overvoltage trend over the remaining cycles shows good electrolyte material stability to the lithium electrode. To analyze the mechanism for voltage increase, impedance was measured at different cycles as shown in Figure 3.6. Total resistance values were determined from the impedance responses at low frequency and were compared to those determined from the galvanostatic lithium plating/stripping cycling, showing good agreement (Figure 3.7(a)). The galvanostatic resistance was obtained by dividing the average cycle overvoltage by the current applied. The impedance plots were fitted using an equivalent circuit consisting of a resistance element ( $R_E$ ) in series with two R/C elements (Figure 3.7(b) *insert*).  $R_E$  represents the conductive resistance of the electrolyte;  $R_{SEI}$  and  $R_{CT}$  represent the high

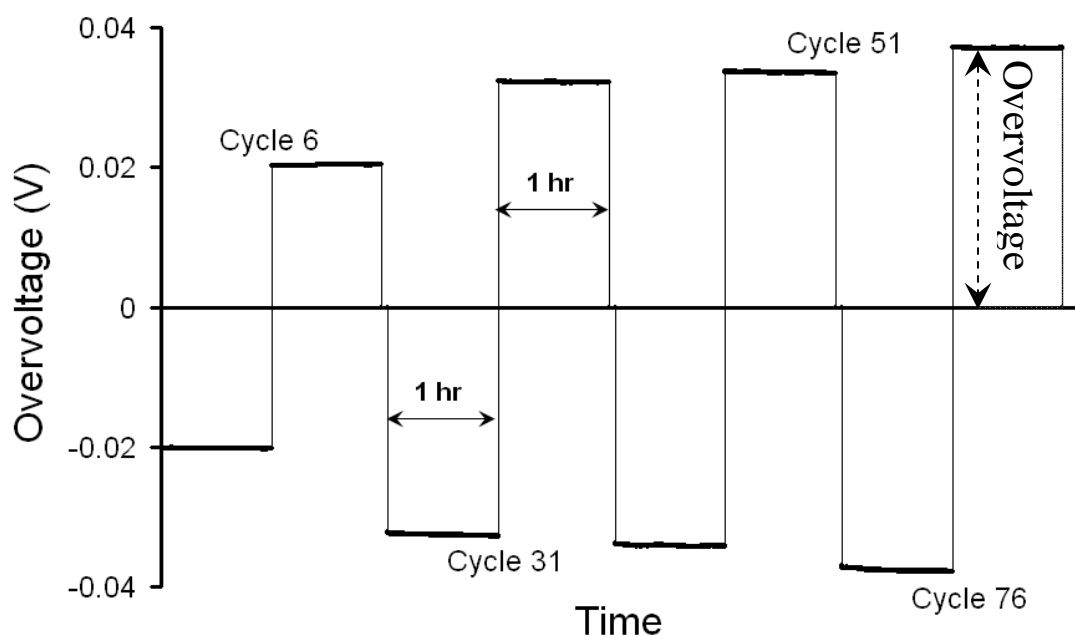


Figure 3.4: Overvoltage profiles of certain cycles during the Li plating/stripping tests of Li/ PEO-*b*-(PMMA-*ran*-PMAALi) + LiBOB (EO:LiBOB = 3:1)/Li cell at room temperature (21–23°C).

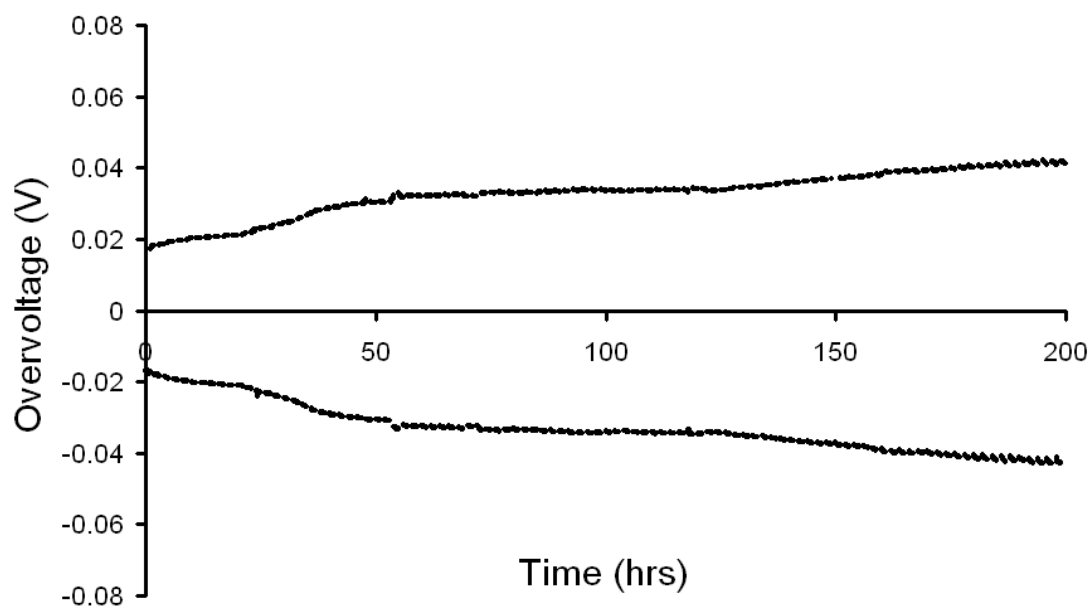


Figure 3.5: Overvoltage vs. time profile of Li/ PEO-*b*-(PMMA-*ran*-PMAALi) + LiBOB (EO:LiBOB = 3:1)/Li cell at room temperature (21–23°C). A current flux of 0.1mA/cm<sup>2</sup> was applied on the film with the polarity being reversed every hour.

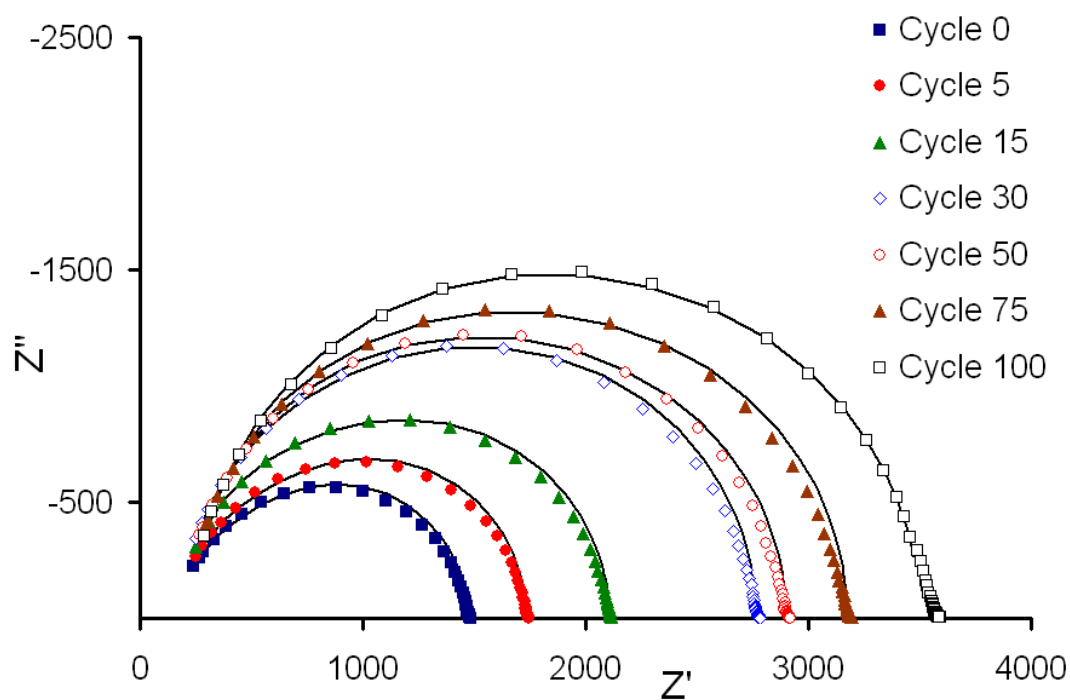


Figure 3.6: Impedance responses of the Li/ PEO-*b*-(PMMA-*ran*-PMAALi) + LiBOB (EO:LiBOB = 3:1)/Li cell at room temperature (21–23°C) obtained at the end of different cycles. The solid lines represent the corresponding data fitting of the impedance scans.

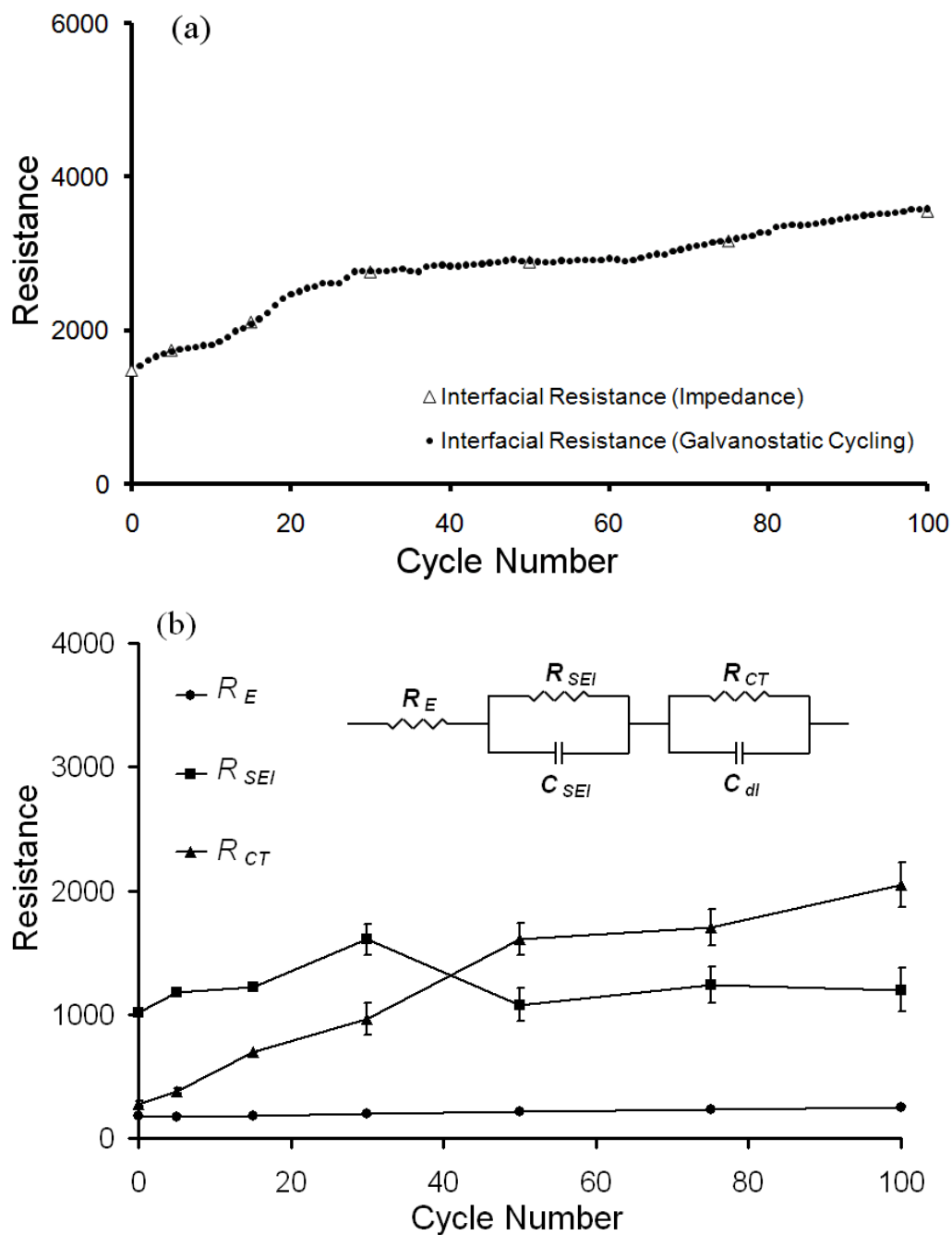


Figure 3.7: Overvoltage studies of Li/ PEO-*b*-(PMMA-*ran*-PMAALi) + LiBOB (EO:LiBOB = 3:1)/Li cell at room temperature (21–23°C): (a) interfacial resistance profile of the cell from impedance scans and galvanostatic cycling, (b) resistance values obtained from data fitting of the impedance profiles to an equivalent circuit (see *insert*).

frequency interfacial resistance (formation of a solid-electrolyte interface (SEI) passivation layer) and charge transfer resistance.  $C_{SEI}$  and  $C_{dl}$  are the corresponding interfacial capacitances due to the SEI film and double layer. As shown in Figure 3.7(b), the ion conductive behavior of the polymer membrane is stable during the Li plating/stripping cycles. LiBOB-based electrolytes have already been shown to exhibit good conduction retention even at elevated temperatures [53, 81, 82]. The high frequency interfacial resistance ( $R_{SEI}$ ) does not show much change over the number of cycles and is attributed to the formation of a stable passivation layer. The charge transfer resistance ( $R_{CT}$ ) shows an initial rise and then stabilizes. In addition to the profile of the overall interfacial resistance, the individual trends of  $R_E$ ,  $R_{SEI}$  and  $R_{CT}$  validate good electrolyte stability towards the lithium metal.

### 3.4 Conclusions

The tailored solid self-assembled diblock copolymer electrolyte matrix exhibits an exceptionally high lithium-ion transference number of 0.9, compared to a value between 0.2 and 0.5, shown by typical polymer-lithium salt materials. Even at elevated temperatures of 60°C average transference number values  $\geq 0.75$  is observed. The results reported here demonstrate the effects that the use of a bulky anion lithium salt and a partially charged polymer backbone have on the transference ( $T_{Li+}$ ) behavior of the solid-state polymer electrolyte. The electrolyte membrane also has a wide electrochemical stability window and excellent interfacial behavior with the lithium metal electrode. The synergy of these properties make electrolyte

membranes composed of the diblock copolymer PEO-*b*-(PMMA-*ran*-PMAALi) and LiBOB salt viable candidates for flexible lithium ion based energy conversion/storage devices.

## Chapter 4

### Conclusions and Future Work

The tendency of PEO to act as a solid-state solvent for alkali salts has been the cornerstone for all the research into its development as a solvent-free electrolyte for battery applications. The semi-crystalline property of PEO, however, has been the constraining factor behind the realization of acceptable levels of room temperature ionic conductivity. In this work, we have shown that designing the electrolyte matrix to utilize the benefits of block copolymers can have distinct improvements on the performance of the electrolyte. It is hoped that the suggestions offered in this section will aid in furthering the initiatives being made in the development of flexible lithium-ion energy storage/conversion materials.

In this work, we have developed spherically microphase separated block copolymers of very low molecular weight (3.5 k). Experiments with similar molecular weight PEO homopolymer and salt loading often resulted in materials with extremely low mechanical integrity. The diblock copolymer PEO-*b*-(PMMA-*ran*-PMAALi) and LiBOB salt not only showed better mechanical integrity as a polymer film; it was also capable of much higher levels of salt loading. PEO based electrolytes of high molecular weight have been researched extensively with much lower levels of



salt loading (molar compositions of ethylene oxide:lithium salt from 10:1 to 20:1) based on system specific salt compositional optimizations. In comparison we were able to obtain a performance optimized molar composition of EO:LiBOB = 3:1. The presence of an ordered microphase separated second block was expected to reduce the free volume available for the PEO chains to crystallize, thus increasing the amorphous content of the material. This allowed for further salt loading (LiBOB) which acted as a plasticizer and resulted in additionally suppressing the crystallinity of the material (Figure 2.5). While all this aided in boosting the ionic conductivity of the material, it comes with certain limitations.

The use of a low molecular block copolymer makes it difficult to incorporate supplementary additives to the electrolyte material without severely compromising its mechanical integrity. Addition of ceramic fillers, which have been shown to improve the electrolyte-lithium electrode interfacial properties, becomes challenging under these circumstances. Higher molecular weight spherically microphase separated block copolymers of PEO-*b*-(PMMA-*ran*-PMAALi) could provide viable candidates to overcoming these limitations.

The developed block copolymer shows the expected high electrochemical stability window. It also shows a surprisingly high transference number. It is hypothesized that complexation of the salt anion (BOB<sup>-</sup>) with the secondary block (PMMA-*ran*-PMAALi) may be the reason behind this phenomenon, but the mechanism is not explicitly understood. As emphasized in the work by Doyle *et al.*, transference number ( $T_{Li+}$ ) behavior of the electrolyte material also has a significant impact on the performance of a battery [71]. Determination of the mechanism behind

achieving a high cation ( $\text{Li}^+$ ) transference number while avoiding the use of anion trappers and tethered polyanions (which often result in a lower ionic conductivity) will greatly aid the design of future electrolyte matrices. Investigating similar PEO based block copolymer matrices containing different percentages of PMAALi and block copolymers of PEO-*b*-PMAALi could aid in a better understanding of the transference number mechanism.

The physical characteristics of the diblock copolymer electrolyte [PEO-*b*-(PMMA-*ran*-PMAALi)] also differed with varying salt content. Polymer electrolyte films with high salt loading (EO:LiBOB = 2:1) and low salt loading (EO:LiBOB  $\geq$  10:1) were brittle and opaque, whereas intermediate salt content films were flexible and translucent in nature (Figure 3.1). Upon removal from the argon glovebox and exposure to normal atmospheric conditions, the polymer film shows a distinct physical transition due to the absorption of moisture by the LiBOB salt. With time, the electrolyte membrane turns opaque due to the decomposition of LiBOB and crumbles (Figure 4.1). This is in stark contrast to the formation of hydrofluoric acid (HF) resulting from the hydrolysis of  $\text{LiPF}_6$ .

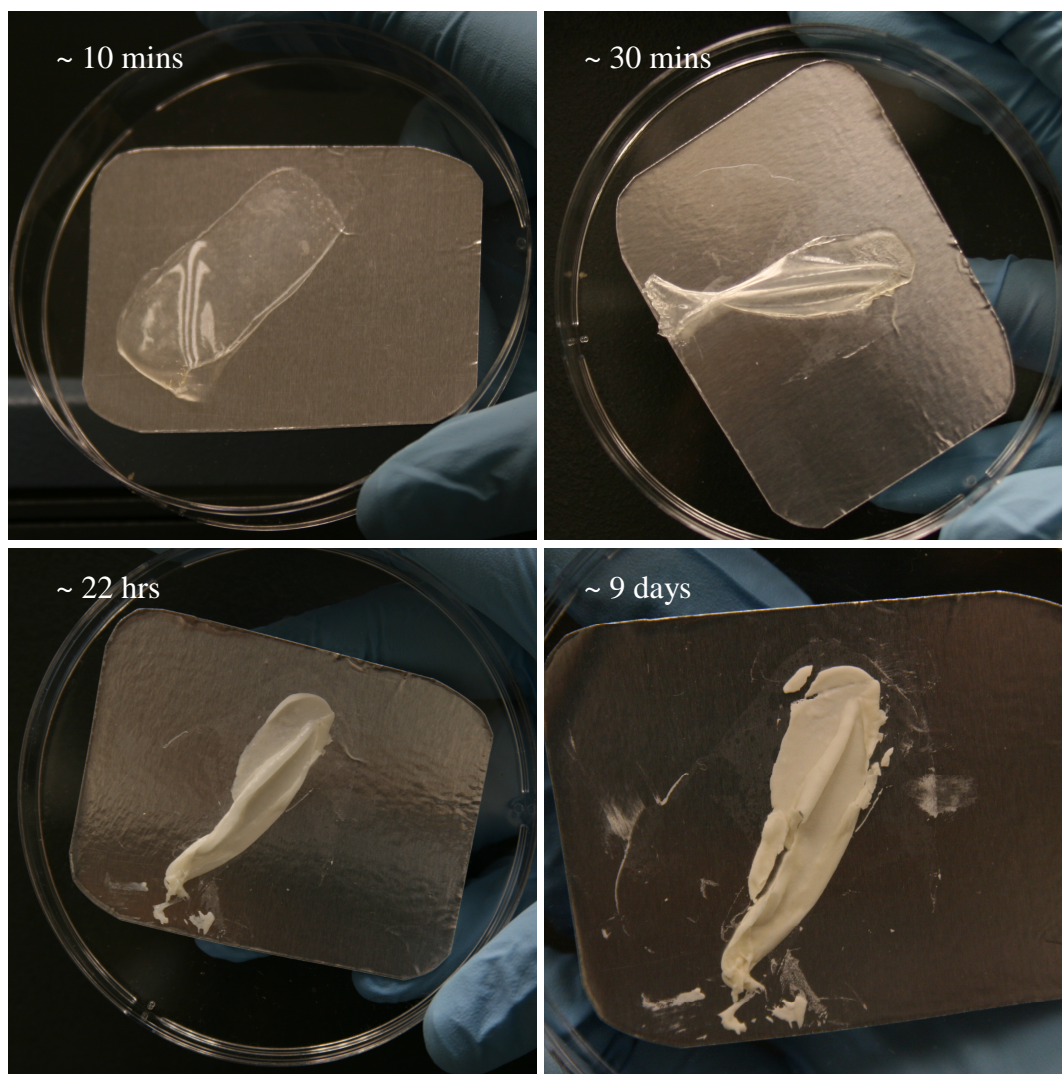


Figure 4.1: Environmental degradation of an electrolyte membrane constructed from the diblock copolymer PEO-*b*-(PMMA-*ran*-PMAALi) and the LiBOB salt upon exposure to normal atmospheric conditions.

The incorporation of room temperature ionic liquids (RTILs) to improve the ionic conductivity of the polymer matrix has been garnering a lot of interest lately. The use of RTILs consisting of N-alkyl-N-methylpyrrolidinium cations and bis(trifluoromethanesulfonyl) imide anions (PYR<sub>1R</sub>TFSI) in PEO, have been shown to

achieve room temperature conductivities greater than  $10^{-4} \text{ S cm}^{-1}$  [29-33]. These RTILs also possess additional desirable properties like negligible vapor pressure and low room temperature viscosity. These advantages, however, are offset by poor interfacial stability towards lithium metal, low transference numbers and inadequate electrochemical stability window. Research into the development of new ionic liquid chemistries is required to counter the conductivity limitations of current solid-state polymer electrolytes. Similar to pyrrolidine, saturated heterocyclic analogs of sulfur (alkylthiolanium) and phosphorous (alkylphospholanes) may serve as possible cation candidates for future ionic liquid chemistries.

## BIBLIOGRAPHY

- [1] Loeb, G. E.; Peck, R. A.; Moore, W. H.; Hood, K. "BION (TM) system for distributed neural prosthetic interfaces". *Medical Engineering & Physics* **2001**, 23, (1), 9-18.
- [2] Iddan, G.; Meron, G.; Glukhovsky, A.; Swain, P. "Wireless capsule endoscopy". *Nature* **2000**, 405, (6785), 417-417.
- [3] Glukhovsky, A. "Wireless capsule endoscopy". *Sensor Review* **2003**, 23, (2), 128-133.
- [4] Goodenough, J. B. "Fast Ionic-Conduction in Solids". *Proceedings of the Royal Society of London Series a-Mathematical Physical and Engineering Sciences* **1984**, 393, (1805), 215-234.
- [5] Bruce, P. G., Electrical Measurements on Polymer Electrolytes. In *Polymer Electrolyte Reviews-I*, MacCallum, J. R.; Vincent, C. A., Eds. Elsevier: London, 1987; pp 237-274.
- [6] Fenton, D. E.; Parker, J. M.; Wright, P. V. "Complexes of Alkali-Metal Ions with Poly(Ethylene Oxide)". *Polymer* **1973**, 14, (11), 589-589.

- [7] Armand, M.; Chabagno, J. M.; Duclot, M. J. In *Poly-Ethers as Solid Electrolytes*, Fast Ion Transport in Solids, Electrodes and Electrolytes, Lake Geneva, Wisconsin, U.S.A., 1979; Vashishita, P.; Mundy, J. N.; Shenoy, G. K., Eds. Elsevier: Lake Geneva, Wisconsin, U.S.A., 1979; pp 131-136.
- [8] Capuano, F.; Croce, F.; Scrosati, B. "Composite Polymer Electrolytes". *Journal of the Electrochemical Society* **1991**, 138, (7), 1918-1922.
- [9] Croce, F.; Gerace, F.; Dautzemberg, G.; Passerini, S.; Appetecchi, G. B.; Scrosati, B. "Synthesis and Characterization of Highly Conducting Gel Electrolytes". *Electrochimica Acta* **1994**, 39, (14), 2187-2194.
- [10] Croce, F.; Appetecchi, G. B.; Persi, L.; Scrosati, B. "Nanocomposite polymer electrolytes for lithium batteries". *Nature* **1998**, 394, (6692), 456-458.
- [11] Scrosati, B.; Croce, F.; Persi, L. "Impedance spectroscopy study of PEG-based nanocomposite polymer electrolytes". *Journal of the Electrochemical Society* **2000**, 147, (5), 1718-1721.
- [12] Appetecchi, G. B.; Croce, F.; Scrosati, B. "Kinetics and Stability of the Lithium Electrode in Poly(Methylmethacrylate)-Based Gel Electrolytes". *Electrochimica Acta* **1995**, 40, (8), 991-997.
- [13] Osaka, T.; Momma, T.; Ito, H.; Scrosati, B. "Performances of lithium gel electrolyte polypyrrole secondary batteries". *Journal of Power Sources* **1997**, 68, (2), 392-396.

- [14] Ostrovskii, D.; Brodin, A.; Torell, L. M.; Appetecchi, G. B.; Scrosati, B. “Molecular and ionic interactions in poly(acrylonitrile)- and poly(methylmethacrylate)-based gel electrolytes”. *Journal of Chemical Physics* **1998**, 109, (17), 7618-7624.
- [15] Appetecchi, G. B.; Croce, F.; De Paolis, A.; Scrosati, B. “A poly(vinylidene fluoride)-based gel electrolyte membrane for lithium batteries”. *Journal of Electroanalytical Chemistry* **1999**, 463, (2), 248-252.
- [16] Appetecchi, G. B.; Croce, F.; Romagnoli, P.; Scrosati, B.; Heider, U.; Oesten, R. “High-performance gel-type lithium electrolyte membranes”. *Electrochemistry Communications* **1999**, 1, (2), 83-86.
- [17] Appetecchi, G. B.; Romagnoli, P.; Scrosati, B. “Composite gel membranes: a new class of improved polymer electrolytes for lithium batteries”. *Electrochemistry Communications* **2001**, 3, (6), 281-284.
- [18] Appetecchi, G. B.; Croce, F.; Hassoun, J.; Scrosati, B.; Salomon, M.; Cassel, F. “Hot-pressed, dry, composite, PEO-based electrolyte membranes I. Ionic conductivity characterization”. *Journal of Power Sources* **2003**, 114, (1), 105-112.
- [19] Croce, F.; Persi, L.; Scrosati, B.; Serraino-Fiory, F.; Plichta, E.; Hendrickson, M. A. “Role of the ceramic fillers in enhancing the transport properties of composite polymer electrolytes”. *Electrochimica Acta* **2001**, 46, (16), 2457-2461.

- [20] Appetecchi, G. B.; Croce, F.; Dautzenberg, G.; Mastragostino, M.; Ronci, F.; Scrosati, B.; Soavi, F.; Zanelli, A.; Alessandrini, F.; Prosini, P. P. "Composite polymer electrolytes with improved lithium metal electrode interfacial properties - I. Electrochemical properties of dry PEO-LiX systems". *Journal of the Electrochemical Society* **1998**, 145, (12), 4126-4132.
- [21] Appetecchi, G. B.; Croce, F.; Mastragostino, M.; Scrosati, B.; Soavi, F.; Zanelli, A. "Composite polymer electrolytes with improved lithium metal electrode interfacial properties - II. Application in rechargeable batteries". *Journal of the Electrochemical Society* **1998**, 145, (12), 4133-4135.
- [22] Gadjourova, Z.; Andreev, Y. G.; Tunstall, D. P.; Bruce, P. G. "Ionic conductivity in crystalline polymer electrolytes". *Nature* **2001**, 412, (6846), 520-523.
- [23] Gadjourova, Z.; Marero, D. M.; Andersen, K. H.; Andreev, Y. G.; Bruce, P. G. "Structures of the polymer electrolyte complexes PEO6 : LiXF6 (X = P, Sb), determined from neutron powder diffraction data". *Chemistry of Materials* **2001**, 13, (4), 1282-1285.
- [24] Christie, A. M.; Lilley, S. J.; Staunton, E.; Andreev, Y. G.; Bruce, P. G. "Increasing the conductivity of crystalline polymer electrolytes". *Nature* **2005**, 433, (7021), 50-53.



- [25] Henderson, W. A.; Passerini, S. "Ionic conductivity in crystalline-amorphous polymer electrolytes - P(EO)(6): LiX phases". *Electrochemistry Communications* **2003**, 5, (7), 575-578.
- [26] Seki, S.; Kobayashi, Y.; Miyashiro, H.; Ohno, Y.; Usami, A.; Mita, Y.; Kihira, N.; Watanabe, M.; Terada, N. "Lithium secondary batteries using modified-imidazolium room-temperature ionic liquid". *Journal of Physical Chemistry B* **2006**, 110, (21), 10228-10230.
- [27] Seki, S.; Kobayashi, Y.; Miyashiro, H.; Ohno, Y.; Usami, A.; Mita, Y.; Watanabe, M.; Terada, N. "Highly reversible lithium metal secondary battery using a room temperature ionic liquid/lithium salt mixture and a surface-coated cathode active material". *Chemical Communications* **2006**, (5), 544-545.
- [28] Seki, S.; Ohno, Y.; Kobayashi, Y.; Miyashiro, H.; Usami, A.; Mita, Y.; Tokuda, H.; Watanabe, M.; Hayamizu, K.; Tsuzuki, S.; Hattori, M.; Terada, N. "Imidazolium-based room-temperature ionic liquid for lithium secondary batteries - Effects of lithium salt concentration". *Journal of the Electrochemical Society* **2007**, 154, (3), A173-A177.
- [29] Shin, J. H.; Henderson, W. A.; Passerini, S. "Ionic liquids to the rescue? Overcoming the ionic conductivity limitations of polymer electrolytes". *Electrochemistry Communications* **2003**, 5, (12), 1016-1020.

- [30] Shin, J. H.; Henderson, W. A.; Passerini, S. "An elegant fix for polymer electrolytes". *Electrochemical and Solid State Letters* **2005**, 8, (2), A125-A127.
- [31] Shin, J. H.; Henderson, W. A.; Passerini, S. "PEO-based polymer electrolytes with ionic liquids and their use in lithium metal-polymer electrolyte batteries". *Journal of the Electrochemical Society* **2005**, 152, (5), A978-A983.
- [32] Shin, J. H.; Henderson, W. A.; Scaccia, S.; Prosini, P. P.; Passerini, S. "Solid-state Li/LiFePO<sub>4</sub> polymer electrolyte batteries incorporating an ionic liquid cycled at 40 degrees C". *Journal of Power Sources* **2006**, 156, (2), 560-566.
- [33] Shin, J. H.; Henderson, W. A.; Tizzani, C.; Passerini, S.; Jeong, S. S.; Kim, K. W. "Characterization of solvent-free polymer electrolytes consisting of ternary PEO-LiTFSI-PYR14 TFSI". *Journal of the Electrochemical Society* **2006**, 153, (9), A1649-A1654.
- [34] Soo, P. P.; Huang, B. Y.; Jang, Y. I.; Chiang, Y. M.; Sadoway, D. R.; Mayes, A. M. "Rubbery block copolymer electrolytes for solid-state rechargeable lithium batteries". *Journal of the Electrochemical Society* **1999**, 146, (1), 32-37.
- [35] Ruzette, A. V. G.; Soo, P. P.; Sadoway, D. R.; Mayes, A. M. "Melt-formable block copolymer electrolytes for lithium rechargeable batteries". *Journal of the Electrochemical Society* **2001**, 148, (6), A537-A543.

- [36] Sadoway, D. R.; Huang, B. Y.; Trapa, P. E.; Soo, P. P.; Bannerjee, P.; Mayes, A. M. "Self-doped block copolymer electrolytes for solid-state, rechargeable lithium batteries". *Journal of Power Sources* **2001**, 97-98, 621-623.
- [37] Ryu, S. W.; Trapa, P. E.; Olugebefola, S. C.; Gonzalez-Leon, J. A.; Sadoway, D. R.; Mayes, A. M. "Effect of counter ion placement on conductivity in single-ion conducting block copolymer electrolytes". *Journal of the Electrochemical Society* **2005**, 152, (1), A158-A163.
- [38] Niitani, T.; Shimada, M.; Kawamura, K.; Dokko, K.; Rho, Y. H.; Kanamura, K. "Synthesis of Li<sup>+</sup> ion conductive PEO-PSt block copolymer electrolyte with microphase separation structure". *Electrochemical and Solid State Letters* **2005**, 8, (8), A385-A388.
- [39] Niitani, T.; Shimada, M.; Kawamura, K.; Kanamura, K. "Characteristics of new-type solid polymer electrolyte controlling nano-structure". *Journal of Power Sources* **2005**, 146, (1-2), 386-390.
- [40] Niitani, T.; Amaike, M.; Nakano, H.; Dokko, K.; Kanamura, K. "Star-Shaped Polymer Electrolyte with Microphase Separation Structure for All-Solid-State Lithium Batteries". *Journal of the Electrochemical Society* **2009**, 156, (7), A577-A583.
- [41] Singh, M.; Odusanya, O.; Wilmes, G. M.; Eitouni, H. B.; Gomez, E. D.; Patel, A. J.; Chen, V. L.; Park, M. J.; Fragouli, P.; Iatrou, H.; Hadjichristidis, N.; Cookson, D.; Balsara, N. P. "Effect of molecular weight on the mechanical

- and electrical properties of block copolymer electrolytes”. *Macromolecules* **2007**, 40, (13), 4578-4585.
- [42] Bullock, S. E.; Kofinas, P. “Nanoscale battery materials based on the self-assembly of block copolymers”. *Journal of Power Sources* **2004**, 132, (1-2), 256-260.
- [43] Bullock, S. E.; Kofinas, P. “Synthesis of an A/B/C triblock copolymer for battery materials applications”. *Macromolecules* **2004**, 37, (5), 1783-1786.
- [44] Angell, C. A.; Liu, C.; Sanchez, E. “Rubbery Solid Electrolytes with Dominant Cationic Transport and High Ambient Conductivity”. *Nature* **1993**, 362, (6416), 137-139.
- [45] Iijima, T.; Toyoguchi, Y.; Eda, N. “Quasi-Solid Organic Electrolytes Gelatinized with Polymethyl-Methacrylate and Their Applications for Lithium Batteries”. *Denki Kagaku* **1985**, 53, (8), 619-623.
- [46] Rajendran, S.; Mahendran, O.; Kannan, R. “Investigations on poly(methyl methacrylate)-poly(ethylene oxide) hybrid polymer electrolytes with dioctyl phthalate, dimethyl phthalate and diethyl phthalate as plasticizers”. *Journal of Solid State Electrochemistry* **2002**, 6, (8), 560-564.
- [47] Miyoshi, T.; Takegoshi, K.; Hikichi, K. “High-resolution solid-state C-13 nuclear magnetic resonance study of a polymer complex: Poly(methacrylic acid) poly(ethylene oxide)”. *Polymer* **1996**, 37, (1), 11-18.

- [48] Ramos, A. R.; Cohen, R. E. "Influence of Diblock Copolymers on Structure and Properties of Polybutadiene-Polyisoprene Blends". *Polymer Engineering and Science* **1977**, 17, (8), 639-646.
- [49] Cohen, R. E.; Ramos, A. R. "Homogeneous and Heterogeneous Blends of Polybutadiene, Polyisoprene, and Corresponding Diblock Copolymers". *Macromolecules* **1979**, 12, (1), 131-134.
- [50] Cohen, R. E. "Homogeneous and Heterogeneous Rubbery Rubbery Diblock Copolymers and Polymer Blends - a Unified View". *Acs Symposium Series* **1982**, 193, 489-499.
- [51] Lischka, U.; Wietelmann, U.; Wegner, M. German Patent DE 19829030 C1, 1999.
- [52] Xu, W.; Angell, C. A. "LiBOB and its derivatives - Weakly coordinating anions, and the exceptional conductivity of their nonaqueous solutions". *Electrochemical and Solid State Letters* **2001**, 4, (1), E1-E4.
- [53] Xu, K.; Zhang, S. S.; Jow, T. R.; Xu, W.; Angell, C. A. "LiBOB as salt for lithium-ion batteries - A possible solution for high temperature operation". *Electrochemical and Solid State Letters* **2002**, 5, (1), A26-A29.
- [54] Yang, H.; Zhuang, G. V.; Ross, P. N. "Thermal stability of LiPF<sub>6</sub> salt and Li-ion battery electrolytes containing LiPF<sub>6</sub>". *Journal of Power Sources* **2006**, 161, (1), 573-579.

- [55] Yu, B. T.; Qiu, W. H.; Li, F. S.; Xu, G. X. "The electrochemical characterization of lithium bis( oxalato) borate synthesized by a novel method". *Electrochemical and Solid State Letters* **2006**, 9, (1), A1-A4.
- [56] Jow, T. R.; Ding, M. S.; Xu, K.; Zhang, S. S.; Allen, J. L.; Amine, K.; Henriksen, G. L. "Nonaqueous electrolytes for wide-temperature-range operation of Li-ion cells". *Journal of Power Sources* **2003**, 119, (SI), 343-348.
- [57] Gray, F. M.; Maccallum, J. R.; Vincent, C. A.; Giles, J. R. M. "Novel Polymer Electrolytes Based on ABA Block Copolymers". *Macromolecules* **1988**, 21, (2), 392-397.
- [58] Harris, D. J.; Bonagamba, T. J.; Schmidt-Rohr, K.; Soo, P. P.; Sadoway, D. R.; Mayes, A. M. "Solid-state NMR investigation of block copolymer electrolyte dynamics". *Macromolecules* **2002**, 35, (9), 3772-3774.
- [59] Kim, D. W.; Park, J. K.; Gong, M. S.; Song, H. Y. "Effect of Grafting Degree and Side Peo Chain-Length on the Ionic Conductivities of Nbr-G-Peo Based Polymer Electrolytes". *Polymer Engineering and Science* **1994**, 34, (17), 1305-1313.
- [60] Croce, F.; Sacchetti, S.; Scrosati, B. "Advanced, lithium batteries based on high-performance composite polymer electrolytes". *Journal of Power Sources* **2006**, 162, (1), 685-689.

- [61] Kurian, M.; Galvin, M. E.; Trapa, P. E.; Sadoway, D. R.; Mayes, A. M. "Single-ion conducting polymer-silicate nanocomposite electrolytes for lithium battery applications". *Electrochimica Acta* **2005**, 50, (10), 2125-2134.
- [62] Borghini, M. C.; Mastragostino, M.; Passerini, S.; Scrosati, B. "Electrochemical Properties of Polyethylene Oxide-Li[(Cf<sub>3</sub>so<sub>2</sub>)(<sub>2</sub>)N]-Gamma-Lialo<sub>2</sub> Composite Polymer Electrolytes". *Journal of the Electrochemical Society* **1995**, 142, (7), 2118-2121.
- [63] Appetecchi, G. B.; Henderson, W.; Villano, P.; Berrettoni, M.; Passerini, S. "PEO-LiN(SO<sub>2</sub>CF<sub>2</sub>CF<sub>3</sub>)(<sub>2</sub>) polymer electrolytes - I. XRD, DSC, and ionic conductivity characterization". *Journal of the Electrochemical Society* **2001**, 148, (10), A1171-A1178.
- [64] Mikes, F.; Pecka, J. "Determination of the Tacticity of Poly(Methyl Methacrylate) by Hydrolysis Rate Measurements". *Collection of Czechoslovak Chemical Communications* **1992**, 57, (2), 349-356.
- [65] Kawai, H.; Nagata, M.; Tukamoto, H.; West, A. R. "High-voltage lithium cathode materials". *Journal of Power Sources* **1999**, 81, 67-72.
- [66] Park, S. B.; Eom, W. S.; Cho, W. I.; Jang, H. "Electrochemical properties of LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> cathode after Cr doping". *Journal of Power Sources* **2006**, 159, (1), 679-684.
- [67] Han, D. W.; Kang, Y. M.; Yin, R. Z.; Song, M. S.; Kwon, H. S. "Effects of Fe doping on the electrochemical performance of LiCoPO<sub>4</sub>/C composites for

- high power-density cathode materials”. *Electrochemistry Communications* **2009**, 11, (1), 137-140.
- [68] Appetecchi, G. B.; Zane, D.; Scrosati, B. “PEO-based electrolyte membranes based on LiBC<sub>4</sub>O<sub>8</sub> salt”. *Journal of the Electrochemical Society* **2004**, 151, (9), A1369-A1374.
- [69] Evans, J.; Vincent, C. A.; Bruce, P. G. “Electrochemical Measurement of Transference Numbers in Polymer Electrolytes”. *Polymer* **1987**, 28, (13), 2324-2328.
- [70] Watanabe, M.; Nishimoto, A. “Effects of Network Structures and Incorporated Salt Species on Electrochemical Properties of Polyether-Based Polymer Electrolytes”. *Solid State Ionics* **1995**, 79, 306-312.
- [71] Doyle, M.; Fuller, T. F.; Newman, J. “The Importance of the Lithium Ion Transference Number in Lithium Polymer Cells”. *Electrochimica Acta* **1994**, 39, (13), 2073-2081.
- [72] Rey, I.; Lassegues, J. C.; Baudry, P.; Majastre, H. “Study of lithium battery by confocal Raman microspectrometry”. *Electrochimica Acta* **1998**, 43, (10-11), 1539-1544.
- [73] Thomas, K. E.; Sloop, S. E.; Kerr, J. B.; Newman, J. “Comparison of lithium-polymer cell performance with unity and nonunity transference numbers”. *Journal of Power Sources* **2000**, 89, (2), 132-138.



- [74] Fujinami, T.; Tokimune, A.; Mehta, M. A.; Shriver, D. F.; Rawsy, G. C. "Siloxyaluminate polymers with high Li<sup>+</sup> ion conductivity". *Chemistry of Materials* **1997**, 9, (10), 2236-2239.
- [75] Tsuchida, E.; Kobayashi, N.; Ohno, H. "Single-Ion Conduction in Poly[(Oligo(Oxyethylene)Methacrylate)-Co-(Alkali-Metal Methacrylates)]". *Macromolecules* **1988**, 21, (1), 96-100.
- [76] Mehta, M. A.; Fujinami, T. "Novel inorganic-organic polymer electrolytes - preparation and properties". *Solid State Ionics* **1998**, 113, 187-192.
- [77] Blazejczyk, A.; Wieczorek, W.; Kovarsky, R.; Golodnitsky, D.; Peled, E.; Scanlon, L. G.; Appetecchi, G. B.; Scrosati, B. "Novel solid polymer electrolytes with single lithium-ion transport". *Journal of the Electrochemical Society* **2004**, 151, (10), A1762-A1766.
- [78] Blazejczyk, A.; Szczupak, M.; Wieczorek, W.; Cmoch, P.; Appetecchi, G. B.; Scrosati, B.; Kovarsky, R.; Golodnitsky, D.; Peled, E. "Anion-binding calixarene receptors: Synthesis, microstructure, and effect on properties of polyether electrolytes". *Chemistry of Materials* **2005**, 17, (6), 1535-1547.
- [79] Mazor, H.; Goodnitsky, D.; Peled, E.; Wieczorek, W.; Scrosati, B. "A search for a single-ion-conducting polymer electrolyte: Combined effect of anion trap and inorganic filler". *Journal of Power Sources* **2008**, 178, (2), 736-743.
- [80] Ghosh, A.; Kofinas, P. "Nanostructured block copolymer dry electrolyte". *Journal of the Electrochemical Society* **2008**, 155, (6), A428-A431.

- [81] Xu, K.; Zhang, S. S.; Poesse, B. A.; Jow, T. R. "Lithium bis(oxalato)borate stabilizes graphite anode in propylene carbonate". *Electrochemical and Solid State Letters* **2002**, 5, (11), A259-A262.
- [82] Chen, Z. H.; Lu, W. Q.; Liu, J.; Amine, K. "LiPF<sub>6</sub>/LiBOB blend salt electrolyte for high-power lithium-ion batteries". *Electrochimica Acta* **2006**, 51, (16), 3322-3326.