

PREPARATION AND CHARACTERIZATION OF POLY (METHYL
METHACRYLATE) / 50% EPOXIDISED NATURAL RUBBER BASED SOLID
ELECTROLYTES FOR LITHIUM-ION SECONDARY BATTERY

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To my beloved husband and families

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ABSTRACT

This research focused on the development of new thin film electrolytes based on Poly(methyl methacrylate)(PMMA) / 50% epoxidised natural rubber (ENR 50) blend by solvent casting method. Lithium nitrate (LiNO_3), lithium triflate (LiCF_3SO_3) and lithium imides ($\text{LiN}(\text{CF}_3\text{SO}_2)_2$) salts were used as the doping material to provide lithium ion for the ionic conduction. Dimethyl carbonate (DMC), ethylene carbonate (EC) and propylene carbonate (PC) plasticizers were used to improve the physical properties and the morphology of the films. Freestanding films were obtained when PMMA was blended with 10% and 20% of ENR 50. Above these compositions, the films became brittle and bonded strongly to the glass substrate. The blend films were not homogeneous in which the phase separation can be observed in their FESEM micrographs even in the presence of plasticizers. Though the films were not homogeneous, the brittle properties of PMMA film have been improved. The DSC thermograms of these films further confirmed the in-homogeneity of the blends by exhibiting two glass transition temperatures, T_g . The infra red (IR) spectra established the PMMA-ENR 50 interactions and the polymer-salt complexation. Doped PMMA / ENR 50 films with LiNO_3 salt were observed to be unstable where by the films obtained became damp and opaque when exposed to the ambient environment. It was observed that the best salt for this PMMA / ENR 50 blend was LiCF_3SO_3 in which the highest conductivity of 10^{-5} S/cm at room temperature were obtained. On the other hand, PMMA / ENR 50 / $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ electrolyte exhibited the lowest ionic conductivity of 10^{-7} S/cm at room temperature. The effect of plasticizers differs from one electrolyte system to another. The ionic conduction behaviour in the electrolyte systems depends on the salt and the plasticizers used. The transference number and the modulus formalism showed that the PMMA / ENR 50 blend based electrolytes were ionic conductor. The equivalent circuit for the highest conducting film from each plasticized or non-plasticized electrolyte system was determined using Autolab software. Films with 10^{-5} S/cm at room temperature were fabricated into LiNiCoO_2 / polymer electrolyte / mesocarbon microbeads (MCMB) cell. It was observed that these cells exhibit poor charge-discharge characteristic and can be improved.

ABSTRAK

Kajian ini memfokuskan kepada penyediaan filem baru elektrolit polimer berasaskan campuran poli(metil metakrilat) (PMMA) / 50% getah terepoksida (ENR 50) dengan kaedah “solvent casting”. Garam litium nitrat (LiNO_3), litium triflat (LiCF_3SO_3) dan litium imida ($\text{LiN}(\text{CF}_3\text{SO}_2)_2$) telah digunakan sebagai dopan dalam penyediaan elektrolit polimer berasaskan PMMA / ENR 50. Dimetil karbonat, (DMC) etilena karbonat, (EC) dan propilena karbonat (PC) telah digunakan sebagai bahan pemplastik untuk membantu memperbaiki morfologi filem elektrolit. Filem elektrolit polimer ini telah berjaya dihasilkan apabila 10% dan 20% ENR 50 ditambah ke dalam campuran. Filem menjadi semakin rapuh dan sukar dipisahkan daripada acuan apabila komposisi ENR 50 dalam campuran melebihi 20%. Kesemua filem berasaskan PMMA/ ENR 50 ini adalah tidak homogen yang mana pemisahan fasa dapat dilihat dengan jelas pada permukaan filem. Malahan, ianya telah dapat dibuktikan melalui analisis permukaan menggunakan mikroskop pengimbasan elektron, FESEM. Walau bagaimanapun, penyediaan elektrolit berasaskan campuran ini diteruskan kerana kerapuhan filem PMMA telah dapat diperbaiki. Analisis pengimbas kalorimetri, DSC pula telah menunjukkan kehadiran dua suhu peralihan kaca, Tg. Daripada analisis spektrum infra merah (IR), didapati telah terbentuknya interaksi antara kedua-dua polimer dan pembentukan kompleks antara polimer dan garam. Dopan LiNO_3 memberikan filem yang paling tidak stabil yang mana filem menjadi lembab dan bertukar opak apabila didedahkan kepada sekitaran. Garam LiCF_3SO_3 telah menunjukkan konduktiviti filem terbaik dengan nilai 10^{-5} S/cm pada suhu bilik manakala filem PMMA / ENR 50 / $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ pula menunjukkan nilai yang sangat rendah dengan konduktiviti tertinggi yang dapat dicapai hanyalah 10^{-7} S/cm. Kehadiran bahan pemplastik telah menunjukkan kesan yang berbeza-beza antara satu sistem elektrolit dengan sistem elektrolit yang lain. Modul pergerakan ion di dalam campuran polimer ini juga bergantung kepada garam dan bahan pemplastik yang digunakan. Daripada penentuan nombor angkutan dan analisis modulus didapati elektrolit polimer ini adalah konduktor ionik. Kesepadanan litar bagi kesemua sistem dengan kekonduksian ionik tertinggi telah ditentukan dengan menggunakan perisian Autolab. Filem dengan kekonduksian minima 10^{-5} S/cm telah digunakan sebagai elektrolit bateri sekunder dalam sel LiNiCoO_2 / elektrolit polimer / “mesocarbon microbeads” (MCMB). Didapati sel ini telah menunjukkan sedikit kelemahan dalam prestasi cas-discasnya dan masih boleh diperbaiki.

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LIST OF SYMBOLS

π	-	Pie
Z	-	Impedance
R	-	Resistance
R_b	-	Bulk Resistance
σ	-	Conductivity
E_a	-	Activation Energy
ϵ'	-	Dielectric Constant
ϵ''	-	Dielectric Loss
M	-	Electrical Modulus Formalism
τ	-	Conductivity Relaxation Time
C	-	Capacitor
Q	-	Constant Phase Element
W	-	Warburg Impedance

LIST OF ABBREVIATIONS

PMMA	-	Poly(methyl methacrylate)
ENR 50	-	50% Epoxidized Natural Rubber
PVC	-	Poly(vinyl chloride)
PEO	-	Poly(ethylene oxide)
PAN	-	Polyacrylonitrile
PVdF	-	Poly(vinylidene difluoride)
PPO	-	Poly(propylene oxide)
EC	-	Ethylene Carbonate
PC	-	Propylene Carbonate
DMC	-	Dimethyl Carbonate
DBP	-	Dibutyl Phthalate
PEM	-	Proton Exchange Membrane
SPE	-	Solid Polymer Electrolyte
SPEFC	-	Solid Polymer Electrolyte Fuel Cell
FESEM	-	Field Emission Scanning Electron Microscope
FTIR	-	Fourier Transform Infrared
DSC	-	Differential Scanning Calorimetry
VTF	-	Vogel-Tammam-Fulcher
WLT	-	Williams-Landel and Ferry
MCMB	-	Mesocarbon Microbeads
OCV	-	Open Circuit Voltage
UNIPEM		Unit Perkhidmatan Makmal

LIST OF PUBLICATIONS

No	Journal / Proceedings	Place/Date	Paper Published	Page	Authors
1	Journal of Power Sources	2006	THE ROLE AND IMPACT OF RUBBER IN POLY(METHYL METHACRYLATE) / LITHIUM TRIFLATE ELECTROLYTE	Article in Press	Famiza Latif, Madzlan Aziz, Nasir Katun, Ab Malik Marwan Ali, Muhd Zuazhan Yahya
2	Solid State Phenomena. Volume 3	2006	THE IMPEDANCE SPECTROSCOPY STUDIES OF PVC/ ENR 50 / LICF ₃ SO ₃ AND PMMA / ENR 50 / LICF ₃ SO ₃ ELECTROLYTES	67-70	M. Aziz, F. Latif, C.L. Chew and N. Katun,
3	Journal Of solid State Science And Technology Letters. Volume 10, No.2 (Abstract) The XX Regional Conference On Solid State Science And Technology.	The Orient Star Resort, Lumut, Perak. (12-14 Disember 2003)	CONDUCTIVITY STUDY FOR PMMA/ENR 50 BASED ELECTROLYTES	61	Famiza Latif and Madzlan Aziz

4	Proceedings Regional Symposium On Membrane Science And Technology.	Putri Pan Pacific Hotel, Johor Bahru, Johor. (21-25 April 2004)	THIN FILM PMMA / ENR 50 BASED ELECTROLYTE FOR LITHIUM ION CONDUCTOR	-	Famiza Latif, Madzlan Aziz and Nasir Katun
5	Proceedings International Conference And Exhibition On Macromolecular Science And Its Impact On Industries.	Sunway Pyramid Convention Centre, Bandar Sunway, Petaling Jaya, Selangor. (27-29 Sept 2004).	THE EFFECT OF DIMETHYL CARBONATE PLASTICIZER ON POLY (METHYL METHACRYLATE)/ ENR 50 / LITHIUM TRIFLATE ELECTROLYTE	-	Famiza Latif, Madzlan Aziz and Nasir Katun
6	Proceedings International Conference And Exhibition On Macromolecular Science And Its Impact On Industries.	Sunway Pyramid Convention Centre, Bandar Sunway, Petaling Jaya, Selangor. (27-29 Sept 2004).	PREPARATION OF THIN FILM ELECTROLYTE BASED ON POLY (METHYL METHACRYLATE) / ENR 50 BLEND BY CASTING METHOD	-	Famiza Latif, Madzlan Aziz and Nasir Katun
7	Journal Of solid State Science And Technology Letters. Volume 11, No.2 (Abstract) The XXI Regional Conference On Solid State Science And Technology.	Hyatt Regency Kinabalu, Kota Kinabalu, sabah, Malaysia. (10-13 October 2004)	THE CONDUCTIVITY OF ENR 50-POLY (METHYL METHACRYLATE)-LITHIUM TRIFLATE SEMI SOLID ELECTROLYTE FOR LITHIUM ION BATTERY	97	Famiza Latif, Madzlan Aziz and Nasir Katun
8	Journal Of solid State Science And Technology Letters. Volume 11, No.2 (Abstract) The XXI Regional Conference On Solid State Science And Technology.	Hyatt Regency Kinabalu, Kota Kinabalu, sabah, Malaysia. (10-13 October 2004)	PREPARATION OF THIN FILM ELECTROLYTE BASED ON POLY (METHYL METHACRYLATE) / ENR 50 BLEND BY CASTING METHOD	131	Madzlan Aziz, Famiza Latif, and Nasir Katun

CHAPTER 1

INTRODUCTION

Conventional liquid electrolytes had been extensively studied and their potential had also been proven and discussed elsewhere. However, liquid electrolytes are facing major problems that are to date remain unsolved. Among the major problems are leakage of corrosive, flammable and toxic liquids or gaseous. For safety and environmental reasons, solid electrolytes are the potential candidates to overcome these problems and soon to replace all liquid-based electrolytes for practical electrochemical devices such as power sources, smart window and displays (Gray, 1991).

The development of new solid electrolyte material is creating opportunities for new types of electrical power generation and storage system. There are many types of solid electrolyte systems, which include solid crystalline electrolytes, glass electrolytes, molten electrolytes and polymeric electrolytes. This work will focus on fabricating and characterizing solid polymer-based thin film electrolytes for secondary battery application.

Although, polymeric materials are not single-ion conductors, they are not hard and brittle materials like solid crystalline and glassy electrolyte. It has mechanical properties that make it suitable to be constructed in all solid-state electrochemical cells. At macroscopic level, high molecular weight amorphous polymer may exhibit properties that are attributes of a true solid, but at atomic level,

local relaxation provides liquid-like degree of freedom that is not significantly different to a conventional liquid.

Below are the critical characteristics that a polymeric material should possess before considering them as practical replacements for their liquid counterparts:

- a) Can easily be fabricated into thin flexible films using existing plastic-film production plant.
- b) They must exhibit adequate ionic conductivity with low electronic conductivity for practical purposes
- c) Compatible with the battery electrode. Chemically and electrochemically stable towards the electrodes.
- d) Large voltage / over voltage stability to achieve complete recharge in rechargeable system.
- e) Also stable against other degradation such as impurities and environment parameters such as temperature.

Since a cell is designed for operations at elevated temperature, therefore it is important that the macroscopic and molecular properties of the polymer material remain constant.

This chapter will discuss some fundamental aspects in the research area of polymer electrolytes to understand why certain materials are selected and a particular technique is employed in this work.

1.1 Classification of Polymer Electrolytes

Polymer electrolytes can be defined or classified as one of the following categories:

a) *A Solvent Free System*

The ionically conducting solid phase systems are formed by dissolution of salts in high molecular weight polar polymer matrix by ion-coordination. This class of material is the most extensively studied because of ease of preparation. Examples of this kind of polymers are poly(vinyl chloride) (PVC) / LiClO₄ (Ramesh *et al.*, 1998) and poly(ethylene oxide) (PEO) / NaNO₃ (Ramalingaiah *et al.*, 1998) complexes.

b) *A Gel Electrolyte System*

This material is formed by dissolving a salt in a polar liquid and an inactive polymeric material is added to improve the mechanical stability. The basic polymer host swelled in the electrolyte solutions and the dopant ionic solute is accommodated in the swollen lattice sites. The ionic motion takes place in this solvent rich swollen region of the polymer. However, these materials are generally unstable since their conductivity is highly dependent on the concentration of the solvent in the swollen region (Chandra and Chandra, 1994). Examples of this class of materials are poly(methyl methacrylate) (PMMA) in liquid electrolyte ethylene carbonate (EC) / propylene carbonate (PC) containing benzoic acid (Ericson *et al.*, 2000), poly(acrylonitrile) (PAN) / dimethyl sulfoxide (DMSO) / AgCl (Lewandowski and Stepniak, 2000) systems.

c) *A Plasticized Electrolyte System*

This system is similar to a gel electrolyte except a small amount of high dielectric constant of solvent is added to the system to enhance the

conductivity of the conducting polymer electrolyte. Example of this type of system is PAN / EC/PC/ LiClO₄ (Rajendran *et al.*, 2001a).

d) *A Membrane Ionomer / Proton-conducting Polyelectrolyte System:*

This class of polymer has self ion-generating groups attached to the main chain of the polymer host that are responsible for the ionic conductivity (Slade *et al.*, 1983). These materials normally consisted of a material comprising a fluorocarbon polymer backbone to which sulfonic acid groups have chemically bonded. A plasticizer (typically water) is also required to achieve excellent conductivity levels. The unique property of this material is that only single ion transport, either the anions or the cations that are responsible for the ionic conduction that occur in the bulk. Example of this type of material is sodium polystyrene sulphate.

The original concept of polymer electrolyte is the solvent-free electrolyte system. However, electrochemical cells based on this type of materials are currently under development because of their relatively low ionic conductivity especially at room temperature. This is due to their poor electrode-electrolyte contact. Therefore, many researchers had turn to gel and plasticized type electrolytes for commercialization purposes. These systems exhibited relatively high ionic conductivity. In fact, gel electrolyte systems had been developed and tested in electrochemical cells by the industrial community.

All the first three classes of polymer electrolytes mentioned above are being developed for battery applications. However, polyelectrolyte membranes are more concerned in the development of fuel cell technology. This type of polymer electrolytes is used in proton- exchange membrane (PEM) fuel cells, which also known as solid polymer electrolyte fuel cell (SPEFC).

1.2 Polymer Electrolytes Background

For many years polymers are known as insulators i.e. unable to conduct electricity and widely used as cable protector, *etc.* As the technology in synthesizing polymers was advancing, a new class of material called conducting polymers was produced. These materials usually had conjugated bonds in their polymer chain. The delocalization of the pie (π) electrons along the polymer backbones produced metal-like conductivity. Examples of these types of polymers are polyacetylene, polyphenylene, *etc.*

However, in the 70's researchers had found that a non conducting polymer, polyethylene oxide, PEO became conducting when lithium salt was added into the polymer matrix. This class of material is called polymer electrolyte. Fenton and co-workers (1973) was the first group to discover polymer electrolyte material. However, the finding has not been appreciated until Armand *et al.* (1978) realized the potential of this material in electrochemical system. In their early work, they had discovered conducting potential of PEO when doped with lithium salts. To date PEO has been the most widely studied (Kim and Smotkin, 2002; Choi *et al.*, 1997) polymer host because it contains only unstrained CO, CC and CH bonds. Moreover, it is chemically and electrochemically stable. A wide variety of salts based on alkali metal, alkaline earth metal, transition metal and lanthanide ions with concentrations exceeding 2 mol/dm^3 are also soluble in the pure polymer (Bruce *et al.*, 1993). However, this material has been excluded from practical applications due to its high melting points of crystalline phase and low ionic conductivity at room temperature (Wright *et al.*, 1975).

Since the potential of these materials have been realized for commercial exploitation, other polymers such as PAN (Ileperuma *et al.*, 2002; Rajendran *et al.*, 2001a), poly(vinylidene fluoride) (PVdF) (Wang and Gu, 2002; Jiang *et al.*, 1997), PMMA (Bohnke *et al.*, 1993a, 1993b; Chen *et al.*, 2002), PVC (Langmaier *et al.*, 1997; Ramesh *et al.*, 2002a, 2002b) had been proposed as a host in electrolyte system. Recently, natural polymer such as chitosan (Yahya *et al.*, 2000; Subban *et al.*, 1996) had also been studied.

1.3 Why Polymer Electrolytes

Polymer electrolytes had played an important role in solid state ionics due to their unique properties (Chandra and Chandra, 1994) such as:

- a) Ease of fabrication into thin film with large surface area hence giving high energy density,
- b) The ability to accommodate a wide range of doping compositions of ionic salts,
- c) Provide good electrode-electrolyte contact,
- d) Exhibited high ionic conductivity,
- e) Mouldability that allows a battery to be fabricated in any shape and design of various dimensions,
- f) The flexible nature of the polymer can also accommodate volume changes in the cell during cycling without physical degradation at the electrode-electrolyte interfacial.

1.4 The Characteristics of a Polymer Host

Below are the essential characteristics that a polymer or the active part of a copolymer must satisfy in order to become a successful polymer host (Ratner, 1987, Gray, 1991). These are the main guidelines when choosing a polymer as a host in an electrolyte system.

- a) Atoms or groups of atoms with lone pair electrons to form coordinate bonds with the cations of the doping salt. Therefore, the polymer is able to solvate the salt via the interaction between the lone pair electrons and the cations of the salt,
- b) The segmental motion of the polymer chain can take place readily,
- c) A flexible polymer chain to ensure effective solvation of cations and to provide favourable solvation entropy,
- d) Low glass transition temperature.

1.5 Characteristic of the Doping Salt

Most pure polymers are non-conducting materials. Their conductivities are way below the significant value. By incorporating additives such as salts, they are able to become ionic conductor. The additive added into the polymer is called a dopant and the process is called doping.

The lattice energy of the salts should also be put into consideration when choosing a doping material since it plays an important role in the formation of polymer-salt complex. The lattice energy of the salts should be low so that the salts can easily be dissolved in the polymer matrix. Usually salts with large anions such as CF_3SO_3^- , $(\text{CF}_3\text{SO}_2)_2^-$, ClO_4^- , NO_3^- , SCN^- , I^- have low lattice energy. Most attention has focused principally on a small group of lithium and sodium salts that form polymer electrolytes of potential commercial interest.

1.6 Preparation Of Polymer Electrolytes

There are several methods in the preparation of polymer electrolyte thin film:

a) *Solvent Casting Technique*

Solvent casting is the most common and easiest method of preparing thin film polymer electrolyte. This involves dissolving polymer and salt in an appropriate solvent. The solution is then cast into specific petri dish and left to dry. Thin film is obtained after solvent evaporation. There are two significant stages in the electrolyte formation. In the dissolution process, the casting solvent overcomes the lattice energy of the salt. Then the salt is transferred from the casting solvent to the polymer that acts as an immobile solvent (Vincent, 1987). In this technique, the crystal formation may be affected by the nature of the solvent, evaporation rate, and by the solvent

residue. The final drying temperature also plays an important role in the structure of the polymer film.

b) *Melt or Hot Pressing*

This method was developed by Gray *et al.* (1986; Patent No. 8619049). In this technique, the polymer is grind into a fine powder under liquid nitrogen and appropriate quantities of polymer and salt are then milled together to form an intimate mixture. The mixture is then annealed at 120-150°C and cooled under pressure to form thin films. This method avoids the presence of residual solvent in the resulting films and is best employed when dealing with co-mixed polymer systems.

c) *Plasma Polymerization*

Ultra thin polymer electrolyte films of the order of 1 μm thick can be fabricated using this method (Uchimoto *et al.*, 1990).

1.7 Modification of Polymer Host

There are several methods that had been adopted in order to enhance the conductivity or the structure of the polymer:

a) *Copolymerization*

Polymer-salt systems may be amorphous, crystalline or amorphous-crystalline mixtures depending on the polymer, salt, and preparative conditions. Originally ionic conductivity was considered to occur in the regular crystalline lattices. However, it is now known that such phases are electrical insulators and that ion transport occurs principally in amorphous regions (Berthier *et al.*, 1983). Simple linear homopolymers are prone to

crystallization and form stoichiometric crystalline phases with salt. Therefore, by adding another polymer that has a lower T_g to the original polymer host will lead to the formation of a flexible polymer backbone hence increasing the conductivity. PEO-poly(propylene oxide) (PPO) copolymer complexed with alkali metal salt (Passimiemi *et al.*, 1988) is one of the example of this type of polymer.

b) *Plasticization*

A plasticizer helps to assist in the dissolution and dissociation of salts and thus increase the number of mobile charges. It is also able to reduce the viscosity of the electrolyte and therefore help to facilitate the movement of charge carriers along the polymer backbone and thereby enhancing the ionic conductivity (Kelly *et al.*, 1985). The most important advantage of plasticized polymer electrolytes is that they exhibit relatively higher ionic conductivity compared to other polymer electrolyte groups. However, its major drawbacks are poor mechanical properties due to high degree of plasticization, solvent volatility and reactivity of polar solvent with the lithium electrode. Examples of these systems are PEO/EC/LiClO₄ (Qian *et al.*, 2002) and PVC / dibutyl phthalate (DBP) / LiBF₄ (Golodnitsky *et al.*, 1996).

c) *Blending*

Polymer blending is one of the useful techniques for designing new materials with various properties. Among the advantages of employing this method are simplicity of preparation and easy to control physical properties by compositional change (Acosta and Morales, 1996; Rocco *et al.*, 2001). The new polymer blends often exhibit properties that are superior compared to the properties of each individual component polymer (Rho *et al.*, 1997; Oh and Kim, 1999; Pielichowski, 1999; Stephen *et al.*, 2000; Tang *et al.*, 2000; Pielichowski and Hamerton, 2000). Examples of polymer blending systems are poly (vinyl chloride)/polypyrrole (Pruneanu *et al.*, 1997), PVC/PMMA (Stephan *et al.*, 2000). Recently blending of polyaniline with nitrilic rubber has also been reported (Vallin *et al.*, 2000).

d) *Addition of Ceramic Fillers/Additive*

The addition of ceramic/inorganic fillers has been reported not only to improve the ionic conductivity but also the mechanical stability of the system. Some examples of inorganic fillers that had been used for this purpose are SiO₂ (Quartrone *et al.*, 1998) and Al₂O₃ (Golodnitsky *et al.*, 1996).

1.8 Applications Of Polymer Electrolyte

The unique properties of these materials make them possible to be applied in a wide range of electrochemical devices especially in primary and secondary batteries and ambient temperature fuel cells. Other practical applications that are under consideration include electrochromic devices, modified electrodes/sensors, solid-state reference electrode systems, supercapacitors, *etc.*

However, the main concern of many solid state researchers is the development of secondary lithium batteries. The major advantages in developing polymer based electrolyte batteries are:

- a) The internal resistance of a cell may be reduced when the electrolytes are fabricated into large-area thin films. Uniquely, this can still be possible even at a moderate conductivity.
- b) A complete thin large-area cell can be operated at relatively low current density, while still permitting the battery to be operating at practical rates. Typical cell dimensions are ~15 – 30 μm thick electrolyte, 25 – 50 μm thick Li electrode and 20 – 100 μm composite cathode are a good combination of a unique battery cell structure that permit high values of specific energy and power to be achieved.
- c) Intimate contact with the cell electrode can be established hence facilitate good interfacial transport.

- d) The incorporation of elastomeric electrolyte phase will help to accommodate volume changes during cycling.

The polymer electrolyte plays three important roles in the solid polymer electrolyte (SPE) battery:

- a) It is a lithium ion carrier
- b) It acts as an electrode spacer, which eliminates the need to incorporate an inert porous separator.
- c) It is a binder, which ensures good electrical contact with the electrodes and can be maintained at all times through charging and discharging.

The replacement of the liquid electrolyte by plastic material solved the problems associated with corrosive or powerful solvents that may react with seals and containers. The absence of gas formation and any significant vapour pressure during operation, permit the battery to be packaged in low-pressure containers such as plastic-metal barrier. The SPE batteries should then be readily manufactured using highly automated existing plastic film techniques.

1.9 Problem Statements

- a) The conventional liquid electrolytes are facing leakage toxic and corrosive liquids or gaseous problems which are to date remain unsolved.
- b) Solid base polymer electrolytes are currently under development due to its poor electrode-electrolyte contact.
- c) To the best of our knowledge, solid PMMA film has not been realized in SPE batteries due to its brittle properties that gave poor electrode-electrolyte contact.

1.10 Objectives

The objectives of this work are:

- a) To prepare soft and flexible freestanding films of PMMA / ENR 50 blend by solvent casting method.
- b) To obtain a minimum ionic conductivity of 10^{-5} S/cm at room temperature from PMMA / ENR 50 based electrolytes. The minimum conductivity of 10^{-5} S/cm has been used as the criterion for possible application purposes (Gray,1991).
- c) To investigate the performance of PMMA / ENR 50 electrolyte in solid polymer electrolyte lithium batteries.

1.11 Research Scope

1.11.1 Selection of Materials

In this work poly (methyl methacrylate), PMMA is used as the main polymer host. PMMA is chosen because it has oxygen atoms in its polymer chain. These oxygen atoms have lone pair electrons that are expected to form coordinate bonds with lithium salts hence establish the PMMA-lithium salt complex. From previous literatures, this material exhibited acceptable conductivity value. However, the high ionic conductivities are achieved when the material is fabricated into a gel form. This material also is found to give better interfacial properties towards lithium electrodes (Appetecchi *et al.*, 1995, Abraham *et al.*, 1990).

In this work solid PMMA based electrolyte in a form of thin free standing films are to be fabricated by solution cast technique. This technique is the most

common method of preparing polymer electrolyte because of ease of preparation. The solvent used in this work is tetrahydrofuran, THF, which is the best solvent to dissolve both PMMA and ENR 50 and a film can be formed after solvent evaporation.

Since PMMA alone form a brittle film, therefore 50% epoxidised natural rubber (ENR 50) is added to improve the brittle properties of PMMA films and therefore a freestanding film of PMMA can be obtained. ENR 50 is chosen based on its soft elastomeric, good elasticity and adhesion properties. In addition, it contains oxygen atom(s) in their structure. These oxygen atoms may provide extra coordinating sites for lithium ions. In fact, Idris *et al.* (2001) and Glasse *et al.* (2002) had worked on various types of epoxidised natural rubber i.e. ENR 25, ENR 50 and ENR 60. The conductivities achieved for the systems are between 10^{-6} to 10^{-4} S/cm. Various amount of ENR 50 will be added into fixed amount of PMMA until the best compositions that produced a thin, flexible and free standing films of PMMA / ENR 50 are obtained. Note that the term “blending” is adopted to explain the process of mixing of the two polymers. However, the homogeneity of the blending is not the main concern. The good contact between the PMMA /ENR 50 electrolyte and the electrode is hoped to compensate the inhomogeneity of the blend. The homogeneity of the blend can be improved in the future work if the minimum conductivity of 10^{-5} S/cm is obtained from the blend.

Compositions that produced free standing films will be doped with various amounts of lithium salts namely lithium nitrate (LiNO_3), lithium triflate (LiCF_3SO_3) and lithium imides ($\text{LiN}(\text{CF}_3\text{SO}_2)_2$) to supply lithium ion for the ionic conduction. LiCF_3SO_3 salt is used because it has helped to improve the conductivity of rubber-based electrolyte system (Idris *et al.*, (2001), Glasse *et al.* (2002). $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ is a new lithium salt that has not been extensively used in polymer electrolyte systems (Sakaebe and Matsumoto, 2003, Deepa *et al.*, 2004). It has several advantages such as excellent safety and stability characteristics as well as its ability to provide polymer electrolytes with ionic conductivity comparable to ClO_4^- and much higher than CF_3SO_3^- can offer (Deepa, 2002; Webber, 1991). LiNO_3 salt is used for its hygroscopic characteristic that is suitable for electrolyte membrane in Fuel Cell. These salts are also chosen because they contain large anions that usually have low

lattice energy. The lattice energy of the salts plays an important role in the formation of polymer-salt complex. It gives a rough indication of the solubility of the salt which reflects the energy required to separate the positive and negative ions in a solid ionic compound. The lattice energies for LiNO_3 , LiCF_3SO_3 and $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ salts are 848 kJ/mol (Lide, 1993), 735 kJ/mol (Kim *et al.*, 2001) and 489.4 kJ/mol (Jenkins, 2006) respectively.

Single plasticizers of ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC) and mixed plasticizer of EC-PC, EC-DMC and PC-DMC will be added to PMMA / ENR electrolyte solutions to further improve the morphology and enhance the conductivity of the films. These plasticizers are among the most extensively studied in polymeric systems due to their low molecular weight, low viscosity, high dielectric constant and high boiling point properties. Furthermore, it has shown tremendous effect on improving the properties and also the conductivity of their respective systems (Jacob *et al.*, 1998).

1.11.2 Selection Of Material Characterizations

When additives such as ENR 50, salts or plasticizers are added to the main polymer host of PMMA, the material will definitely show at least a slight change in its internal structure and properties.

To study the effect of adding ENR 50, salts or plasticizers on the morphology of PMMA and the blend, Field Emission Scanning Electron Microscopy (FESEM) will be performed. To confirm polymer-polymer interactions or polymer-salt complexation or ion-ion interactions, Fourier Transform Infrared (FTIR) will be carried out. Differential scanning calorimetry (DSC) will be implemented to study the thermal properties of the new materials in which the glass transition temperature, T_g of the new materials will be determined.

Conductivity of a sample cannot be measured directly from specific equipment. Therefore, the impedance of each film prepared will be firstly measured by impedance spectroscopy at room and elevated temperature. From the impedance measurements, Cole-Cole plots will be obtained and the bulk resistance for each sample will be determined. Finally, the conductivity of the samples can then be calculated. Besides impedance, the dielectric constant and the electrical modulus will also be calculated and analyzed in order to understand the effects of salts and plasticizer on the electrical conductivity of the materials. Finally the impedance plots will be fitted to an equivalent circuit model by software fitting.

Since the conductivity of a polymeric material is due to the ionic and electronic conduction, it is therefore important to determine the ionic transference number (t_i) of the material. Films with appreciable conductivity value of at least 10^{-5} S/cm will be selected for the determination of transport number. The determination of transference number (t) will be carried out manually.

1.11.3 Selection Of Test Cell

Once the samples have been characterized and showed complexation with high ionic transference number and sufficient conductivity (10^{-5} S/cm) at room temperature, it is then necessary to test the electrolytes in a complete battery system. In this study the battery system of the type LiNiCoO_2 / polymer electrolyte / MCMB will be considered. Here industrial grade LiNiCoO_2 and MCMB (mesocarbon microbeads) are the cathode and anode electrodes respectively. LiNiCoO_2 is chosen because it is able to deliver a reasonably high voltage and high discharge capacity (Koksang *et al.*, 1996; Zhang *et al.*, 2000; Zhechera *et al.*, 1993; Caurant *et al.*, 1996). However, these electrodes are readily prepared by other groups. The charge discharge characteristic will be carried out to determine the battery performance.

1.12 Expectations

At the end of this work, it is hope that the right compositions of PMMA / ENR 50 blend can be obtained to form thin, freestanding films. It is also hope that the solvent casting technique is the right method in preparing PMMA / ENR 50 based electrolytes films.

It is expected that complexation occurred between the polymer and salt. For possible application purposes, a minimum conductivity of at least 10^{-5} S/cm (Gray,1991) can be obtained at room temperature when salts are doped into the polymeric films. The presence of plasticizers will improve the morphology of the electrolyte films and hence enhance the conductivity of the resulting films.

High ionic transference number will be obtained from films that exhibited high ionic conductivity. The complete cells will give good charge-discharge characteristic and show stability towards lithium electrode when test on battery system.

1.13 Technical Challenge and Limitations

It is difficult to obtain a homogeneous phase in freestanding polymer electrolyte films. Therefore, it is difficult to qualitatively characterize the polymer via IR or FESEM techniques since it does not represent the whole systems.

A freestanding type polymer based electrolyte for battery application has not yet been commercialized due to their poor electrode-electrolyte contact that impedes the ion exchange at the interface. Furthermore, the addition of plasticizers, though helps to increase the conductivity, has a poor electrochemical stability against cell electrodes and yet has to be established.

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