PHASE DIAGRAM APPROACH TO CONTROL OF IONIC CONDUCTIVITY AND ELECTROCHEMICAL STABILITY OF SOLID POLYMER ELECTROLYTE MEMBRANE FOR LI-ION BATTERY APPLICATION

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PHASE DIAGRAM APPROACH TO CONTROL OF IONIC CONDUCTIVITY AND ELECTROCHEMICAL STABILITY OF SOLID POLYMER ELECTROLYTE MEMBRANE FOR LI-ION BATTERY APPLICATION

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ABSTRACT

Binary and ternary phase diagram of poly(ethylene glycol) dimethacrylate (PEGDMA), bis(trifluoromethane)sulfonimide (LiTFSI), and succinonitrile (SCN) blends have been established by means of differential scanning calorimetry and polarized optical microscopy. The binary phase diagram of PEGDMA/SCN mixture is of typical eutectic type, whereas the binary phase diagram of PEGDMA/LiTFSI mixture exhibits a wide single-phase region at the intermediate compositions. The ternary phase diagram of PEGDMA/SCN/LiTFSI mixture shows a wide isotropic region. The polymer electrolyte membrane (PEM), which is formed by ternary blends in this region after UV-crosslinking, remains in the isotropic phase and performs. The room temperature ion conductivity as evidenced in AC impedance measurement, was found to be extremely high (i.e., $10^{-3}$ S/cm). This ionic conductivity increases to $10^{-2}$ S/cm at 60 °C that continues to improve further up to 135 °C investigated. More importantly, the high ionic conductivity behavior is reproducible in repeated heating/cooling cycles. Those PEM are solid-state, stretchable, nonflammable, and light weight, which may be applicable to lithium ion battery as a replacement of commercial liquid electrolyte. SCN in ternary blends affords not only dissociation of the lithium salt, but also plasticization to the cross-linked PEGDMA network. Last not least, thermal and electrochemical stability of these membranes were examined for further application probability.
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CHAPTER I
INTRODUCTION

The world’s growing demand for energy storage devices has driven the research to new directions in energy storage systems, for the sake of reducing energy crisis. Li-ion battery is one of the most viable systems for various uses such as electronic devices and, most attractively, electric vehicles. Traditional electrolytes are found to be no longer suitable for future Li-ion systems, whereby series of novel cathode and anode materials with higher energy storage abilities were applied. Innovations of Li-ion battery electrolytes have to catch up with the evolutions on electrode materials. On the other hand, traditional solvent electrolytes have some drawbacks especially serious safety problems due to the flammable essential of solvents.

Chapter II reviews a series of novel electrolytes that have been studied for their potential application on Li-ion batteries. Those researches focus on solid polymer electrolytes, polymer gel electrolytes, ionic liquids and so on. All of them need to be further improved for industrial application although they have surprising performances in certain aspects. For example, the nonflammable nature of solid polymer electrolytes made them much safer than solvent electrolyte, but most of their ionic conductivities are not sufficient for industrial application.

In this thesis, efforts have been made to improve the ionic conductivity of solid polymer electrolytes. A system of ternary mixtures with poly(ethylene oxide)
dimethacrylate (PEGDMA), succinonitrile(SCN) and bis(trifluoromethanesulfonyl)imide (LiTFSI) has been studied. Binary and ternary phase diagram of PEGDMA, LiTFSI and SCN blends have been firstly established by means of differential scanning calorimetry and polarized optical microscopy in Chapter IV. Those ternary mixtures formed into polymer electrolyte membranes (PEMs) after UV cross-linking. Ionic conductivities of those PEMs in relation to ternary phase diagram are investigated in Chapter V. As a consideration for further application probability, thermal and electrochemical stability of those PEMs are examined in Chapter VI.
CHAPTER II
BACKGROUND AND LITERATURE SURVEY

2.1 General introduction to energy storage system

The global shortage of fossil fuels results in series of energy crisis. This attracts world’s attention on ways of reducing energy crisis such as the exploitation of sustainable energy and replacing burning fuel for electricity to support ground transportations. Nowadays the exploitation of sustainable energy mainly focuses on the development of solar energy, wind, and renewable biofuel systems. And to reduce the use of burning fuel, electric vehicles and hybrid vehicle are urgently needed, which mostly depend on the development of higher energy storage devices. Fuel cells have the highest energy density compared to common battery systems. At present, fuel cell technology is not mature enough for practical application on EVs due to some problems such as hydrogen storage for H$_2$/O$_2$ fuel cells. Supercapacitors attract a lot of attention for their application in hybrid vehicles because of their high power density. Li-ion battery is one of the most reliable battery systems for EVs as they have both considerable power density and energy density.

2.2 Introduction to lithium ion batteries

Lithium metal is a preferred choice for high energy density battery system because it is the most electropositive (-3.04V versus standard hydrogen electrode) and the lightest (equivalent weight M=6.94g mol$^{-1}$, and specific gravity $\rho$=0.53g cm$^{-3}$) metal. $^1$
Figure 2.1 Scheme of basic structure of a Li-ion cell, taking an example of graphite-LiCoO$_2$ electrode system and solvent electrolyte.

Although primary lithium ion batteries were used during 1970s as power sources for watches, calculators and implantable medical devices, the commercial products of secondary (rechargeable) lithium ion batteries did not emerge until early 1990s. The early generation of rechargeable lithium ion batteries included Li-TiS$_2$, Li-MoS$_2$ and Li-Li$_x$MnO$_2$ systems. Li-TiS$_2$ was the best intercalation (will be discussed later) compound available at that time with layered-type structure but it did not go far due to safety issues. Dendritic lithium grows on the Li-metal surface during repeated charge-discharge cycles due to a reaction between Li-metal and electrolyte, which would further lead to the explosion of the battery. Same safety problem also exists with Li-MoS$_2$ system. The Li-Li$_x$MnO$_2$ system performs well on safety issue, but not quite well in the
prolonged cycle life.\textsuperscript{6,7} The concept of the so-called rocking-chair technology, i.e., back and forth shuttling of ions, was brought into lithium ion battery during the end of 1980s to early 1990s. It helps to solve the dendrite problem of lithium cells as lithium in this case is its ionic rather than the metallic crystalline state. It was realized that transition metal oxides and sulfides could be a good choice for cathode materials as three-dimensional transition-metal oxides have higher potentials than layered transition-metal sulfides.\textsuperscript{5} Then with the introduction of graphite to replace Li-metal as an anode material, the new generation of lithium ion battery system came to graphite-LiCoO\textsubscript{2}, which is also a rocking-chair system. This kind of cell has a potential over 3.6 V and gravimetric energy densities as high as 120-150 Whkg\textsuperscript{-1}, which make graphite-LiCoO\textsubscript{2} becoming a leading electrode system for rechargeable lithium ion batteries even nowadays. A basic cell structure of graphite-LiCoO\textsubscript{2} system is illustrated in Figure 2.1

Now let us take a look at the basic structure of a Li-ion cell and the reactions between cathode and anode material with the example of graphite-LiCoO\textsubscript{2} system. A basic Li-ion cell should have a cathode, an anode and an electrolyte with or without a separator. The electrochemical reaction between graphite and LiCoO\textsubscript{2} is called a Li-ion intercalation - de-intercalation reaction. The cathodic reaction is:

\[
\text{LiCoO}_2 \leftrightarrow 0.5\text{Li}^+ + 0.5\text{e}^- + \text{Li}_{0.5}\text{CoO}_2
\]  

(2.1)

The anodic reaction is:

\[
\text{C}_6 + \text{Li}^+ + \text{e}^- \leftrightarrow \text{LiC}_6
\]  

(2.2)

LiC\textsubscript{6} is the final product of intercalation reaction between Li\textsuperscript{+} and graphite. As charging step moves forward, electrons are released into external circuit due to the oxidation of Co and Li-ions are released from LiCoO\textsubscript{2} into electrolyte on the cathode side, namely the oxidation and delithiation of LiCoO\textsubscript{2}. On the anode side, graphite undergoes intercalation
and reacts with lithium ions to form LiC₆ with electron obtained from the external circuit, namely the reduction and lithiation of graphite. The discharging step is just the opposite as both cathodic and anodic reactions are reversible.

Figure 2.2 (a) Structure of alkyl carbonate solvents; (b) The electrochemical windows of various solvent families mixed with tetraalkyl ammonium (TAA) salts. (c) The electrochemical windows of Li salt-dissolved solutions in various solvent families.

The role of electrolyte is to serve as a medium that transports charges, which are in the form of ions, between two electrodes. The major types of electrolyte that used in battery are salts-dissolved solvents. It can be classified as aqueous (if the solvent is water) and aprotic (if the solvent is organic). In Li-ion batteries the electrolyte is always aprotic. Early in the 1950s, it was reported that a passivation film could form on the surface of lithium metal when lithium metal is put into certain nonaqueous solvent. This passivation film would prevent further reaction between lithium metal and solvent, which gives lithium metal stability in such solvents. This discovery served as a starting point for further research on electrolyte candidates for Li-ion batteries. In 1990s, it was found that
solvents from alkyl carbonate analogues, like propylene carbonate and dimethyl carbonate, could be usable for Li-ion batteries. Figure 2.2b and Figure 2.2c exhibit the electrochemical window of a series of alkyl carbonates when dissolved with tetraalkyl (TAA) salts and lithium salts, respectively. This shows the electrochemical window, which is the voltage range between oxidative and reductive decomposition limits, of those electrolytes in Li-ion cells. These lithium salt-dissolved alkyl carbonates are still widely used nowadays in Li-ion batteries as conventional electrolytes.

2.3 Solid electrolyte interphase (SEI) layer

Before moving on to any further topics on Li-ion battery, no matter cathode materials or anode materials, there is a critical issue in Li-ion cells that must be firstly discussed. A thin film called “solid electrolyte interphase (SEI)” would form on the surface of anode, which plays the role of a protective layer that ensures the reversibility of Li-ion cell. The mechanism this phenomenon can be described as follows:

(1) In the reduction process, electrolyte solvents decompose on the surface of the anode and form a thin film that finally covers the anode surface. This thin film, on the other hand, prevents further decompositions of solvent.

(2) Li ions can be transferred through the SEI layer while electrons cannot be blocked.

(3) SEI layer only forms during the first charge cycle; the subsequent cycles would be reversible with anode being stable.

This SEI layer works for both carbonaceous and lithium metal anode, ensuring their stability in most aprotic, lithium salt-dissolved solvent electrolyte. The exact mechanism of SEI layer is still a complicated problem for battery engineers and some details still
remain unclear. Its importance to Li-ion battery system makes it one of the key topics in today’s research.

2.4 Electrolyte materials

As the society’s demand for Li-ion batteries increases tremendously with the rapid development on portable electronics and electric vehicles, people are trying to find new cathode and anode materials that with higher energy density. Meanwhile, our electrolyte continuously needs improvement to meet the demanding electrochemical environment that was created by the more oxidizing cathode and more reducing anode, namely, a wider electrochemical window. Modern electrolytes are designed under the following basic requirements:

(1) It should have a good ionic conductivity so that Li-ion can be transported easily between two electrodes. However it must be an electron insulator to minimize self-discharge process.

(2) Its electrochemical window should be wide that it can survive under working potential range without degradation.

(3) In a working cell, it should not react with cathode, anode or any other components like a separator under a given working potential range.

Besides, other properties, such as thermal stability, mechanical integrity, non-flammability, and room-temperature ionic conductivity, are also some important factors that make the battery desirable even it faces extreme environment.

In this thesis, electrolytes will be mainly classified into several categories: solvent (conventional) electrolytes, polymer electrolytes, and ionic liquids (molten salts).
Furthermore, polymer electrolytes can be divided into two subgroups: solid polymer electrolyte and gel polymer electrolyte.

2.5 Conventional electrolyte

Solvent electrolytes for Li-ion battery are mixtures of lithium salt and solvent. Mostly one or two lithium salts and more than two kinds of solvent are chosen as a combination to meet different applications that cannot be achieved by single salt and/or solvent, for example, both high dielectric constant and low viscosity. A desired solvent or solvent mixtures should be evaluated in such ways:

(1) Lithium salt must be easily dissolved to ensure that the electrolyte would have a high dielectric constant.

(2) In the working temperature range of a battery, solvent should remain liquid. Take the battery in an electric vehicle for example, melting temperature of the solvent mixtures should at least be below -20 °C to guarantee the batteries’ performance in winter. On the other hand, boiling (evaporation) temperature of solvent mixtures should above 100 °C to survive the harsh environment temperature in a car.

(3) Low viscosity in the working temperature range is also a crucial property as it is closely related to the ionic conductivity.

(4) High flash point of solvent mixtures to alleviate safety issues. However, most solvent have a relatively low flash point (generally below 100 °C) and that makes the safety issue to be a major drawback for conventional electrolytes.

Any solvents that have active protons would not be suitable although they have a good ability to dissolve lithium salts. The essential point is that the oxidation and
reduction reaction voltage range of these solvent is 2.0-4.0 V versus Li$^+/\text{Li}$,\textsuperscript{11} which falls into the general working potential range of Li-ion battery. These solvents would not have stability if applied to Li-ion batteries. Then aprotic solvents with polar groups are taken into consideration for suitable electrolyte solvents.

Table 2.1 and 2.2 lists two groups of commonly used solvents as electrolyte.\textsuperscript{12-16} However, due to a series of problems such as internal short circuit, leaking and possibility of forming flammable reaction product, serious safety hazards become great impediment to the application of solvent electrolyte. Considerable efforts have been made to gradually substitute solvent electrolytes by a set of novel electrolytes.

Table 2.1 Organic Carbonates and Esters as Electrolyte Solvents\textsuperscript{10}
Table 2.2 Organic Ethers as Electrolyte Solvents

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Structure</th>
<th>M. Wt</th>
<th>T_m/°C</th>
<th>T_β/°C</th>
<th>η/P 25°C</th>
<th>e 25°C</th>
<th>Dipole Moment/debye</th>
<th>T_β/°C</th>
<th>d/gem², 25°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMM</td>
<td></td>
<td>76</td>
<td>-105</td>
<td>41</td>
<td>0.33</td>
<td>2.7</td>
<td>2.41</td>
<td>-17</td>
<td>0.86</td>
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<tr>
<td>DME</td>
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<td>-58</td>
<td>84</td>
<td>0.46</td>
<td>7.2</td>
<td>1.15</td>
<td>0</td>
<td>0.86</td>
</tr>
<tr>
<td>DEE</td>
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<td>118</td>
<td>-74</td>
<td>121</td>
<td>20</td>
<td>0.84</td>
<td></td>
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<td></td>
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<tr>
<td>THF</td>
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<td>72</td>
<td>-109</td>
<td>66</td>
<td>0.46</td>
<td>7.4</td>
<td>1.7</td>
<td>-17</td>
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<td>2-Me-THF</td>
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<td>80</td>
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<td>6.2</td>
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<td>1,3-DL</td>
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<td>6.8</td>
<td>1.43</td>
<td>-2</td>
<td>0.983</td>
</tr>
<tr>
<td>2-Me-1,3-DL</td>
<td></td>
<td>88</td>
<td></td>
<td>0.54</td>
<td>4.39</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

2.6 Polymer electrolytes

2.6.1 Models for ion transport

Due to the large variety of systems involved and the complicated structure of polymers, the ion transport model has yet to achieve as a comprehensive description. The ionic conductivity can be generally analyzed in the context of Arrhenius and/or Vogel-Tammann-Fulcher (VTF) models. The Arrhenius behavior is described by equation (2.3)

$$\sigma = \sigma_0 \exp\left(\frac{-E_a}{kT}\right)$$  (2.3)

where $\sigma_0$ is related to the number of charge carriers, $E_a$ is the activation energy. The VTF model is a better fit for polymer electrolytes, which is described by equation (2.4)

$$\sigma = \sigma_0 T^{-\frac{1}{2}} \exp\left(\frac{-B}{T-T_0}\right)$$  (2.4)

where B represents pseudo-activation energy for the conductivity and $T_0$ is the reference temperature, which is about 10-50K lower than the kinetic glass transition temperature.
2.6.2 Solid polymer electrolyte

The term “Solid polymer electrolyte” refers to such kind of electrolyte in which high molecular polymers take the place of solvent, playing both the roles of ion conductor and separator.\(^\text{19}\) Those polymers not only can dissolve lithium salts but also processable into a matrix to impart mechanical strength. Those non-flammable solid polymers electrolytes are much safer compared with solvent electrolyte such as LiPF\(_6\)/ethylene carbonate (EC). They can be fabricated in various ways such as solvent casting, melt-pressing, lamination, extrusion, and in-situ-polymerization.\(^\text{20}\)

In 1973, Wright and co-workers found that the mixture of poly(ethylene oxide)(PEO) and alkali metal salt was able to exhibit high ion conductivity at room temperature.\(^\text{21}\) This launched the new direction in research on polymer electrolyte. PEO is a semi-crystalline polymer with glass transition temperature, \(T_g\), at -60 °C and melting temperature, \(T_m\), at 65 °C. It can also dissolve salt owing to its high dielectric constant (\(\varepsilon = 8\) in the amorphous phase). In early researches, it was perceived that it was crystalline domains that gave SPEs high ionic conductivity, where Li-ions were transported along PEO helices; but later it was conjectured that the amorphous phase mainly took the job of ion transport.\(^\text{22}\) The ion-transport of PEO takes place in the polymer amorphous region based on an “oxygen-assisted hopping” mechanism when temperature is raised above \(T_g\).\(^\text{20}\) Scheme in Figure 2.3 shows a generally accepted model to describe the mechanism of Li-ion transport in PEO based polymer electrolyte. The ether oxygen atoms on the PEO backbones coordinate the Li-ions. Long-range net displacement of Li-ions is carried out by segmental rearrangement and gradual replacement of ligands.\(^\text{23}\) The ionic conductivity is thus related to the local segmental motion of the polymer chain, which is always characterized by their glass transition temperature (\(T_g\)). On the other hand, lithium salts
can also plasticize the PEO matrix, resulting in a lower $T_g$ and better processability. Figure 2.4 shows the ionic conductivity of various PEO-LiN(CF$_3$SO$_2$)$_2$ and PEO-LiClO$_4$ mixtures at different temperatures.$^{24}$

One crude expression of ionic conductivity is $\sigma = n e \mu$, where $n$, $e$, and $\mu$ are the effective number of mobile ions, the elementary electric charge, and the ion mobility, respectively.$^{25}$ From this expression it can be seen that the degree of dissociation of the lithium salts, which is related to $n$, in host polymers is one of the key issue to influence the ionic conductivity. However, the degree of dissociation decreases with increasing salt concentration, but the salt concentration has to keep above a certain amount to provide sufficient number of ions. This implies that an optimal salt concentration should be achieved to maximize the ion conductivity. Generally, the molar ratio Li/O locates around 0.04.$^{25}$

![Figure 2.3 Schematic presentation of the mechanism of Li-ion transport in SPEs$^{10}$](image)
Figure 2.4 The conductivity measured on melted or supercooled mixtures of LiN(CF$_3$SO$_2$)$_2$ and LiClO$_4$ with PEO at 50 and 100 °C as a function of the salt concentration (in mol/kg of mixture)$^{24}$

Since most of room temperature ionic conductivity of simple PEO-LiX complexes fall between $10^{-5}$ and $10^{-9}$ S/cm, which is far short of supporting normal workable criteria in Li-ion cells, great effort has been made to improve the ionic conductivity of solid polymer electrolytes. As the $T_g$ is intimately related to ion transport, the major way to increase the ionic conductivity is to lower the $T_g$ of the electrolyte mixture.

Li-ion conductive polymer like polypropylene oxide (PPO), having a lower $T_g$ had been employed. Another approach was to employ branched polymer, in which PEO side chains were attached to the backbones of polymers with low $T_g$. Polysiloxanes with PEO branches were first synthesized and these system exhibited an ionic conductivity around $10^{-4}$ S/cm at room temperature.$^{26,27}$ However the chemical stability of Si-O-C bonds were of major concern in the electrochemical environment, so Smid and co-workers replaced
Si-O-C with Si-C bond. Shriver and co-workers studied the system based on polyphosphazene (MEEP) backbones and PEO side chains whose $T_g$ was around -80 °C. However, the branched system above failed due to lack of chemical stability.

Besides, in most of the systems with lower $T_g$, mixtures became “liquid like” as they turned into amorphous state to raise ionic conductivity. Their mechanical properties also turned into “liquid like” as solvent electrolytes, which conflicts with the basic motivation of applying solid polymer electrolytes. The introduction of cross-linkable polymer hosts greatly improved the dimensional stability of SPEs. Kang et al. photo-cured polyethylene glycol acrylates (PEGM) mixture with LiCF$_3$SO$_3$ and low molecular weight poly(ethylene glycol) dimethylether (PEGDME). The photo-cured network exhibited a maximum conductivity of $5.1 \times 10^{-4}$ S/cm at 30 °C and displayed oxidation stability up to 4.5V against a lithium reference electrode. Echeverri et al. fabricated polymer electrolyte membranes with ionic conductivities as high as $10^{-3}$ S/cm at room temperature through photo-cured mixtures of poly(ethylene glycol diacrylate) (PEGDA), succinonitrile(SCN) and Lithium bis(trifluoromethane sulfonyl)imide (LiTFSI). The ionic conductivity of fabricated membranes with high SCN contents exceeded the value of $3 \times 10^{-3}$ S/cm at room temperature.

Although the ionic conductivity of SPEs has rapidly increased, it still needs improvement for practical applications. Further more, ionic conductivity is not the only obstacle that challenges the design of SPEs:

1. Most of their mechanical property should be improved against mechanical abuse in real battery since they do not offer superior mechanical strength compared to presently used polyolefin separators.
(2) A more severe problem comes from their interfacial contact with electrode materials. For solvent electrolytes, liquid are accessible to fill into porous materials. However for polymer electrolytes, the surface area of electrolytes-electrode interface are much smaller. As porous materials are applied to both cathode and anode in Li-ion batteries, the high interfacial impedance creates a severe problem.

(3) SPEs still have to face the complex surface chemistry on each electrode in an electrochemical environment.

2.6.3 Gel polymer electrolytes (GPEs)

GPEs are much closer to application as compared with SPEs. The term “gel polymer electrolytes” refers to electrolytes that are based on solvent-swollen polymers mixed with lithium salts. Solvent plays a major role of conducting Li-ions and fully swollen polymers, with a small percentage, acts only to provide dimensional stability. The ionic conductivity of such electrolytes is much higher than most SPEs while the mechanical strength is poorer. Chemical or physical cross-linking is always necessary for GPEs in order to provide greater dimensional stability. Lowering the concentration of polymer eliminates some electrochemical stability issues that might be caused by the oxidative or reductive degradation of polymer segments. However, due to the residual high concentration of solvent, safety issues like leaking, ignition, and combustion, could not be eliminated.

In 1975, Feuillade and Perche came up with the idea that a polymer gel, in which salt-dissolved aprotic solutions trapped in polymer matrix, could be used in lithium cells.32 This idea opened up the new research direction in gel type polymer electrolytes. In these systems, organic solvents play a pivotal role of plasticizer to decrease the Tg of polymer matrix. PEO-LiX gels with PC and/or EC exhibited a room temperature as high
as the order of $10^{-3}$ S/cm while their mechanical property was quite poor according to Chintapalli et al.\textsuperscript{33} Low molecular weight cross-linked PEO with 50\% PC showed good tensile property and ionic conductivity of the order $10^{-4}$ S/cm at 20 °C according to Borghini et al.,\textsuperscript{34} which was two orders of magnitude higher than the amorphous cross-linked PEO-LiClO$_4$. General ionic conductivity of cross-linked gel polymer and/or copolymer fell in the range of $10^{-5}$ to $10^{-4}$ S/cm,\textsuperscript{34} according to Borghini et al.

Another series of polymer matrix was found to exhibit high ionic conductivity in gel electrolytes, PAN\textsuperscript{35-37} and PVDF\textsuperscript{38}. They could reach a conductivity as high as $10^{-3}$ S/cm at 20 °C. Jiang et al. studied PVDF-based gels with EC, PC and a LiX salt and room temperature conductivities of the mixtures with LiN(CF$_3$SO$_2$)$_2$ salt reached $2.2 \times 10^{-3}$ S/cm.\textsuperscript{39}

### 2.7 Ionic liquids (ILs)

Ionic liquids (ILs) refer to salt melt near or below room temperature. Generally, the cations of ILs are linear amines or cyclic amines and the anions can be both inorganic and organic. Their cations can be functionalized thus giving ILs versatile properties. ILs have been recently attracted considerable attention owing to their unique properties. They have good chemical and electrochemical stability, low or no toxicity, low vapor-pressure, non-flammability and ionic conductivity so that they have been studied as potential electrolyte candidates for Li-ion batteries,\textsuperscript{40} fuel cells and solar cells. The main drawback relates to their relatively high viscosity, which results in a low ionic conductivity especially at low temperatures. Ionic conductivities of an ether-based ILs are shown in Figure 2.5.\textsuperscript{41}
Figure 2.5 Plot ionic conductivity of an ester-based ILs against the concentration of LiTFSI$^{40}$
CHAPTER III
MATERIALS AND EXPERIMENTAL TECHNIQUES

3.1 Materials

3.1.1 Poly(ethylene glycol) dimethacrylate

PEGDMA is a photo-curable semi-crystalline polymer whose melting transition temperature \( T_m \) is located at around 9 °C and a glass transition temperature \( T_g \) appears around -64 °C. With the same repeating unit as PEO, it has the ability to transport Li-ions. The structure of PEGDMA is shown in Figure 3.1. PEGDMA was purchased from Sigma-Aldrich. The number average molecular weight, \( M_n \), is 750 g/mol.

3.1.2 Succinonitrile (SCN)

SCN is one of the plastic crystals that can be used as plasticizers to lower the \( T_g \) of polymers. The crystalline structure of SCN is a monoclinic unit cell with completely gauche conformation below its crystal-plastic crystal transition temperature (around -40 °C). Upon transforms into plastic crystal, the SCN turns to a mixed guache and trans-conformation with a body centered cubic (bcc) structure. The structure of SCN is shown in Figure 3.2. SCN (>99%) used in this thesis was purchased from Sigma-Aldrich.

3.1.3 Lithium bis(Trifluoromethanesulfonyl)imide (LiTFSI)

LiTFSI has a large anionic group, TFSI⁻, which attributes a lot to ionic conductivity. It is thermally stable and does not decompose until 360 °C. The melting transition
temperature of LiTFSI is around 234 °C. It dissociates well even in low-dielectric-constant solvents, namely, a higher dissociation. The oxidation potential of LiTFSI is found to be 4.3V versus Li/Li$^+$ in ethylene carbonate/diethyl carbonate (1:1) solution, which indicates a high stability. The structure of PEGDMA is shown in Figure 3.3. LiTFSI (>99.95%) was purchased from Sigma-Aldrich.

Figure 3.1 The structure of PEGDMA

Figure 3.2 The structure of SCN

Figure 3.3 The structure of LiTFSI

Figure 3.4 The structure of photo initiator Irgacure® 819

Figure 3.5 The structure of TEGDME
3.1.4 Other materials used

Solvents, methylene chloride (99.9%) and acetone (99.9%), were bought from Fisher Scientific and Mallinckrodt, respectively. These solvents were used as received without further purification.

Photo initiator, Irgacure® 819, was bought from CIBA. The structure of Irgacure® 819 is depicted in Figure 3.4.

Tetraethylene glycol dimethyl ether (TEGDME) is a kind of low-molecular solvents that can be used as electrolyte in Li-ion batteries. The melting transition temperature ($T_m$) of TEGDME is around -30 °C. TEGDME (≥99%) was purchased from Sigma-Aldrich. Its chemical structure has been shown in Figure 3.5.

3.2 Experimental techniques

3.2.1 Differential scanning calorimetry (DSC)

The melting temperature of PEGDMA, SCN, LiTFSI and their binary, ternary blends were determined using DSC (Model Q200, Thermal Analysis instruments, TA). Samples were sealed hermetically in into aluminum pans with lids using a crimping machine. An empty aluminum pan with a lid was used as a reference pan. Scan was made at a rate of 10 °C/min unless indicated otherwise under constant nitrogen flow to maintain inert atmosphere.

3.2.2 Polarized optical microscope (POM)

In order to study the morphology of coexistence regions, POM (BX60, Olympus) pictures were taken at various regions. Pictures of microstructures were taken using a 35
mm digital camera (EOS 5D Mark II, Canon) and a sample hot stage (TMS93, Linkam) with continuous nitrogen flow.

3.2.3 AC impedance measurement

Ionic conductivities were measured for various PEGDMA/SCN/LiTFSI ternary mixtures using impedance analyzers (Solatron, Model 1260 + 1287). A temperature ramping was made to various PEGDMA/SCN/LiTFSI concentrations to determine the change of conductivity upon temperature and morphology evolution.
CHAPTER IV

BINARY AND TERNARY PHASE DIAGRAM OF PEGDMA, SCN AND LITFSI BLENDS

4.1 Introduction

The rapid evolution of Li-ion battery system and the growing demand for more efficient electrolyte compels the researchers to look for new electrolyte. Single PEM material will neither survive the harsh electrochemical environment nor meet stringent demands of Li-ion batteries. As discussed before, in conventional liquid electrolyte, two or more kinds of solvents are usually mixed together to afford electrolyte diverse properties. Likewise, this idea can also be employed to solid polymer electrolytes in order to enhance its ionic conductivity, mechanical property, and electrochemical stability. The technique of polymer blending is one of the most common and effective ways to improve certain properties of materials. PEGDMA is a kind of semi-crystalline polymer like PEO that can transport the dissociated lithium ions. The mechanism of ion transport is similar to that of PEO-LiX (X refers to an anion group of lithium salt) blend in which amorphous phase take the major responsibility for enhanced ionic conductivity. SCN is a kind of plasticizer having a crystal-plastic crystal transition at -40 °C and a plastic crystal-isotropic transition at 60 °C, i.e., the melting temperature. Moreover, SCN is capable of solubilizing LiTFSI salt and eventually dissociating the Li ions from its bulky anion. So it is of great importance to first establish the binary and ternary phase diagrams
of PEGDMA, SCN and LiTFSI blends to provide guidance to processing window for amorphous PEM.

In this chapter, phase diagrams of binary blends PEGDMA/SCN, SCN/LiTFSI and ternary blends PEGDMA/SCN/LiTFSI have been determined by means of DSC. Morphology of the above blends is investigated by POM to confirm these consistence regions.

4.2 Experimental section

As-received pure LiTFSI was annealed in a vacuum oven for 24 hours at 100 °C to remove all residual moisture prior to blending. The blending was carried out in a glove-box under dry nitrogen gas circulation to avoid moisture absorption. Various concentrations of PEGDMA/SCN binary blends were first simultaneously dissolved in a methylene chloride/acetone solution (40:1 w/w). Then those solutions were cast by evaporating solvent under continuous nitrogen flow at 80 °C for 1 h. The blend samples were kept in a glove-box under nitrogen environment until use.

In the case of PEGDMA/LiTFSI binary blends, various concentrations of PEGDMA/LiTFSI blends were simultaneously dissolved in a methylene chloride/acetone solution mixture (40:1 w/w). Then the binary blend films were solvent cast under continuous nitrogen flow at 100 °C for 1 h. Right after this, those blends were sealed hermetically in DSC aluminum pans with lids and placed under continuous nitrogen flow for morphology investigation.

In the preparation of PEGDMA/SCN/LiTFSI ternary blends, various concentrations of PEGDMA/SCN/LiTFSI blends were simultaneously dissolved in a mixed methylene chloride/acetone solution (40:1 w/w). The same sample preparation protocol of the binary
blends was followed in the present ternary blends. Regarding POM investigation, the solution was poured on glass-slides and films were casted under nitrogen flow.

Differential scanning calorimetry (DSC) experiment was performed to determine the melting points of those blend samples. Samples were weighed in an amount of 5-10 mg and subsequently sealed hermetically into aluminum pans using lids in a glove-box under nitrogen circulation to prevent moisture absorption. One reference pan was made without the samples. The DSC scan rate was kept at a constant ramping rate of 10/min, unless indicated otherwise.

In the case of PEGDMA/SCN binary blends and ternary PEGDMA/SCN/LiTFSI blends, samples were firstly cooled to -50 °C and equilibrated for 15 min, and then ramped to 80 °C. The same procedure was followed in the PEGDMA/LiTFSI blends, except that the sample was ramped to 250 °C to ensure the complete melting of LiTFSI in the blends.

Polarized optical microscopic (POM, Olympus BX60) pictures were taken using a 35 mm digital camera (EOS 5D Mark II, Canon) and a sample hot stage (TMS93, Linkam) by subjecting to nitrogen flow. After solvent casting, the blend samples were covered with a glass-slide and cooled to -50 °C at 5 °C /min and held isothermally for 10 min. Then, samples were heated to desired experimental temperatures at 2 °C/min to examine the blend morphology as a function of temperature.
4.3 Results and discussion

4.3.1 Binary phase diagram

Figure 4.1 Binary phase diagram of SCN/LiTFSI blends and their morphological POM pictures, corresponding to various coexistence regions. A wide isotropic region can be observed.\(^\text{43}\)

It is important to find out the phase behavior of individual binary blends of PEGDMA/SCN, PEGDMA/LiTFSI and LiTFSI/SCN prior to studying the ternary blend of PEGDMA/SCN/LiTFSI. The binary phase diagram of SCN/LiTFSI was already established by Echeverri et al.,\(^\text{43}\) showing various coexistence regions encompassing SCN plastic crystal + liquid, SCN crystal + liquid along with their neat crystalline phases in the extreme SCN-rich regions (Figure 4.1). However, the crystalline structures were clearly
identifiable under the POM investigation at temperatures below SCN’s degradation temperature of 135 °C, e.g., 100 °C (see Figs. 4.1.c and 4.1.d).

Figure 4.2 DSC thermograms of PEGDMA/SCN blends, exhibiting melting point depression of SCN plastic crystals with increasing PEGDMA concentrations and vice versa lowering of PEGDMA crystal melting temperature with increasing SCN concentrations.

To examine the phase behavior of each binary pair, we shall now determine the binary phase diagrams of PEGDMA/SCN and LiTFSI/PEGDMA blends. Figure 4.2 exhibits a set of DSC thermograms of various PEGDMA/SCN blends with compositions varying at 10%wt intervals. The pure SCN exhibits two phase transition temperatures at -40 °C and 58 °C. The former one can be ascribed to a solid crystal-to-plastic crystal (solid-solid) transition, while the latter one corresponds to the plastic crystal-isotropic (solid-liquid) transition. The term “solid crystal” refers to crystals having both positional
and orientational orderings, whereas the term “plastic crystal” refers to crystals having positional ordering only. Upon mixing with PEGDMA, the melting transition temperature of SCN decreased with increasing PEGDMA concentration. However, the solid crystal-to-plastic crystal transition temperature remains almost invariant. The melting transition temperature of pure PEGDMA was found to locate at 9 °C. This transition temperature shifted to a lower temperature after mixing with SCN. In the 50/50, 40/60 and 30/70 blends, neither melting transition nor crystal-plastic crystal transition can be discerned in the DSC thermograms. Upon further increasing SCN to 20/80 PEGDMA/SCN, one exothermic peak was observed around -25 °C, attributable to the cold crystallization of PEGDMA, which may be caused by fast cooling resulting in incomplete crystallization of PEGDMA. Because of its nonequilibrium nature, the above cold crystallization temperature is not included in the present phase diagram; only the endothermic peaks have been considered.

Plotting melting temperatures of those PEGDMA/SCN samples against the weight fraction of PEGDMA establishes the binary phase diagram of PEGDMA/SCN (Figure 4.3). The phase diagram of PEGDMA/SCN blends is of a typical eutectic type, which shows a wide region of isotropic liquid phase ($L$). In this region, there is no identifiable morphology in the POM micrographs, because the picture is totally dark under the cross-polarization (Figure 4.3c). The micrograph shown in Figure 4.3b was taken under the parallel polarization configuration. The picture corresponding to region B shows the coexistence of plastic crystal of SCN forms surrounded by the PEGDMA-rich amorphous (liquid) phase. On the other hand, the region rich in PEGDMA concentration reveals needle type lamellar crystals of PEGDMA were well developed, which correspond to the coexistence of crystal PEGDMA and amorphous SCN.
In order to study the phase behavior of LiTFSI/PEGDMA mixtures, thermograms of various LiTFSI/PEGDMA blends are shown in Figure 4.4. The melting transition temperature of pure LiTFSI and PEGDMA locates at 235°C and 9°C, respectively. A melting transition temperatures depression of samples with high PEGDMA concentration can be observed as increasing the concentration of LiTFSI. On the other hand, the melting transition temperatures of pure LiTFSI move to low temperatures upon mixing with PEGDMA. The endothermic peak around 155°C in the 95/5 sample and pure LiTFSI are
related to the α-crystal to crystal transition of LiTFSI. In the case of mixtures with 10-70%wt PEGDMA, neither melting transition peaks nor α-crystal to crystal transition peaks can be observed from Figure 4.4. The exothermic peaks in mixtures with more than 60%wt PEGDMA can be ascribe to the thermal cross-linking of PEGDMA thus would be excluded from phase diagram.

Figure 4.4 DSC thermograms of LiTFSI/PEGDMA blends, melting temperature of PEGDMA and LiTFSI shifted to lower temperatures by mixing with each other. α-crystal to crystal transition temperature remains at the same place for pure LiTFSI and blend 95/5.
Figure 4.5 Binary phase diagram and morphology of PEGDMA/LiTFSI blends, various coexistence region are verified by POM morphological pictures.

Similarly, we now plot melting temperatures of those LiTFSI/PEGDMA samples against the weight fraction of PEGDMA to establish the binary phase diagram of LiTFSI/PEGDMA mixtures (Figure 4.5). Binary phase diagram of LiTFSI/PEGDMA shows a wider isotropic region ($L$) (Figure 4.5d) compared with that of PEGDMA/SCN blends. In the region where PEGDMA exceeded 80wt%, needle like crystal PEGDMA formed below melting temperatures and the morphology shown in Figure 4.4e indicates the coexistence of crystal PEGDMA and amorphous LiTFSI ($L$)-rich phase. Crystal LiTFSI and amorphous PEGDMA ($L$) coexisted in sample with more than 95%wt LiTFSI at temperatures between 155 °C and $T_m$ (Figure 4.5b). Figure 4.5c reveals the formation of LiTFSI $\alpha$-crystal at temperatures lower than 155 °C.
4.3.2 Ternary phase diagram

With the help of three binary phase diagram established above, further study on phase behavior of PEGDMA/SCN/LiTFSI blends was carried out by means of DSC. Ternary phase diagrams at 25 °C and 0 °C of PEGDMA/SCN/LiTFSI are shown in Figure 4.6 and Figure 4.7, respectively. For both ternary phase diagrams established 0 °C and 25 °C, most part of the triangular concentration plane is covered by the wide isotropic region, which indicates that a processing composition window for highly conductive polymer electrolyte membranes (PEMs). With temperature elevated to 25 °C, the crystal region B \((Cr_{PEGDMA}+L)\) located at high PEGDMA concentration area at 0 °C disappears due to the melting of PEGDMA crystals at 25 °C. Micrographs of blends located at region C captured morphologies of LiTFSI crystal coexisted with liquid SCN and PEGDMA in both phase diagrams at 25 °C and 0 °C. Micrographs of the blends located at region A were taken under parallel polarization since they were totally dark under cross polarization, which indicates the coexistence of plastic crystal SCN with amorphous phase.

4.4 Conclusions

The binary phase diagrams of PEGDMA/SCN blend is of typical eutectic type whereas the binary phase diagram of LiTFSI/PEGDMA blend exhibits a wide single phase region at the intermediate compositions. The ternary phase diagram of PEGDMA/LiTFSI/SCN blend shows a wide isotropic region. As temperature increased from 0 °C to 25 °C, the crystal region at the high PEGDMA concentration corner disappears while the other two coexistence regions contract, but are still discernible. The
ternary phase diagram thus established will provide guidance to studying on room-temperature ionic conductivity of PEMs within this system.

Figure 4.6 Ternary phase diagram of PEGDMA/SCN/LiTFSI at 25 °C shows a wide isotropic region, and two coexistence region are crystal LiTFSI+ liquid and plastic crystal SCN+ liquid
Figure 4.7 Ternary phase diagram and morphology of PEGDMA/SCN/LiTFSI blends at 0 °C, coexistence region of crystal PEGDMA+ liquid is shown at right bottom corner. Morphological POM pictures verified the coexistence regions.
CHAPTER V
IONIC CONDUCTIVITY OF UV-CROSSLINKED SOLID POLYMER ELECTROLYTES

5.1 Introduction

In the previous chapter, we have demonstrated that the ternary phase diagram of PEGDMA/SCN/LiTFSI blends shows a wide isotropic region at room temperature, which indicates that the PEMs formed from this region may possibly have high ion transport. On the other hand, although the crystal phase of PEGDMA can impede ion transport, the ionic conductivity of SCN plastic crystal phase still needs further investigation. It is of great importance to carry out an ionic conductivity study of PEMs at various compositions based on ternary phase diagram.

As mentioned in the previous chapters, the amorphous phase takes the major responsibility of ion transport in the PEO-LiX (X refers to anions, such as PF$_6^-$, ClO$_4^-$ and TFSI) polymer electrolyte. Due to the similarity in the backbone structures, the mechanism of ion conduction in PEGDMA/SCN/LiTFSI electrolyte is similar to that in PEO-LiX electrolytes. As a result, completely amorphous blends are anticipated to exhibit considerably higher ionic transport. However, those amorphous blends, like liquids, will lose mechanical strength and integrity. Hence, a photo curing technique has been sought to form cross-linked networks, termed as polymer electrolyte membranes (PEMs), which can afford much better mechanical strength and integrity.
Ionic conductivity measurement was firstly undertaken in the isotropic regions according to the room temperature ternary phase diagram of PEGDMA/SCN/LiTFSI mixtures that was established in chapter IV. The weight concentration ratio of SCN/LiTFSI was kept at 1:1. Ionic conductivities of PEMs were measured by varying the amount of PEGMDA. To find out how SCN affects the ionic conductivities, the weight concentration ratio of PEGDMA/LiTFSI was kept at 0.5 and ionic conductivities of PEMs were measured as a function of SCN amount. After that, the ionic conductivity variation with temperatures was carried out on PEMs at several compositions.

5.2 Experimental section

Various PEGDMA/SCN/LiTFSI ternary blends were melt-blended in the isotropic region at 50 °C till completely mixed. To be kept away from moisture, blends were kept in a glovebox under continuous nitrogen flow prior to use. Before fabricating polymer electrolyte membranes (PEMs), 2%wt of Irgacure 819® in reference to the PEGDMA amount was added into each mixture as a photo-initiator. A special cell was made in order to prepare PEM samples for AC impedance measurement, whose geometry is shown in Figure 5.1.

Upon fabricating, the mixtures were poured into the square slot whose dimension was $1 \times 10$ mm$^2$ and subsequently exposed to UV-light by using a UV Cure Lamp (Bondwand 350 nm) at an intensity of 5 mW/cm$^2$ for 15 min to fully realize complete polymerization of PEGDMA. Then the upper and bottom parts of the cell were sealed together using screws with a rubber O-ring placed in the circular slot in order to avoid the moisture absorption. All the procedures above were performed in a glovebox under continuous nitrogen flow.
Figure 5.1 Geometry scheme of the cell used for AC impedance measurement. Cell dimension is 10mm(length) × 10mm(width) × 1mm(depth).

Those free-standing PEMs formed after cross-linking were flexible, homogenous and transparent. Ionic conductivities of those membranes were measured by AC impedance measurement using the combination of Solartron 1287 electrochemical interface and 1260 impedance analyzer. Frequency ranges from 1MHz to 0.1Hz with an applied voltage of 200mV. For the measurements that need temperature control, a hot stage with temperature controller was applied. To measure ionic conductivities of PEMs at a certain temperature, all PEMs were kept at this temperature for at least 20 min to ensure uniform temperature throughout the membrane.

5.3 Results and discussion

PEMs that follow the composition line depicted in Figure 5.2 have equal weight concentration (i.e., 1:1 ratio) of LiTFSI and SCN. In the case of AC impedance measurement, Cole-Cole plots in Figure 5.3 recorded the imaginary impedance component Z'' versus real component Z' (defined as Z*=Z’-iZ’'). The complex
impedance $Z^*(j\omega)=Z'$ when $Z''=0$, which means the value $Z'$ equals to bulk resistance $R$ of the membranes when $Z''=0$. Ionic conductivity thus can be calculated according to $\sigma=L/(A\times R)$.

Figure 5.2 Composition plots of PEM0/50/50(black), PEM10/45/45(red), PEM20/40/40(orange), PEM30/35/35(blue), PEM40/30/30(purple), PEM50/25/25(dark yellow) on room temperature ternary phase diagram
Figure 5.3 Cole-cole plots of PEM0/50/50(black), PEM10/45/45(red), PEM20/40/40(orange), PEM30/35/35(blue), PEM40/30/30(purple) and PEM50/25/25(dark yellow) at 25 °C.
The ionic conductivities of each PEM related in Figure 5.3 were calculated in Table 5.1 applied by a membrane size of $0.1\text{cm} \times 1\text{cm}^2$. The ionic conductivity of PEM10/45/45 (i.e., the PEMs was formed from ternary blends having 10wt% PEGDMA, 45wt% SCN and 45wt% LiTFSI, similarly thereafter) was higher than PEM0/50/50, reaching a value of $1.62 \times 10^{-3}$ S/cm (Figure 5.4). The added PEGDMA polymer chain provided an ion-conductive network that helped increase the ionic conductivity of SCN/LiTFSI binary mixtures. However the ionic conductivities of those membranes decreases with further increase of PEGDMA amount. This might be partly due to decreasing Li$^+$ concentration in the PEMs with higher PEGDMA concentration. Another possible explanation could be made by paying attention on the increased PEGDMA/SCN ratios, from PEM10/45/45 to PEM50/25/25, which reflects a weaker plasticization (or dissociation) effect of SCN. This leads to a higher $T_g$, namely less mobility of polymer chains, and as a result ionic conductivity drops. Although lower PEGDMA concentration may result in a higher ionic conductivity, the critical issue is PEGDMA offers the major mechanical strength to the PEMs. A balance of ionic conductivity and mechanical strength should be kept by adjusting the amount of PEGDMA and other two ingredients.

Ionic conductivity of PEM10/45/45, PEM30/35/35 and PEM50/25/25 were measured at temperatures range from room temperature (25 °C) to 65 °C and the results were plotted in Figure 5.5. Each PEM shows an almost linear increase of ionic conductivities in logarithm scale with reciprocal temperature.
Table 5.1 Bulk resistances R of various PEMs and their room-temperature ionic conductivities of the blends.

<table>
<thead>
<tr>
<th>Compositions PEGDMA/SCN/LiTFSI</th>
<th>A (cm^2)</th>
<th>L (cm)</th>
<th>R (Ω)</th>
<th>Ionic conductivity (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0/50/50</td>
<td></td>
<td></td>
<td>87.7</td>
<td>1.14 × 10^{-3}</td>
</tr>
<tr>
<td>10/45/45</td>
<td></td>
<td></td>
<td>61.7</td>
<td>1.62 × 10^{-3}</td>
</tr>
<tr>
<td>20/40/40</td>
<td></td>
<td></td>
<td>103.5</td>
<td>9.66 × 10^{-4}</td>
</tr>
<tr>
<td>30/35/35</td>
<td>1.00</td>
<td>0.1</td>
<td>199.7</td>
<td>5.00 × 10^{-4}</td>
</tr>
<tr>
<td>40/30/30</td>
<td></td>
<td></td>
<td>659.7</td>
<td>1.52 × 10^{-4}</td>
</tr>
<tr>
<td>50/25/25</td>
<td></td>
<td></td>
<td>801.9</td>
<td>1.25 × 10^{-4}</td>
</tr>
</tbody>
</table>

Figure 5.4 Ionic conductivities of PEMs with a PEGDMA concentration variation from 0% to 50%wt at 10%wt interval. PEM10/45/45 reaches a highest room temperature ionic conductivity value of 1.62 × 10^{-3} S/cm.
Figure 5.5 Arrhenius plots of conductivities versus reciprocal temperature for PEM10/45/45(purple), PEM30/35/35(orange) and PEM50/25/25(green). Ionic conductivity increased linearly in log scale versus reciprocal absolute temperatures.

In order to gain insight into the versatile roles of SCN in PEMs, ionic conductivities of PEMs were measured as a function of SCN concentrations. The selected compositions were plotted in room temperature ternary phase diagram (Figure 5.6).

In those PEMs the concentration ratio of PEGDMA/LiTFSI were kept at 1:2 and the SCN concentration various from 20% to 80%wt at 10%wt interval. Figure 5.6 depicts the Cole-Cole plots from AC impedance measurement and Figure 5.8 correspondingly demonstrated the variation in ionic conductivities of those samples as a function of concentration of SCN. The ionic conductivities markedly increased with the increase of SCN amount till they reached the composition 13.3/60/26.6. A drop in ionic conductivity values occurs at the same time when the composition enters the SCN plastic crystal region. This variation reveals that SCN can significantly increase the ionic conductivity in amorphous phase, which can be ascribed to its plasticization effect and high Li-ion
dissociation ability. However plastic crystal SCN does not work as well as liquid ones do. This might partly contributes to the ionic conductivity decline.

![Image of ternary phase diagram with composition plots](image)

Figure 5.6 Composition plots of PEM26.7/20/53.3(black), PEM23.3/30/46.7 (red), PEM20/40/40(light blue), PEM16.7/50/33.3(green), PEM13.3/60/26.6(pink), PEM10/70/20(dark yellow) and PEM6.7/80/13.3(dark blue) on room temperature ternary phase diagram. The last two PEMs fall into SCN plastic crystal region according to the phase diagram.

In contrast, ionic conductivities of various PEMs with TEGDME at above compositions were measured, where the only difference was a substitution of TEGDME for SCN. TEGDME, a conventional solvent for liquid electrolytes, has a melting transition temperature at -30 °C. The PEMs at above compositions remained totally amorphous. This contrast conveyed information in two aspects: (1) Small molecule
plasticizer such as SCN prominently contributes to Li-ion transport ability of PEMs at lower concentration but excess SCN can be adverse. (2) The presence of plastic crystal SCN would reduce the ionic conductivity of PEMs.

Figure 5.7 Cole-Cole plots of PEMs in which concentration of SCN varies from 20% to 80%wt at 10%wt interval. Color-composition correspondence was identical to those in Figure 5.5
Figure 5.8 Ionic conductivity variations of PEMs depending on the concentration of SCN and TEGDME. SCN can significantly increase the ionic conductivity in the liquid state.

5.4 Conclusions

Totally amorphous free-standing PEMs can be fabricated through amorphous PEGDMA/SCN/LiTFSI mixtures after UV-crosslinking process. PEMs in this region exhibited room temperature ionic conductivity as high as a magnitude of $10^{-3}$ S/cm, which was 2 orders of magnitude higher than that of PEO-LiX complex electrolytes. The ionic conductivities of those PEMs increase with increasing temperature and obeyed the Arrhenius law. Cross-linked PEGDMA not only contributed to ion transportation but also provided a stretchable network. SCN worked as a versatile additive to pure polymer-LiX complex electrolyte, resulting from both its ability to plasticize PEGDMA and dissociate LiTFSI. Above results revealed the great potential application of those PEMs to real batteries.
CHAPTER VI

THERMAL AND ELECTROCHEMICAL STABILITY OF UV-CROSSLINKED POLYMER ELECTROLYTE MEMBRANES

6.1 Introduction

As demonstrated in Chapter V, PEMs formed by UV-curing of PEGDMA/SCN/LiTFSI blends exhibited very high ionic conductivity, which made them applicable to Li-ion batteries from the conductivity perspective. However, PEMs should survive a much stringent environment in practical application, which required further inspection into other properties. Although the substitution of solid polymer in lieu of volatile solvent makes electrolyte non-flammable, the thermal stability of the complex, especially when plasticizer is added, need careful investigations throughout the possible working temperature window of Li-ion batteries. Meanwhile, the complex chemical constitutions of PEMs cause concerns on their electrochemical stability. PEMs should be stable between the working voltage ranges of Li-ion batteries, namely they should have a suitable electrochemical window.

In this chapter, thermal and electrochemical stability of PEMs have been investigated. TGA measurements were undertaken to evaluate the intrinsic thermal stability of PEMs in open condition, while ionic conductivity measurements were conducted in a close environment at evaluated temperatures above 65 °C. Oxidation and reduction voltage limits of PEMs were examined by cyclic voltammetry (CV) scans with
a stainless steel as both working and reference electrode and lithium metal as a counter electrode.

6.2 Experimental section

The procedures to make ternary mixtures were kept identical to those in chapter V. Before fabricating PEMs, 2%wt of Irgacure 819® relative to the PEGDMA amount was added into each mixture as a photo-initiator. Mixtures were subsequently casted onto a glass slide and kept at a thickness of 150µm by three layers of scotch tape spacers. Casted mixtures cured into membranes by exposing to UV-light at an intensity of 5 mW/cm² for 15 min at ambient temperature.

Thermogravimetric analysis (TGA) PEM was performed to investigate its thermal properties in an open cell. Neat PEGDMA, SCN, LiTFSI and PEM20/40/40, PEM10/70/20 were examined using a thermogravimetric analyzer (TGA - Model Q50, TA Instruments) at a heating rate of 10 °C/min from room temperature to 800 °C under nitrogen atmosphere. Isothermal TGA was performed by annealing the samples at various temperatures from 95 to 135 °C at 20 °C interval for 3h.

AC impedance measurements of PEMs were employed to determine the ionic conductivity by using the same experimental method as described in chapter V. Isothermal AC impedance measurement were performed for 3h after a temperature jump to desired temperatures.

To determine the electrochemical stability window of PEMs, all membranes were cut into a proper size for both fitting into the coin cell and covering the electrodes. PEMs were sandwiched between a stainless steel working electrode disc and a lithium foil serving as reference and counter electrode, all of which were assembled into a coin cell
afterwards. Cyclic voltammetry (CV - Model 1260+1287, Solartron) measurements were carried out for at least 5 cycles at a constant scanning rate of 1 mV/s. The effective surface area of electrodes was 1×1 cm².

6.3 Results and discussions

6.3.1 Thermal stabilities

Figure 6.1 reveals an excellent thermal stability up to 370 °C and 340 °C for neat LiTFSI and PEGDMA respectively while SCN appears stable up to 130 °C. Echeverri et al.⁴³ carried out an isothermal TGA for neat SCN at temperatures ranging from 80 to 130 °C and illustrated the weight loss of SCN as a function of time (Figure 6.2). Neat SCN shows no weight change at 80 °C for a duration of 30 min tested, whereas an 8% weight loss after 30min can be witnessed from the isothermal TGA thermogram at 90 °C. At further elevated test temperatures, weight loss becomes more severe. This observation may be attributed to vaporization of SCN at temperatures higher than 90 °C thus raises the concern about thermal properties of PEMs. TGA thermogram of PEM10/70/20 in Figure 6.1 indicates the membrane undergoes a two-stage weight loss which may ascribed to the vaporization of SCN, with an onset temperature of around 135 °C, and degradation of PEGDMA starting around 375 °C, respectively. Similarly, isothermal TGA of PEM10/70/20 were performed to further investigate the thermal stability (Figure 6.3) for an extended duration of 180 min. PEM10/70/20 lost almost 40% of its initial weight at 135 °C for 40min.
Figure 6.1 LiTFSI and PEGDMA are thermal stable up to 370 °C and 340 °C whereas the weight loss of SCN happens from 130 °C.

Figure 6.2 isothermal TGA of SCN at temperatures ranging from 80 °C to 130 °C for 30min⁴³
Figure 6.3 Isothermal TGA at 135 °C of PEM10/70/20 shows a loss of 40% initial weight for 40 min in an open cell.

Being an open system, TGA could not reveal exactly the thermal stability of PEMs in the actual application such as in a sealed lithium cell. AC impedance measurement of PEMs sealed in a cell was then introduced to provide an investigation of the performance in the close system. Figure 6.4 illustrates the ionic conductivity variation of PEM10/70/20 and PEM 13.3/60/26.6 upon temperatures. The slope change around 35 °C of PEM10/70/20 can be ascribed to a melting transition, which was verified by POM morphology pictures. This phenomenon in another aspect indicates that SCN amorphous phase has a better Li⁺ transport capability than the plastic crystal phase. Ionic conductivity of PEMs increases linearly with reciprocal temperature below 95 °C and the slope gradually declines after reaching 115 °C. According to the isothermal TGA results, SCN should undergo vaporization at such high temperatures. AC impedance measurements of PEM10/70/20, carried out isothermally at 60 °C, 95 °C, 115 °C and 135 °C (Figure 6.5), showed no evidence of obvious ionic conductivity change at 95 and
115 °C, but there was a slight decline at 135 °C. Explanation can be made as the close system prevented the escaping of sublimated SCN and blocked further vaporization of SCN remained in the PEM networks.

Figure 6.4 Ionic conductivity variations upon temperature of PEM10/70/20 and PEM 13.3/60/26.6. Two slope changes can be observed for PEM10/70/20. The one around 35 °C is due to the melting of SCN plastic crystals, confirmed by POM pictures A, B and C.
Ionic conductivity variation upon test time exists but was not pronounced.

6.3.2 Electrochemical stability

For the purpose of establishing an electrochemical stability window of PEMs, cyclic voltammetry was performed. Figure 6.6 shows the first 5 scan cycles for PEM30/35/35. Each scan started from the open circuit potential (OCP) and then underwent a cathodic scan to -0.5V versus Li$^+$/Li. An anodic scan followed it, sweeping from -0.5V up to 6.0V versus Li$^+$/Li, and finally went the cathodic way back to OCP.

Lithium platting was observed at a potential in the vicinity of -0.3V and lithium stripping occurred from -0.5V to 0.5V versus Li$^+$/Li in the cathodic and anodic scans, respectively. Lithium platting means Li$^+$ gets reduced to lithium metal and deposits on the surface of the working electrode, i.e., stainless steel in this case. Similarly, lithium
stripping reflects the opposite process, whereby lithium metal deposition undergoes an oxidation reaction, producing Li⁺.

\[
\text{Li}^+ + e^- \rightarrow \text{Li} \quad \text{(Lithium platting)} \quad (6.1)
\]

\[
\text{Li} \rightarrow \text{Li}^+ + e^- \quad \text{(Lithium stripping)} \quad (6.2)
\]

The minor bump occurring around 1.0V versus Li⁺/Li for all 5 cycles was probably associated with residual O₂ in the coin cells. In the first scan, as in Figure 6.6a, a bump came up around 4.3V before the occurrence of large oxidation peak above 5V versus Li⁺/Li, which has not yet been fully understood by investigators. By applying a stainless steel as a working electrode, Dautzenberg et al.⁴⁴ compared the oxidation limits of PC/EC/LiX electrolytes with different lithium salts and similar bump only occurred in LiTFSI. They gave a possible explanation for the observed bump at this potential that it may be due to a partially reversible dissociation of the N(CF₃SO₂)₂⁻ anion, where N(CF₃SO₂)₂⁻ was similar to TFSI⁻. Another comparison was made between two different working electrodes (Ni and stainless steel) by Jiang et al.³⁹, who indicated that stainless steel also contributed to the bump around 4.3V versus Li⁺/Li. To summarize, this small bump reflects oxidation of decomposed TFSI⁻ anions and stainless steel in some degree associated in such reactions. The oxidation peak depressed with increasing cycle numbers, and meanwhile, two reduction peaks appeared around 1.3V and 1.7V versus Li⁺/Li which becoming more pronounced with repeated cycles. This indicates some LiTFSI oxidation products undergo irreversible reduction reactions during the cathodic scan.

In some papers, investigators claimed stabilities up to 5V (the potential larger oxidation peak arose) in similar electrolytes systems even though similar bump did occur around 4.3V. However, the exact oxidation limit depends on the reversibility of reactions
related to this bump. To investigate this, another set of cyclic voltammetry scans was performed with anodic voltage limit reduced to 4.5V versus Li$^+$/Li (Figure 6.7). Two reduction peaks can be observed around 0.8V and 1.4V after the first cycle. The processes related to these peaks have not been fully understood. Bonino et al.$^{45}$ interpreted these peaks as the reactions of the anion or caused by impurities. Aurbach et al.$^{46}$ proposed a series of reduction reactions as follows by investigating reduction product formed through \textit{in-situ} FTIR spectroscopy.

\begin{align*}
\text{Li[N(CF}_3\text{SO}_2)_2] + 4e^- + 4Li^+ & \rightarrow \text{Li}_3\text{N} \downarrow + 2\text{Li(CF}_3\text{SO}_2) \downarrow & (6.3) \\
2\text{Li(CF}_3\text{SO}_2) + ne^- + n\text{Li}^+ & \rightarrow \text{Li}_2\text{S}_2\text{O}_4 \downarrow + C_2\text{F}_3\text{Li}_y + \text{LiF} \downarrow & (6.4) \\
\text{Li}_2\text{S}_2\text{O}_4 + 6e^- + 6\text{Li}^+ & \rightarrow 2\text{Li}_2\text{S} \downarrow + 4\text{Li}_2\text{O} \downarrow & (6.5)
\end{align*}

According to Figure 6.7, although some oxidation reactions occur around 4.3V, the reaction shows a good reversibility since the current density to each peak remain almost the same. PEM 30/35/35 exhibits a good stability in this voltage range. However, conservatively, the stable electrochemical window should be fixed from 0.5V-4.3V versus Li$^+$/Li, which is good enough for application in most Li-ion batteries.

6.4 Conclusions

Thermal and electrochemical stability of PEMs are investigated. Although TGA result indicated evaporation of SCN in membranes could happen at relatively a low temperature, 95 °C for example, no evidence of conductivity change could be found if sealing PEMs hermetically into a cell and kept them isothermally at temperatures up to 135 °C for 3h. Anyway, even 95 °C is far higher than normal working temperature for a Li-ion battery. This indicates the present PEMs with PEGDMA/SCN/LiTFSI are thermally stable for battery applications. In the case of electrochemical stability, PEMs
showed outstanding stabilities in the voltage range of 0.5V-4.3V versus Li+/Li. PEMs are stable by themselves if applied to lithium ion batteries. Electrochemical stability with other reactive electrodes can be determined in future via series of half-cell tests.
Figure 6.6 First 5 cyclic voltammetry scans that goes between -0.5V and 6V for PEM 30/35/35. Working electrode: stainless steel; reference and counter electrode: lithium metal; scan rate: 1mV/s; surface area of electrodes: 1cm$^2$. 
Figure 6.7 cyclic voltammetry result of a scan goes between -0.5V and 4.5V for PEM 30/35/35. Working electrode: stainless steel; reference and counter electrode: lithium metal; scan rate: 1mV/s; surface area of electrodes: 1cm$^2$. Peaks around 0.8V and 1.4V didn’t appear until the second cycle, indicating these peaks may relate to the bump around 4.3V versus Li$^+$/Li.
Highly conductive polymer electrolyte membranes (PEMs) have been fabricated through UV cross-linking of poly(ethylene glycol) dimethacrylate (PEGDMA), succinonitrile (SCN) and bis(trifluoromethane)sulfonimide (LiTFSI) blends. Binary and ternary phase diagram approach was applied to provide control of the ionic conductivities of fabricated PEMs.

In chapter IV, means of differential scanning calorimetry (DSC) and polarized optical microscopy (POM) were carried out in order to establishing binary and ternary phase diagrams of PEGDMA, SCN and LiTFSI mixtures. The room temperature ternary phase diagram exhibited a wide isotropic region on the triangle composition plane, which indicated a wide processing composition window for PEMs.

In chapter V, ionic conductivity of PEMs with varies compositions were investigated by means of AC impedance measurement. Ternary phase diagram worked as an important instruction. The ionic conductivity was found to be as high as \(10^3\) S/cm at room temperature and increases with elevated temperatures, following Arrhenius type. Cross-linked PEGDMA provided a conductive network for PEM and it can increase the ionic conductivity of SCN/LiTFSI binary blends. SCN can significantly improve ionic conductivity within certain concentration range. The presence of plastic crystal phase SCN can probably impede ion transport.
For further application probability study, thermal and electrochemical stability of PEMs were examined in chapter VI. TGA with a heating rate of 10°C/min shows the weight loss onset temperature of PEM was around 135 °C and isothermal TGA observed a significant weight loss within 180 min at temperature as low as 90 °C. This thermal instability was ascribed to the vaporization of SCN. However, by keeping PEMs in an electrochemical cell at 135 °C for 150min, no SCN loss can be evidenced through ionic conductivity value. PEM can be thermally stable in a close system.

To establish the electrochemical stability window, two sets of cyclic voltammetry scans were performed between -0.5V-6V and -0.5V-4.5V, respectively. Lithium foils worked as both reference and counter electrode. Stainless steel was chosen as working electrode. The oxidation voltage limit of PEM was found to be 4.3V versus Li⁺/Li.
REFERENCES


