# CHAPTER 3

# METHODOLOGY

## 3.1 Introduction

In this work, the polymer electrolyte solutions were prepared using reflux method. Reflux method was chosen to dissolve the materials at temperatures higher than ambient in order to provide greater energy in the form of heat to dissolve the materials and mix them until homogeneous solutions were obtained. Besides that, the use of acetone and the action of vigorous stirring to mix the polymer electrolyte materials would result in the evaporation of the solvent even at room temperature, which will cause solvent loss from the samples. Miao et al. (2008) reported that the dissolution of semi–crystalline PVdF–HFP occurs easier at higher temperatures to refrain the growth of PVdF–HFP crystallites. They observed that PVdF–HFP was completely dissolved with heating of about 2 h at temperatures between 50 and 60 °C, which influenced the duration and temperature used to prepare polymer electrolyte films in this work.

Tetrahydrofuran (THF) is a common solvent used to dissolve the components of polymer electrolytes and is often evaporated from the polymer electrolyte solutions by drying at around 50 °C for long duration, i.e. for 12 hours as reported in the preparation of PVdF–HFP–EC–PC containing various Li salts [Manuel Stephan et al., 2005] and for 24 hours as reported in polymer electrolytes based on PEMA–PVdF blend [Sivakumar et al., 2007] and PVdF–HFP–$LiClO_4$ containing $AlO[OH]_n$ and alumina ($\gamma$–$Al_2O_3$) [Wilson et al., 2007]. On the other hand, acetone has a low boiling point (~56 °C). This allows evaporation of acetone to occur easily and polymer electrolyte films can be obtained in a short time (few hours as compared to overnight). Thus, acetone is used as solvent for all materials as it is compatible with the materials used in this work. Another advantage of using acetone as solvent in this work are its high dielectric constant ($\varepsilon$=20.7) which helps the dissolution of the components (i.e. polymers, salt, plasticizers, ionic liquids). Acetone is also non–toxic, available and can be obtained at low cost. Literature in which PVdF–HFP–based polymer electrolytes are formed using acetone as solvent has been reported [Shalu et al., 2012].

To benefit from the advantages of the two polymers, in this work PEMA and PVdF–HFP have been blended at a fixed PEMA:PVdF–HFP weight ratio of 70:30 to produce PEMA/PVdF–HFP blend polymer electrolytes with high transparency and good mechanical stability. Lithium triflate has been added to provide the charge carriers.

## 3.2 Materials

Poly(ethyl methacrylate) (PEMA) ($M_w$ = 515000, CAS = 9003–42–3, density = 1.11 g $cm^{-1}$) in powder form, poly(vinylidene fluoride–*co*–hexafluoropropylene) (PVdF–HFP) (CAS = 9011–17–0, density = 1.78 g $cm^{-1}$) in pellet form, lithium trifluoromethanesulfonate (LiTf) (density = 1.90 g $cm^{-1}$), ethylene carbonate (EC) (98 % purity, density = 1.32 g $cm^{-1}$) and anhydrous propylene carbonate (PC) (99.7 % purity; density = 1.19 g $cm^{-3}$), 1–butyl–3–methyl imidazolium iodide (BMII) (density = 1.49 g $cm^{-1}$) and 1–butyl–3–methyl imidazolium trifluoromethanesulfonate (BMITf) (density = 1.29 g $cm^{-1}$) were purchased from Aldrich. Acetone was obtained from J.T. Baker.

## 3.3 Sample Preparation

### 3.3.1 Solid PEMA/PVdF–HFP–LiTf Polymer Electrolyte Films

PEMA/PVdF–HFP blend polymer electrolyte films were prepared using the reflux method. The PEMA:PVdF–HFP ratio is 70:30 as this composition produces homogenous polymer blend which is suitable to prepare polymer electrolytes. Different amounts (5, 10, 15, 20, 25, 30, 35 and 40 wt. %) of LiTf salt were added to the polymer solution in acetone. The mixtures were magnetically stirred vigorously under reflux at 55 to 65 $^{o}$C for 2 h to form PEMA/PVdF–HFP polymer blend electrolytes. Figure 3.1 illustrates the reflux set–up used to prepare polymer electrolyte films.

**Figure 3.1 Image of reflux set–up during preparation of polymer electrolytes**

LiTf salt was heated at 130 °C for 3 h to eliminate any moisture prior to use. The resultant solutions consisting of salt and the two polymers were cast onto glass petri dish and dried at 45 °C in an oven for several hours to evaporate the solvent until transparent films were obtained. The polymer films formed were kept in the dessicator for several days for further drying before characterization. Figure 3.2 depicts the flow chart of the preparation of PEMA/PVdF–HFP–LiTf polymer electrolyte films.

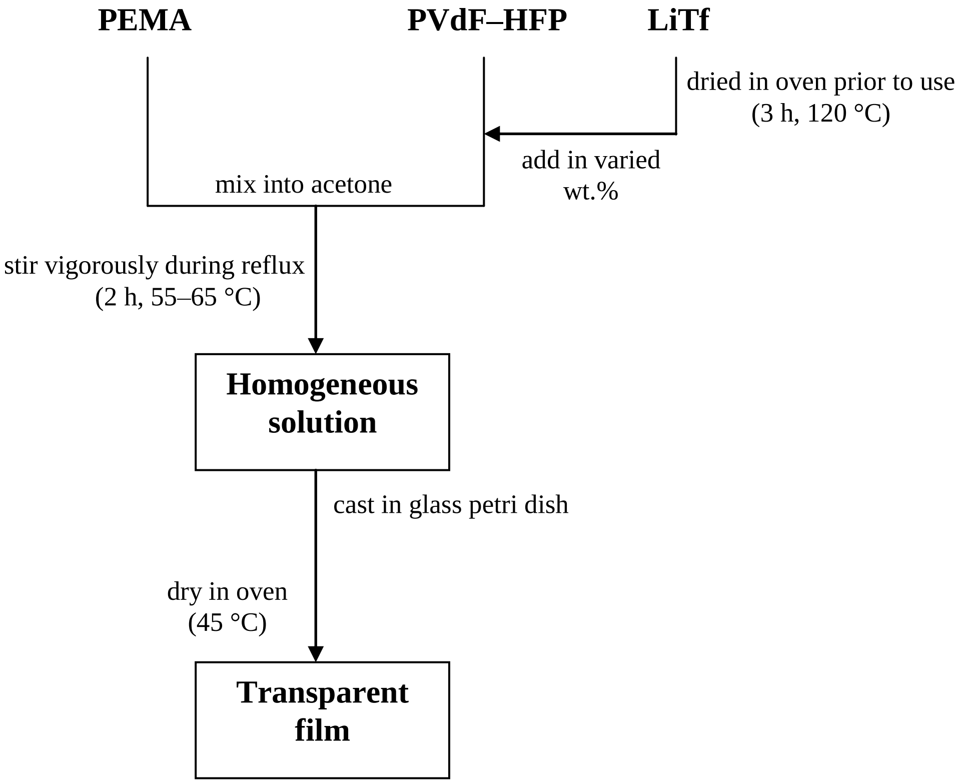

**Figure 3.2 Flow chart showing the preparation procedure of PEMA/PVdF–HFP–LiTf polymer electrolyte films**

The image of the polymer electrolyte films formed is shown in Figure 3.3. The designations of PEMA/PVdF–HFP–LiTf polymer electrolyte samples are listed in Table 3.1. The samples are named with S representing salt, and the number proceeding it is the amount of wt. % of LiTf salt added into the polymer blend.

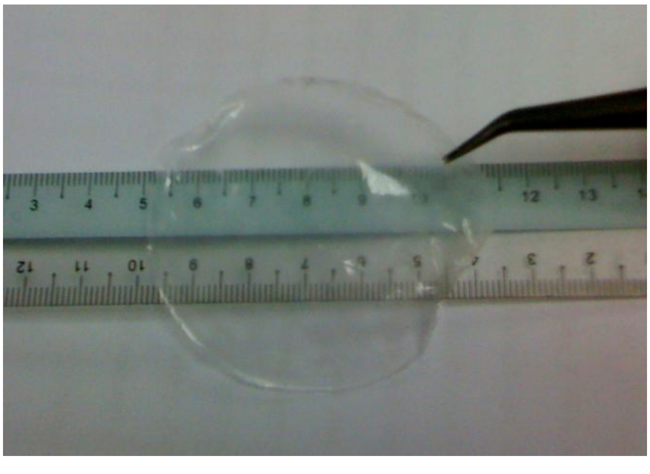

**Figure 3.3 Image of transparent PEMA/PVdF–HFP based polymer electrolytes**

**Table 3.1 Composition of PEMA/PVdF–HFP–LiTf polymer electrolyte system**

| Designation | PEMA (g) | PVdF–HFP (g) | LiTf (g) | PEMA : PVdF–HFP : LiTf (w:w) |
|---|---|---|---|---|
| S–0 | 0.7 | 0.3 | 0.0000 | 70.00 : 30.00 : 0.0 |
| S–5 | 0.7 | 0.3 | 0.0526 | 66.50 : 28.50 : 5.0 |
| S–10 | 0.7 | 0.3 | 0.1111 | 63.00 : 27.00 : 10.0 |
| S–12.5 | 0.7 | 0.3 | 0.1429 | 61.25 : 26.25 : 12.5 |
| S–15 | 0.7 | 0.3 | 0.1765 | 59.50 : 25.50 : 15.0 |
| S–20 | 0.7 | 0.3 | 0.2500 | 56.00 : 24.00 : 20.0 |
| S–25 | 0.7 | 0.3 | 0.3333 | 52.50 : 22.50 : 25.0 |
| S–30 | 0.7 | 0.3 | 0.4286 | 49.00 : 21.00 : 30.0 |
| S–35 | 0.7 | 0.3 | 0.5385 | 45.50 : 19.50 : 35.0 |
| S–40 | 0.7 | 0.3 | 0.6667 | 42.00 : 18.00 : 40.0 |

### 3.3.2 Plasticized PEMA/PVdF–HFP–LiTf–EC and PEMA/PVdF–HFP–LiTf–PC Polymer Electrolyte Films

EC and PC were chosen as plasticizers due to their high dielectric constant and viscosity as listed in Table 2.3. As EC is more viscous compared to PC at room temperature, the use of larger amount of EC should be avoided. The plasticizer containing polymer electrolytes were prepared by adding 2, 4, 6, 8 and 10 wt.% EC and PC into the highest conducting PEMA/PVdF–HFP–LiTf composition. The use of plasticizer(s) in polymer electrolytes tends to produce polymer electrolytes with reduced mechanical stability [Srivastava and Chandra, 2000]. However, this is not the case in our work as mechanically strong EC and PC–plasticized films, no different than unplasticized films were obtained. This could be due to the low content (below 10 wt.%) of plasticizers used.

#### 3.3.2.1 PEMA/PVdF–HFP–LiTf–EC System

EC is present as an odorless and colorless solid at room temperature with a melting point of 36.4 °C. When mixed with acetone, EC will dissolve and then mix with other components i.e. PEMA, PVdF–HFP, LiTf to form a homogeneous mixture. The

EC–containing polymer electrolyte films were prepared using the reflux method. Different amounts (2, 4, 6, 8 and 10 wt. %) of EC were added to the optimized polymer blend–salt composition in acetone. The mixtures were magnetically stirred vigorously at 55 to 65 $^{o}$C for 2 h to form PEMA/PVdF–HFP–LiTf–EC polymer electrolytes. LiTf salt was heated at 130 °C for 3 h to eliminate moisture prior to use. The resultant transparent solutions were cast onto glass petri dish and dried at 45 °C in an oven for several hours to evaporate the solvent until transparent films were obtained. The polymer electrolyte films formed were kept in the dessicator for several days for further drying before characterization. Table 3.2 shows the designation and composition of EC–added polymer electrolytes. Figure 3.4 depicts the flow chart for the preparation of PEMA/PVdF–HFP–LiTf–EC polymer electrolyte films. The EC–added samples are named with EC representing the plasticizer, and the number proceeding it refers to the wt. % of EC added to the optimized polymer blend–salt composition.

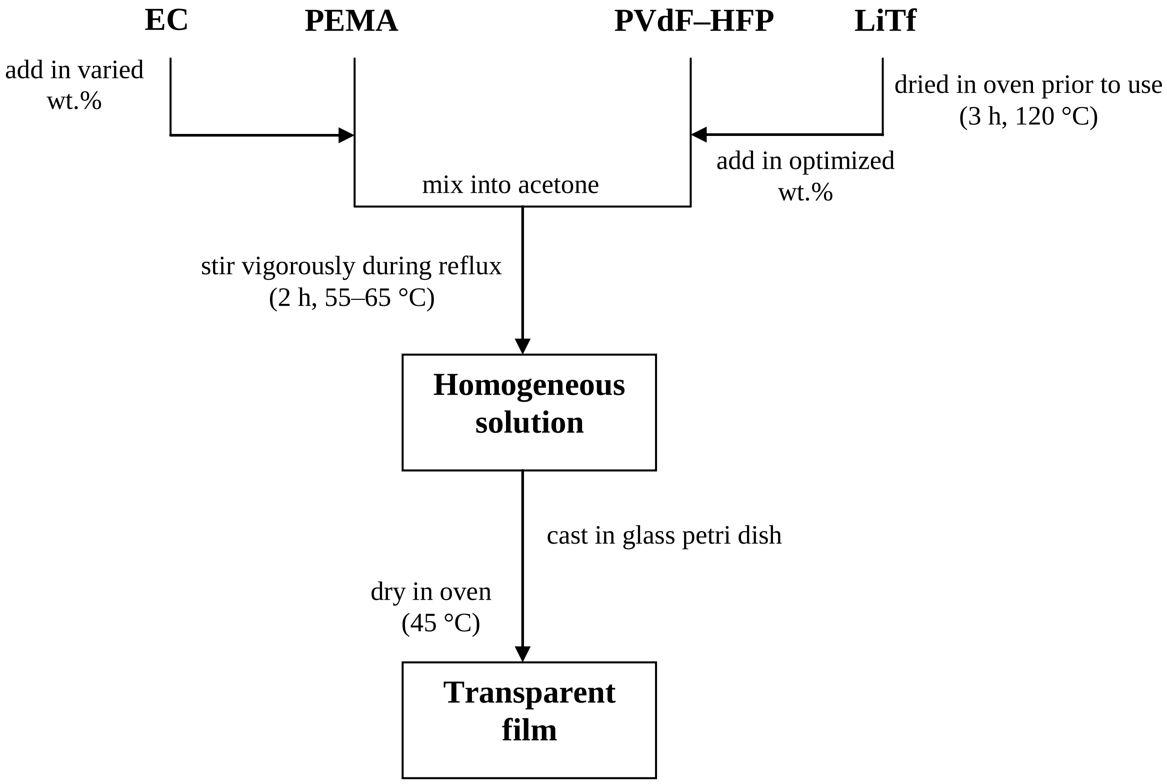

**Figure 3.4 Flow chart for the preparation procedure of PEMA/PVdF–HFP–LiTf–EC polymer electrolyte films**

**Table 3.2 Composition of PEMA/PVdF–HFP–LiTf–EC polymer electrolyte system**

| Designation | PEMA (g) | PVdF–HFP (g) | LiTf (g) | EC (g) | [PEMA:PVdF–HFP] : LiTf : EC (w:w) |
|---|---|---|---|---|---|
| EC–0 | 0.7 | 0.3 | 0.4286 | 0 | 70.0 : 30.0 : 0.0 |
| EC–2 | 0.7 | 0.3 | 0.4286 | 0.02916 | 68.6 : 29.4 : 2.0 |
| EC–4 | 0.7 | 0.3 | 0.4286 | 0.05953 | 67.2 : 28.8 : 4.0 |
| EC–6 | 0.7 | 0.3 | 0.4286 | 0.09119 | 65.8 : 28.2 : 6.0 |
| EC–8 | 0.7 | 0.3 | 0.4286 | 0.1242 | 64.4 : 27.6 : 8.0 |
| EC–10 | 0.7 | 0.3 | 0.4286 | 0.1587 | 63.0 : 27.0 : 10.0 |

#### 3.3.2.2 PEMA/PVdF–HFP–LiTf–PC System

PC is a liquid with density of 1.2 g $cm^{-3}$ at 25 °C. The PC–added polymer electrolyte films were prepared following the same procedure as the EC–added polymer electrolyte films. Table 3.3 shows the designation and composition of PC–added polymer electrolytes.

**Table 3.3 Composition of PEMA/PVdF–HFP–LiTf–PC polymer electrolyte system**

| Designation | PEMA (g) | PVdF–HFP (g) | LiTf (g) | PC (g) | PC (mL) | [PEMA/PVdF–HFP] : LiTf : PC (w:w) |
|---|---|---|---|---|---|---|
| PC–0 | 0.7 | 0.3 | 0.4286 | 0.0000 | 0.0000 | 70.0 : 30.0 : 0.0 |
| PC–2 | 0.7 | 0.3 | 0.4286 | 0.0292 | 0.0245 | 68.6 : 29.4 : 2.0 |
| PC–4 | 0.7 | 0.3 | 0.4286 | 0.0595 | 0.0501 | 67.2 : 28.8 : 4.0 |
| PC–6 | 0.7 | 0.3 | 0.4286 | 0.0912 | 0.0767 | 65.8 : 28.2 : 6.0 |
| PC–8 | 0.7 | 0.3 | 0.4286 | 0.1242 | 0.1045 | 64.4 : 27.6 : 8.0 |
| PC–10 | 0.7 | 0.3 | 0.4286 | 0.1587 | 0.1335 | 63.0 : 27 : 10.0 |

The PC–based samples are named with PC representing the plasticizer, and the number proceeding it is the wt. % of PC present. The flow chart of the preparation of PEMA/PVdF–HFP–LiTf–PC polymer electrolyte films is depicted in Figure 3.5.

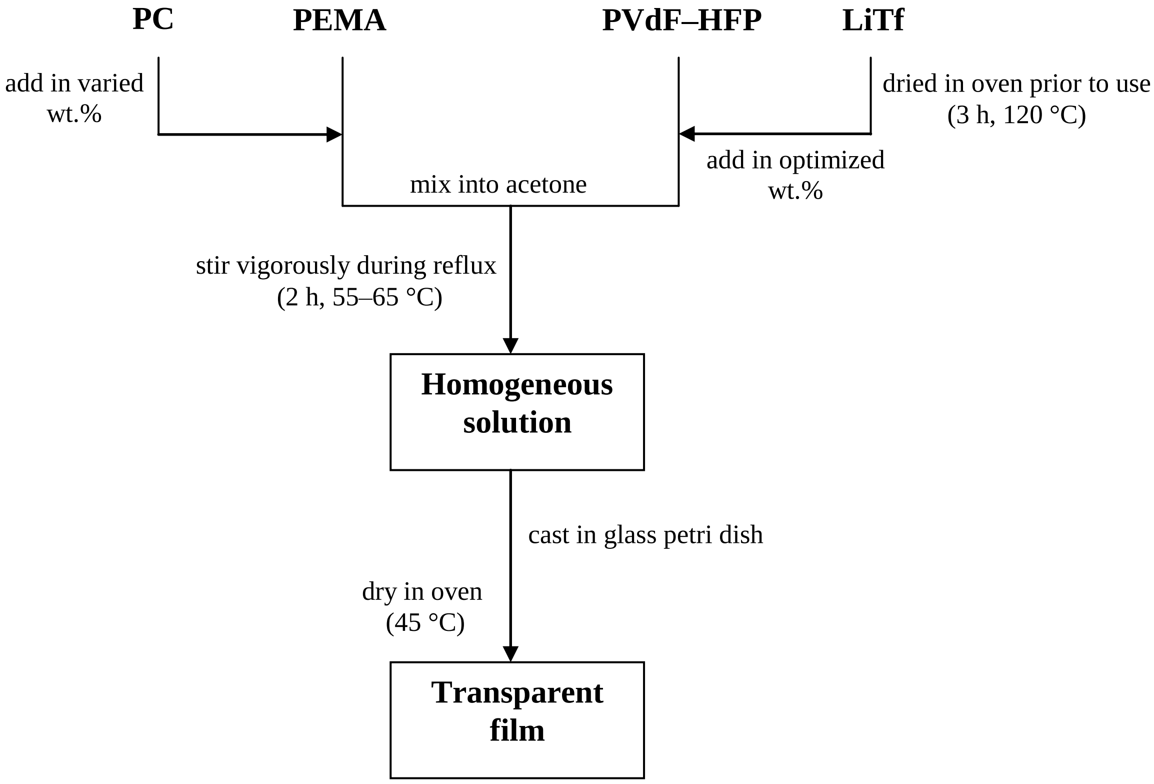

**Figure 3.5 Flow chart for the preparation procedure of PEMA/PVdF–HFP–LiTf–PC polymer electrolyte films**

### 3.3.3 Ionic Liquid Based PEMA/PVdF–HFP–LiTf–BMII and PEMA/PVdF–HFP–LiTf–BMITf Polymer Electrolyte Films

#### 3.3.3.1 PEMA/PVdF–HFP–LiTf–BMII System

BMII is a pale yellow color viscous liquid at room temperature and was used as received. The BMII–containing polymer electrolyte films were also prepared using the reflux method. Different amounts (5, 10, 12.5, 15, 17.5 and 20 wt. %) of BMII were added to the optimized polymer blend–salt composition in acetone. The mixtures were stirred vigorously with a magnetic stirrer at 55 to 65 $^{o}$C for 2 h to form PEMA/PVdF–HFP–LiTf–BMII polymer electrolytes. LiTf salt was heated at 130 °C for 3 h to eliminate any moisture prior to use. The resultant pale yellow coloured solutions were cast onto glass petri dish and dried at 45 °C in an oven for several hours to evaporate the solvent until semi–transparent films of light yellow colour were obtained as shown in Figure 3.7. Highest occupied molecular orbital (HOMO) is the non–bonding orbital localized on iodide ion while lowest unoccupied molecular orbital (LUMO) is mainly localized on the $BMI^+$ ring and is antibonding in nature. Hence, the color of BMII is due to the charge transfer transition from HOMO on iodide anion to the antibonding orbital ($\pi^*$) LUMO on $BMI^+$ cation [Shukla et al., 2011].

The polymer electrolyte films formed were kept in a dessicator for several days for further drying before characterization. Table 3.4 shows the designation and composition of BMII–added polymer electrolytes. The prefix BI represents BMII ionic liquid and the number proceeding it refers to the wt.% of BMII added. Figure 3.6 depicts the flow chart for the preparation of PEMA/PVdF–HFP–LiTf–BMII polymer electrolyte films.

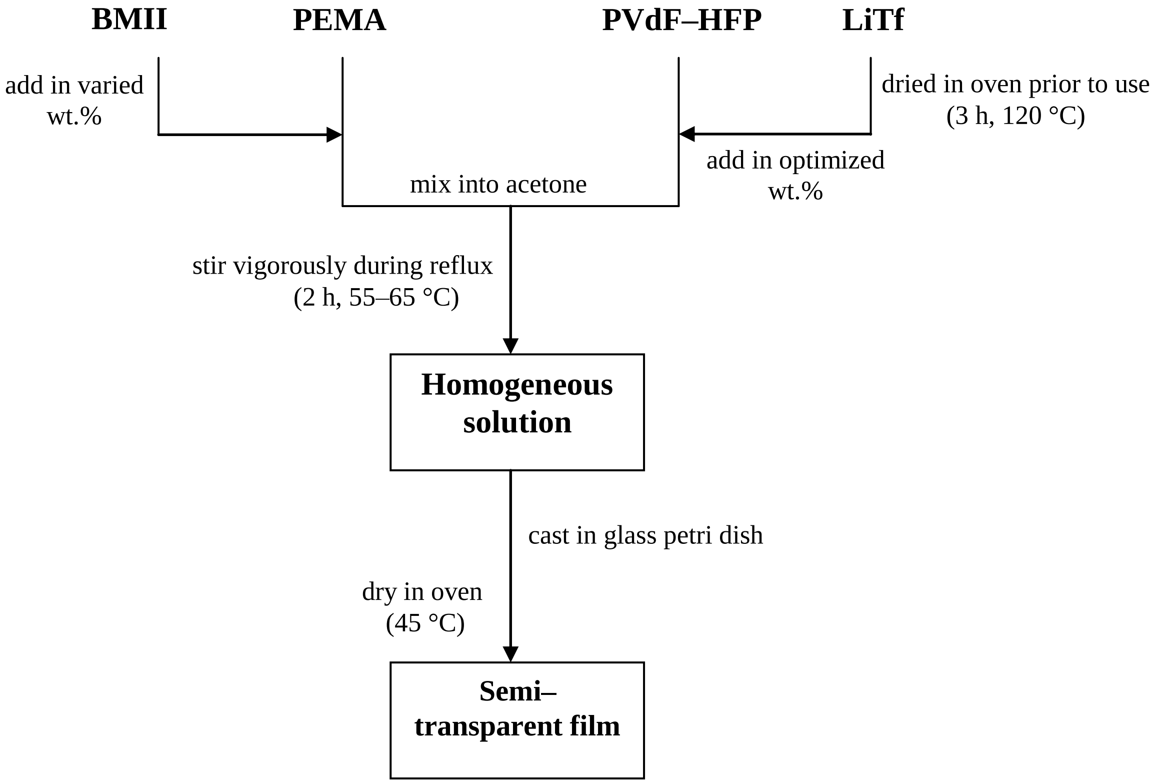

**Figure 3.6 Flow chart for the preparation procedure PEMA/PVdF–HFP–LiTf–BMII polymer electrolyte films**

**Table 3.4 Composition of PEMA/PVdF–HFP–LiTf–BMII polymer electrolyte system**

| Designation | PEMA (g) | PVdF–HFP (g) | LiTf (g) | BMII (g) | [PEMA/PVdF–HFP] : LiTf : BMII (w:w) |
|---|---|---|---|---|---|
| BI–5 | 0.7 | 0.3 | 0.4286 | 0.0752 | 66.50 : 28.50 : 5.0 |
| BI–10 | 0.7 | 0.3 | 0.4286 | 0.1587 | 63.00 : 27.00 : 10.0 |
| BI–12.5 | 0.7 | 0.3 | 0.4286 | 0.2041 | 61.25 : 26.25 : 12.5 |
| BI–15 | 0.7 | 0.3 | 0.4286 | 0.2521 | 59.50 : 25.50 : 15.0 |
| BI–17.5 | 0.7 | 0.3 | 0.4286 | 0.3030 | 57.75 : 24.75 : 17.5 |
| BI–20 | 0.7 | 0.3 | 0.4286 | 0.3572 | 56.00 : 24.00 : 20.0 |

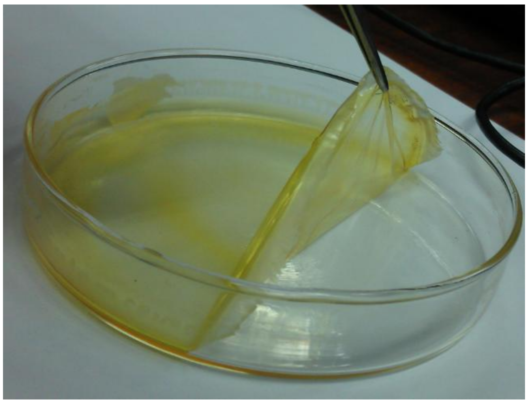

**Figure 3.7 Image of semi–transparent PEMA/PVdF–HFP–LiTf–BMII based polymer electrolytes**

### 3.3.3.2 PEMA/PVdF–HFP–LiTf–BMITf System

BMITf is a clear liquid with a density of 1.2951 g ml$^{-1}$ at room temperature and was used as received. In this system, varied amounts (10, 20, 30, 40, 50 and 60 wt. %) of BMITf were added to the optimized polymer blend–salt composition in acetone. The BMITf–containing polymer electrolyte films were prepared in the same way as the BMII–containing polymer electrolyte films. Transparent PEMA/PVdF–HFP–LiTf–BMITf films were produced. Table 3.5 shows the designation and composition of BMITf–added polymer electrolytes while Figure 3.8 depicts the flow chart for the preparation of PEMA/PVdF–HFP–LiTf–BMITf polymer electrolyte films. The prefix BT represents the BMITf ionic liquid and the number proceeding it refers to the wt.% of BMITf added.

**Table 3.5 Composition of PEMA/PVdF–HFP–LiTf–BMITf polymer electrolyte system**

| Designation | PEMA (g) | PVdF–HFP (g) | LiTf (g) | BMITf (g) | PEMA : PVdF–HFP : LiTf : BMITf (w:w) |
|---|---|---|---|---|---|
| BT–10 | 0.7 | 0.3 | 0.4286 | 0.1587 | 44.1 : 18.9 : 27.0 : 10.0 |
| BT–20 | 0.7 | 0.3 | 0.4286 | 0.3572 | 39.2 : 16.8 : 24.0 : 20.0 |
| BT–30 | 0.7 | 0.3 | 0.4286 | 0.6123 | 34.3 : 14.7 : 21.0 : 30.0 |
| BT–40 | 0.7 | 0.3 | 0.4286 | 0.9524 | 29.4 : 12.6 : 18.0 : 40.0 |
| BT–50 | 0.7 | 0.3 | 0.4286 | 1.4286 | 24.5 : 10.5 : 15.0 : 50.0 |
| BT–60 | 0.7 | 0.3 | 0.4286 | 2.1429 | 19.6 : 8.4 : 12.0 : 60.0 |

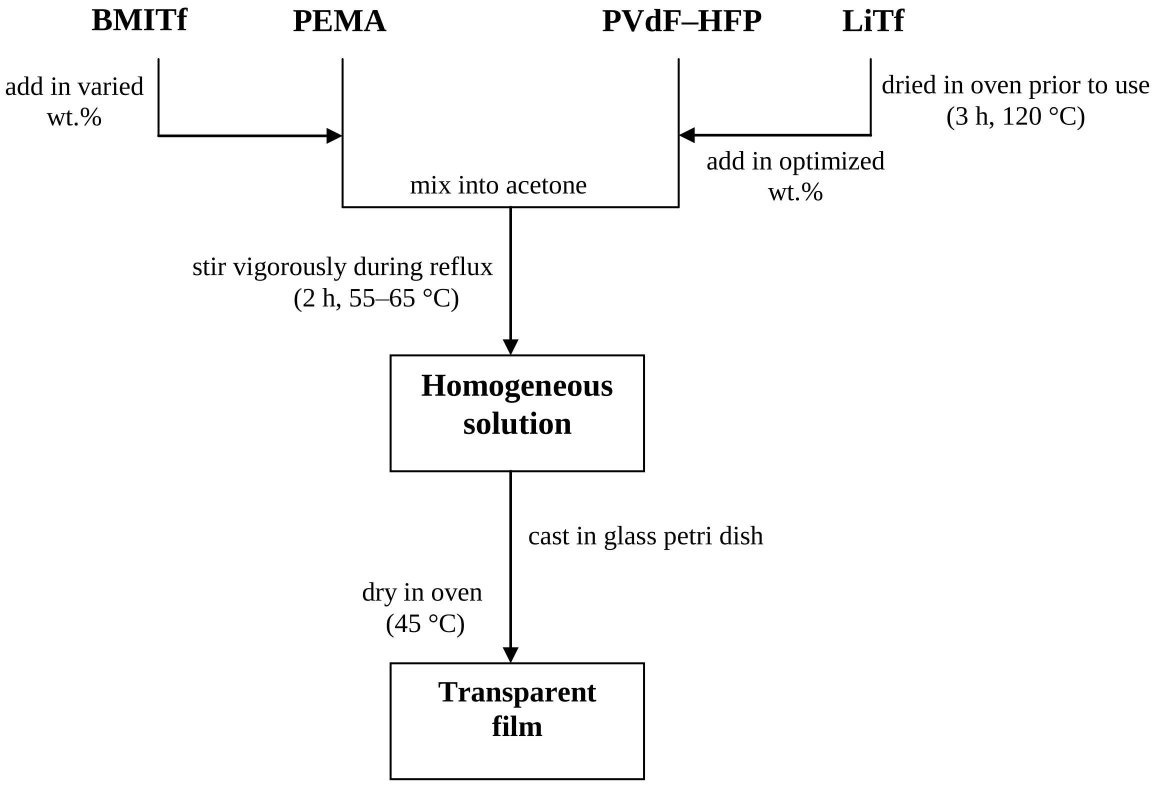

**Figure 3.8 Flow chart for the preparation procedure of PEMA/PVdF–HFP–LiTf–BMITf polymer electrolyte films**

## 3.4 Characterization Methods

### 3.4.1 Fourier Transform Infrared (FTIR) Spectroscopy

Infrared (IR) radiation refers broadly to the part of the electromagnetic spectrum between the visible and microwave regions. FTIR spectroscopy can be used to investigate the structure in polymer electrolytes, to confirm complexation between the salt and the polymer, between the plasticizer or ionic liquid and the polymer, or even between the plasticizer or ionic liquid and salt. Several researchers used this technique to study the interaction between polymer, salt and plasticizers. The complexation, nature and concentration of the various ionic species are important to understand the overall mechanism of conductivity. In all these work, the interaction is determined by the shift in the IR spectrum [Rhodes and Frech, 1999; York et al., 2001].

Figure 3.9 shows the FTIR spectra in the transmittance mode of PEO, LiTf and PEO–LiTf polymer electrolyte samples [Ramesh et al., 2008]. Changes in the IR bands of PEO–LiTf sample are attributed to complexation which occurred between PEO and LiTf.

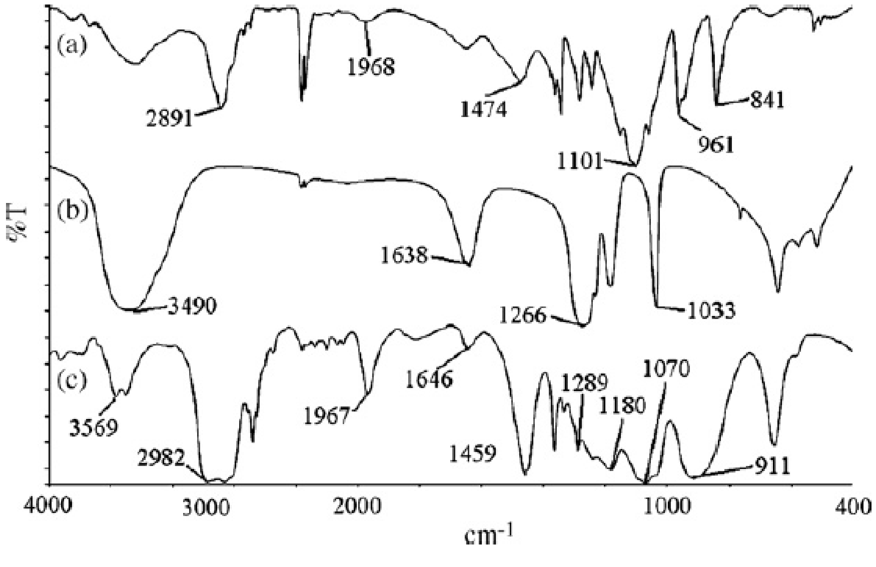

**Figure 3.9 FTIR spectra of (a) pure PEO, (b) pure LiTf and (c) PEO:LiTf (95:5; wt.:wt.) sample [Taken from Ramesh et al., 2008]**

FTIR spectroscopy was carried out on all polymer electrolyte films using the Thermo Scientific Nicolet iS1O Smart iTR* ATR in the transmittance mode over the wavenumber region of 4000–650 cm$^{-1}$ with resolution of 1 cm$^{-1}$. The use of 1 cm$^{-1}$ resolution enables the instrument to dissolve peaks as little as 1 cm$^{-1}$. By utilizing diamond ATR accessory, the effective path length is impacted by the penetration depth of the IR wave and therefore is not influenced by thickness of the sample. The ATR penetration depth is about 0.5 to 2 μm.

In this work, series of deconvolution of IR bands were performed using the OMNIC software. The deconvolution was carried out by fixing the number of IR peaks and line shape, and allowing band parameters such as full width at half height, area, intensity and band shape to vary without constraints during the iteration [Brooksby and Fawcett, 2000]. The Gaussian/Lorentzian function was employed to fit the selected bands of the polymer electrolyte samples [Das and Bhattacharyya, 2010; Fan et al., 2009; Chen et al., 2011] and all the deconvoluted spectra were best fitted using a constant baseline. All resultant peaks created through curve–fitting matches the original spectrum when added together.

Besides studying the effect of EC and PC as plasticizer in the PEMA/PVdF–HFP–LiTf system, polymer–plasticizer and plasticizer–salt interactions were also investigated. In order to investigate the interactions that occur between LiTf salt and the plasticizer (i.e. EC or PC), 6 wt.% LiTf–94 wt.% EC and 6 wt.% LiTf–94 wt.% PC electrolyte compositions were prepared. The low content of LiTf was incorporated into EC or PC was to allow its solvation and dissociation in the absence of acetone as solvent. Individual polymer (i.e. PEMA, PVdF–HFP) and PEMA/PVdF–HFP blend containing only EC or PC (10 wt.%) were used as comparisons in each polymer blend–salt–plasticizer system. As EC and PC are poor anion solvators, any change in the wavenumber of the plasticizer would be due to interaction between cation of the salt ($Li^+$) and not the anion ($Tf^-$). In all the five polymer electrolyte systems, the effect on ion–polymer interactions and ion–pairing in the salt–containing, plasticized and ionic liquid–added PEMA/PVdF–HFP–LiTf complexes were investigated at the microscopic level. By obtaining the area of free ions, ion pairs and ion aggregates of LiTf anion through FTIR deconvolution, we should be able to correlate the FTIR results with the conductivity results obtained.

### 3.4.2 Electrochemical Impedance Spectroscopy (EIS)

Electrochemical impedance spectroscopy (EIS) is a method used to characterize the electrical properties of a material. This method involves the application of a small fixed voltage of 10 mV across two identical electronically conducting electrodes of a sample holder which are placed in contact to the faces of a sample at different frequencies. As a result, current flows through the sample. The processes that take place upon electrical stimulation are: (1) the transport of electrons through the electrodes, (2) the transfer of electrons at the electrode–electrolyte interface and (3) the transport of ions in the electrolyte [Ross Macdonald and Johnson, 2005]. The ratio of the applied voltage to the resulting current passing through the sample at the particular frequency gives impedance of the sample. Impedance changes with frequency and is a complex quantity.

In this work, impedance of the samples was determined using the Hioki 3531 Z HiTester. The measurements were done in the frequency range from 50 Hz to 1 MHz between ambient and 353 K with an interval of 5 K. Six replicates of impedance readings were measured and the average was obtained with error of ±5 ohm. The thickness of each sample was measured six times using a micrometer screw gauge to obtain the average value with error of ±0.0003 cm. The ionic conductivity, $\sigma$ of each sample can be deduced by employing the formula:

$$\sigma = \frac{l}{R_b A} \tag{3.1}$$

where $l$ is the thickness of the electrolyte film, $R_b$ is the bulk resistance and $A$ is the contact area between the electrolyte and the electrodes. The imaginary impedance (Z”) was plotted against the real impedance (Z’) and the bulk resistance was obtained from the intercept with the real–axis.

The number density ($n$), mobility ($\mu$) and diffusion coefficient ($D$) of free ions of all polymer electrolyte systems were calculated using the equations below:

$$n = \%FI \times \frac{m}{M_W} \times \frac{N_A}{V} \tag{3.2}$$

$$\mu = \frac{\sigma}{n \times e} \tag{3.3}$$

$$D = \frac{\mu \times k \times T}{e} \tag{3.4}$$

whereby $\%FI$ refers to percentage of free ions obtained from FTIR deconvolution, $m$ is mass of LiTf used, $M_W$ = molecular mass of LiTf (156.01 g mol$^{-1}$), $N_A$ is Avogadro’s number ($6.02 \times 10^{23}$) and $V$ is total volume of components present in the sample. $\sigma$ is the conductivity of each sample at 298 K and $e$ is electron charge ($1.60 \times 10^{-19}$ C). $k$ is Boltzmann constant ($1.38 \times 10^{-23}$ J K$^{-1}$) and $T$ is 298 K.

### 3.4.3 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) is a versatile thermal analysis to investigate the thermal properties of polymer electrolytes as a function of temperature. The thermal stability of a material can be determined through the onset decomposition temperature. The thermal stability of the polymer electrolyte is also an important parameter to guarantee acceptable performance in electrochemical devices as it affects the upper–limit use temperature and dimentional stability of the electrolyte film. Figure 3.10

shows an example of TGA curves of pure PMMA and PMMA samples containing nanocomposites while Figure 3.11 shows TGA curves of PVdF–HFP containing PEG.

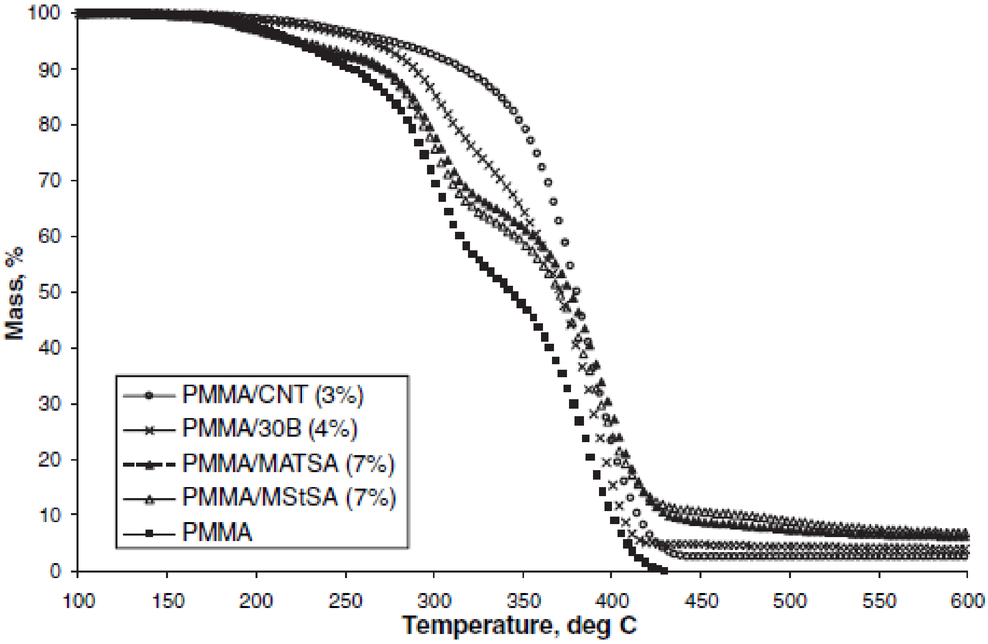

**Figure 3.10 TGA curves of PMMA and its nanocomposites [Taken from Costache et al., 2006]**

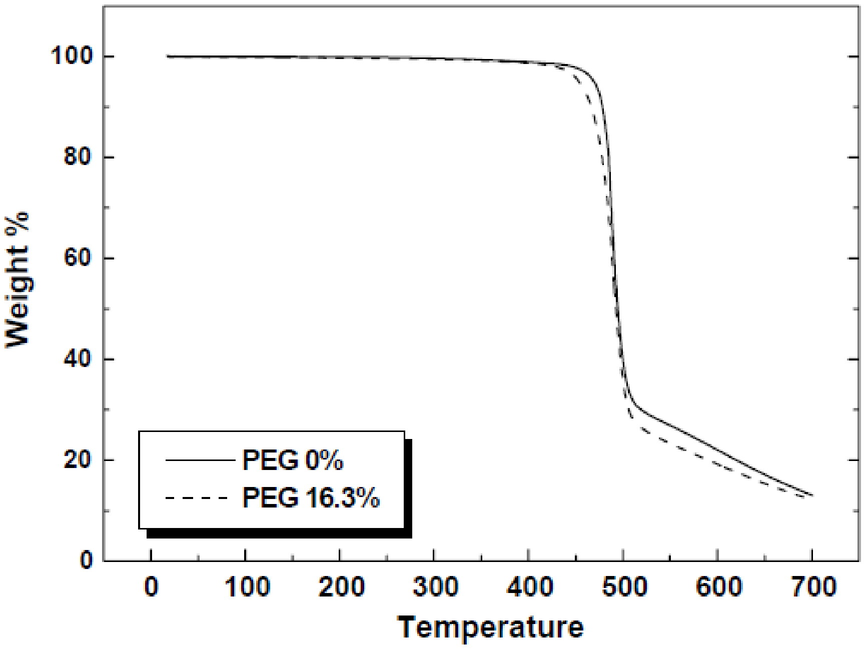

**Figure 3.11 TGA thermograms of PVDF–HFP films containing 0 and 16.3 wt.% PEG [Taken from Chung et al., 2003]**

TGA measurements were carried out using TA Instruments Q500 Thermogravimetric Analyzer. Each sample weighing about 3 mg was placed into a platinum pan and heated from room temperature to 550 °C at 50 °C min$^{-1}$ and resolution of 5 °C in nitrogen atmosphere. In this work, high heating rate (50°C/min) was used during ramp segments where no weight changes occur, but the heating rate is automatically lowered when weight changes occur. Once the weight change(s) are complete, the system returns to the selected ramp heating rate of 50°C min$^{-1}$. The onset decomposition temperatures, $T_\mathrm{d}$ were determined using TA Universal Analysis software.

## 3.5 Summary

Chapter 4 will detail the results from FTIR studies of the salted, plasticized and ionic–liquid added polymer blend electrolytes. The results from EIS studies will be presented in Chapter 5. The thermal stability of polymer electrolyte films obtained from TGA will be presented in Chapter 6.