2.0   EXPERIMENTAL PROCEDURES

2.1   Preparation of Polymer Electrolyte

Films of Poly (Vinyl Chloride) (PVC) based polymer electrolytes were prepared using a ___ by the solution cast technique. The starting materials PVC was obtain ___ Lithium ___ trifluoromethanesulphonate (LiBr) ___ propylene carbonate (PC) and ___ were ___ respectively. Tetrahydrofuran (THF) was obtained from J.T Baker.

Prior to the preparation of polymer electrolyte, LiCF₃SO₃ and LiBF₄ were dried at 70°C for two ___ in order to minimize trace amounts of locks in the material. Certain amounts of ___ ___ ___ ___ ___ PC and these solutions were added together ___ ___ After the different amounts of PC and ___ were mixed and stirred for 4 hours to give a homogeneous viscous solution. The solution that obtain ___ was cast into glass petri and allowed to evaporate slowly to film a developing. This procedure yields mechanically stable and free standing films.

The solution method proposed by Y. Song et al. [87] was used to prepare plasticizer ___ stabilizer PVC electrolyte containing LiCF₃SO₃, ___ LiClO₄ and PC. By this method, the PVC powder was allowed to minimize doses of a ___ dissolution in ___ the ___ ___ ___ at room temperature. After irradiation, the PVC powder was

Chapter 2

Experimental
Procedures

2.0   EXPERIMENTAL PROCEDURES

2.1   Preparation of Polymer Electrolyte

Films of Poly (Vinyl Chloride) (PVC) based polymer electrolytes were prepared using a single solvent by the solution cast technique. The starting materials, PVC was obtained from Fluka and lithium triflate ($LiCF_3SO_3$) as well as lithium tetrafluoroborate ($LiBF_4$) were obtained from Merck. The plasticizers to be used i.e. propylene carbonate (PC) and ethylene carbonate (EC) were procured from Aldrich and Fluka respectively. Tetrahydrofuran (THF) was obtained from J.T.Baker.

Prior to the preparation of polymer electrolytes, $LiCF_3SO_3$ and $LiBF_4$ were dried at 100°C for one hour in order to eliminate trace amounts of water in the material. Desired amounts of PVC and salts were dissolved separately in THF and these solutions were mixed together and stirred. After that, different amounts of PC and EC were mixed and stirred for 24 hours to get a homogeneous viscous solution. The solution thus obtained was cast on a glass plate and allowed to evaporate slowly inside a desiccator. This procedure yields mechanically stable and free standing films.

The mixture method, proposed by Y. Song *et al.* [65] was used to prepare γ - irradiation - induced PVC electrolyte containing $LiCF_3SO_3$, $LiBF_4$ and EC. By this method, the PVC powder was exposed to different doses of γ - irradiation in a ^{60}Co source under vacuum at room temperature. After irradiation, the PVC powder was

mixed with an appropriate amount of PC and doped with $LiCF_3SO_3$ and $LiBF_4$ salts to supply ionic carriers. The polymer electrolyte films were then prepared by the solution cast method as mentioned above. The ionic conductivity of all the polymer electrolytes was measured by using ac – impedance spectroscopy.

2.2   AC - Impedance Spectroscopy

Impedance spectroscopy is a measurement of real and imaginary parts of impedance at different frequencies. This helps in separating out the true bulk conductivity from conduction due to grain boundary, electrode-electrolyte interface and other relaxation phenomena. Earlier, different bridges such as Schering bridge, Anderson's bridge, Wien's bridge and their combination were used for impedance measurements. Now, frequency response analysers are the direct measuring devices in frequency domain which can measure real and imaginary components of impedance in a wide range of frequency.

In Impedance Spectroscopy, when a monochromatic signal $V(t) = V_m \sin(\omega t)$ is applied [101-102], the resulting steady state current is $I(t) = I_m \sin(\omega t + \theta)$ where,

ω $= 2\pi f$

θ = phase difference between voltage and current

V_m = the maximum voltage

I_m = the maximum current

θ is zero for purely resistive behaviour. We can now define the conventional impedance as, $Z(\omega) = V(t) / i(t)$. Its magnitude is $|Z(\omega)| = V_m / I_m(\omega)$ and its phase angle is $\theta(\omega)$.

Since θ, V_m and I_m change with frequency, a set of complex impedance, Z, values will be obtained. From these set of values, a set of real impedance, Z_R and a set of imaginary impedance, Z_I can be calculated.

$$Z_R = Z' = |Z(\omega)| \cos\theta \qquad (2.1)$$

$$Z_I = Z'' = |Z(\omega)| \sin\theta \qquad (2.2)$$

After obtaining the impedance data, the parameters of interest are extracted. There are two types of impedance plots (Nyquist Plot and Bode Plot) which can be considered. Nyquist Plot is also known as Cole-Cole Plot or complex impedance plane plot. In Nyquist Plot, we plotted the imaginary impedance component, Z'', against the real component, Z', at each excitation frequency. The plots have the shape of a perfect semicircle or a "flattened" semicircle. The Bode Plot allows us to examine the absolute impedance, $|Z|$, and the phase shift, θ, each as a function of frequency. In both cases the bulk impedance, R_b, can be determined. By knowing the bulk impedance, the electrical conductivity of the sample can be calculated via the equation,

$$\sigma = \frac{L}{R_b A} \qquad (2.3)$$

where,

       σ = electrical conductivity in S/cm

       L   =the thickness of the sample in cm

       A   =the area of the sample in cm^2

The conductivity measurements was also carried out at different temperatures. The conductivity obtained at different temperatures are plotted in the form of log σT against 10^3/T. This plot will help in the study of the conductivity mechanisms. Experimental data represented in an Arrhenius plot define straight lines for an activated transport and curves for an assisted transport mechanism [103]. Figure 2.1 shows ac-impedance spectrum of poly (methoxy ethoxy ethyl methacrylate) based polymer electrolytes at three different temperatures.
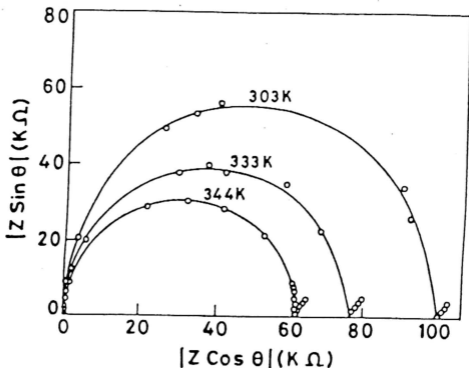

Figure 2.1 : Complex impedance plot for poly (MEEMA) - LiCF$_3$SO$_3$ at three different temperatures [71].

Other related functions besides impedance, used in impedance spectroscopy are complex admittance, $A(\omega)$, complex dielectric constant, $\varepsilon(\omega)$, and complex dielectric modulus, $M(\omega)$. All the parameters are generally called as immittances. The interrelations between the four immittance functions are summarised in Table 2.1.

	M	Z	A	ε
M		μZ	μA^{-1}	ε^{-1}
Z	$\mu^{-1}M$		A^{-1}	$\mu^{-1}\varepsilon^{-1}$
A	μM^{-1}	Z^{-1}		$\mu \varepsilon$
ε	M^{-1}	$\mu^{-1}Z^{-1}$	$\mu^{-1}M$	

Table 2.1 : Relation between immittance functions [102].

Here,

$$\mu = j\omega \, C_c \qquad\qquad (2.4)$$

where $C_c = \varepsilon_0 A/t$, ε_0 = permittivity of free space (8.854×10^{-12} F/m), A = sample electrode contact area and t is the thickness of the sample. Converting the impedance data into the complex permittivity and electrical modulus formalisms enable the understanding of the conductivity mechanism in the samples [104-105].

In our study, the electrical conductivity of the polymer electrolytes were determined by ac-impedance measurements using a HIOKI 3531 Z bridge interfaced with a computer for data acquisition over the frequency range between 40Hz and 5MHz. The thin film polymer electrolyte films were sandwiched between two stainless disk electrodes which acted as a blocking electrode for ions. For the temperature dependant ionic conductivity, measurements were performed in the temperature range of 25°C (RT) up to 100°C.

2.3   Ionic Transference Number Measurement

It has long been recognised that concentration gradients that build up in the polymer electrolyte during the passage of current can be detrimental to cell performance. These gradients develop as a result of the nonunity transference number of the lithium ion. Thus, it is important to have information on transference number as well as on ionic conductivity [106]. It is a natural consequence of the structure of most polymer electrolytes that anions tend to be more mobile than cations [96].

A significant amount of effort has been put to measure the lithium ion transference number in solid polymer electrolytes based on a potentiostatic polarization [107-108].

According to Linford [109], electron conduction can be neglected in polymer electrolytes. Thus, the total current, i_T flowing in a polymer electrolyte can be assumed to consist of cationic and anionic currents,

$$i_T = i_+ + i_- \qquad (2.5)$$

where,

        i_+ = current due to cations

        i_- = current due to anions

When there is current flow, the ions will travel to the electrode connected to the terminal that has an opposite charge to that of their own charge. A back emf is produced and polarization occurs. This method is also known as Wagner's Polarization Method. The polymer film is placed between two blocking electrodes and the current value is taken every 10 seconds until a constant current was obtained. Blocking electrodes which do not allow ions to dissolve in them were used . Polarization concentration impedes the anionic current . Thus, the cationic transference number, t_+ is given by,

$$t_+ = \frac{i_{+\alpha}}{i_T} \qquad (2.6)$$

where,

        $i_{+\alpha}$ = cationic current saturation

        i_T = total current at the beginning of polarization

Most attempts to measure the transference number in lithium salt/polymer systems have led considerable variation in their results. However, it is generally

accepted that the transference number of the lithium ion is less than 0.5 [110]. The transference number seems to vary with salt concentration. The cationic transference numbers show a tendency to decrease with increasing salt concentration, as shown in Figure 2.2.
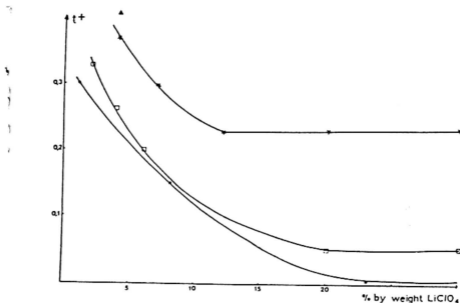

Figure 2.2 : Plot of the cation transport number versus $LiClO_4$ concentration for different PEO networks [30].

2.4 X-Ray Diffraction (XRD)

X - rays used for diffraction are electromagnetic waves with wavelengths in the range 0.05 to 0.25nm (0.5 to 2.5Å). In order to produce x-rays for diffraction purposes, a voltage of about 35kV is necessary and is applied between a cathode and an anode target metal , both of which are contained in a vacuum.

Many researchers have used x-ray diffraction method to study whether a material is amorphous or crystalline [111-112]. Solid state chemistry has proved that polymers may form almost perfect crystals due to the spatial possibilities offered by chain folding. The disruption of the crystalline peaks by some modifications such as the addition of an inorganic salt, addition of plasticizers etc. makes the final material more amorphous. Since only the amorphous phase takes part in conductivity, the materials in amorphous nature will have better ionic conductivity than materials in crystalline nature [30].

X-ray diffraction method can also be used to show that complexation takes place between the salt and the heteroatom of the polymer. Several researchers have shown that complexation occurs between the salt and the polymer host [112,113] although in PEO - AgSCN x-ray diffractogram [114], there is no existence of a new peak. The original peaks of PEO and AgSCN are also not shifted in the complex. By this technique, the diffractogram of the salt, pure polymer and the complex is obtained. The shift in the peaks of pure salt and pure polymer host in the salt-polymer complex and the existence of new peaks confirms the existence of complexation.

Figure 2.3 shows the XRD pictures of PAN (poly acrylonitrile) based polymer electrolytes. It can be clearly observed that the PAN- based lithium salt complex is in amorphous phase. A fully amorphous nature produces greater polymer flow and ionic diffisivity. Thus, a higher ionic conductivity can be obtained in the amorphous nature.

The X-ray diffractogram also shows a shift in PAN peak and the complete absence of salt peaks. This confirms the complexation between the polymer, salt and the plasticizers [86].
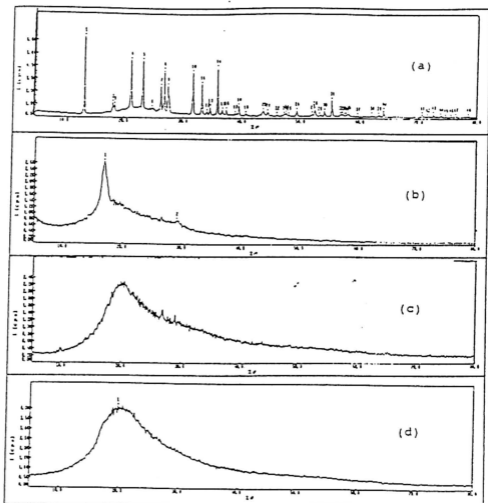

Figure 2.3 : The XRD pattern of a) LiClO$_4$, b) PAN c) PAN-EC-BL-SL-LiClO$_4$
and d) PC-EC-PC-DMF-LiClO$_4$

In this work, X-ray diffraction analysis was performed using Philips 1840 X-ray diffractometer using Cu - Kα radiation of wavelength λ = 1.5418Å in the 2θ range between 10° and 80°. The films were scanned using slit width 0.05 and receiving slit 0.2.

The coherent length was calculated from the Scherrer equation :

$$C \quad = \quad \frac{0.9\lambda}{Cos\,\theta_b\,(\Delta 2\,\theta_b)}\;\text{Å} \qquad (2.7)$$

where,

λ = wavelengths at the X-rays (1.5418Å)

θ_b = glancing angle

$\Delta 2\,\theta_b$ = difference in angle at two ends of FWHM

2.5   Thermal Analysis

Thermal analysis include a number of different techniques, each of which can provide certain useful information of the materials, under specific conditions. These include Differential Scanning Colorimetry (DSC) and Thermogravimetric Analysis (TGA).

2.5.1 Differential Scanning Colorimetry (DSC)

From the chemical thermodynamics point of view, DSC is the most useful instrument, because all chemical and physical changes involving enthalpy change and enthalpy is a state function. DSC instrument can measure the change in heat capacity, C_p as a function of temperature. At a particular state of the material, C_p changes very slightly with temperature. However, when there is a change of physical state, such as melting, C_p would change drastically.

DSC uses the same principles as DTA (Differential Thermal Analysis). DTA is a dynamic method which records the temperature difference between the sample and a reference material against time or temperature.

In general, DSC can be used for the measurement of any transition involving enthalpy change (ΔH) or heat capacity change (C_p). DSC technique has a wide range of applications as described below [115-116] :

i)   Determination of thermodynamic parameters

ii) Determination of glass transition temperature, T_g

iii) Investigation of crystallization

iv) Investigation of melting

v) Rate of thermal degradation and oxidation

vi) Kinetics of reactions

vii) Quality control (QC) on checking raw materials, intermediates or the finished products

DSC was carried out at the Chemistry Department. The samples are heated with a heating rate of $10°C \ min^{-1}$ in the temperature range up to 300°C.

Figure 2.4 shows a typical PVC thermogram with different glass transition temperature, T_g values at different inherent viscosity values [117].
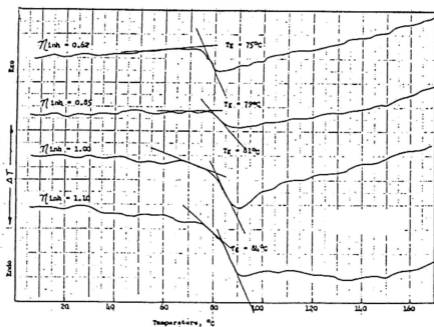

Figure 2.4 : PVC thermogram [117].

2.5.2 Thermogravimetric Analysis (TGA)

TGA measures the change in the mass of a sample as it is heated, cooled or held isothermally (at a constant temperature) [118]. The TGA technique can be used for studying any system that involves weight change with heating, under either inert or oxygen atmosphere. Some of the studies are :

i) General characterization where different components of a mixture can vaporise, decompose or combust at different temperatures.

ii) Comparison of thermal stability of materials

iii) Effect of certain additive on improving thermal stability.

iv) Determination of inorganic complexes where "step-wise" decomposition occur at specific temperatures for certain ligands.

v) Quality control on checking raw materials, intermediates or the finished products.

TGA was carried out at the Department of Chemistry , University of Malaya. Typical thermogravimetric analysis graph for PEO and PEO_nCoBr_2 with n = 8, 16, 32, 64, 128 are shown in Figure 2.5.

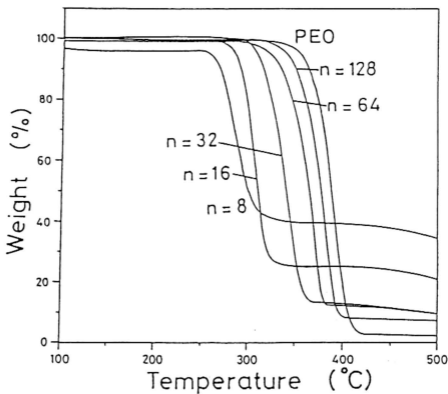Figure 2.5 : TGA data for PEO and PEO$_n$CoBr$_2$ with n = 128, 64, 32, 16, 8 [119].

There is no weight loss observed for all composition in the temperature range 25 to 250°C. In the high temperature, beyond 250°C, different samples are found to begin losing weight at different temperatures. Defining T_d as the temperature at which first derivative of weight loss with respect to temperature maximizes, T_d was found to decrease with increasing salt concentration. Results indicate that adding salt to PEO decreases the thermal stability of PEO.

2.6   Battery Charge/Discharge Characteristics

The polymer-salt-plasticizer complex film with the highest electrical conductivity was used as the electrolyte in the secondary electrochemical cell fabrication. Graphite was chosen as the cathode material and lithium metal was used as the anode material. The cell was assembled into the battery casing with the electrolyte sandwiched between anode and cathode materials under argon atmosphere in a glove box.

Usually, the battery charge / discharge characteristics is performed using the galvanostatic method. The galvanostatic charge / discharge characteristics was studied using the BAS LG50 galvanostatic instrument. Several charging and discharging current were tried until the appropriate current was obtained.

Discharging a cell by draining a constant current out of the cell will give a discharge curve as shown in Figure 2.6.
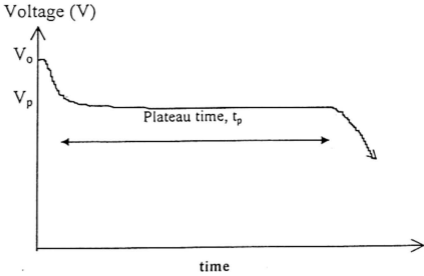
Figure 2.6 : Discharge characteristic

By estimating the plateau time and knowing the mass of the cell and the voltage of the cell, the important cell parameters can be calculated by using the below equations:

$$\text{Current density} \quad = \frac{\text{Current, I}}{\text{Area of electrode, A}} \quad (\text{A}/\text{cm}^2)$$

$$\text{Discharge capacity} = \frac{\text{Current, I x Plateau time, } t_p}{\text{Weight of the cell}} \quad (\text{Ah}/\text{kg})$$

$$\text{Energy density} \quad = \text{Plateau Voltage, } V_p \text{ x discharge capacity } (\text{Wh}/\text{kg})$$

$$\text{Power density} \quad = \frac{\text{Plateau Voltage, } V_p \text{ x Current, I}}{\text{Weight of the cell}} \quad (\text{W}/\text{kg})$$