Chapter 2

Experimental
2. Experimental

2.1 Method of Sample Preparation

The aim of the present study is to develop thin-film polymer based batteries. For the development of plastic battery, the essential requirement is a good polymer electrolyte having high ionic conductivity at ambient condition. The polymer electrolytes for the present study were prepared by solution cast technique that has been described elsewhere [116-117].

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![Diagram of polymer electrolyte preparation method]

Fig 2.1. Polymer electrolyte preparation method
Prior to the preparation of polymer electrolytes, LiBF₄ (high purity from Fluka) was dried at around 100⁰C for two hours. PVDF was obtained from Fluka and used without any drying. The plasticizers DMF and MF (Fluka) were stored in molecular sieves (Linda, pore diameter 4Å) and used in the present study. The plasticizer Ethylene Carbonate (from Fluka) was distilled prior to use in the preparation. The solvent used was high purity grade Acetone from BDH. The polymer electrolyte films were allowed to evaporate slowly inside the desiccator for two days. Then the polymer electrolyte films were dried in an oven for 10 hours at around 50⁰C after which characterization was carried out for the entire polymer electrolyte samples. The structures of the plasticizers used in the present study are shown below.

Since the high ionic conductivity is an immediate requirement of a good polymer electrolyte, the ionic conductivity of the polymer electrolyte was measured using ac-impedance spectroscopy. The ac-impedance spectroscopy will provide all the information necessary for the ionic conductivity studies.
2.2 ac-Impedance Spectroscopy

In impedance spectroscopy a signal $V(t) = V_0 \sin(\omega t + \theta)$ is applied across a sample through which a current $I(t) = I_o \sin(\omega t + \theta)$ is measured. Here

$$\omega = 2\pi f$$

$\theta$ = phase angle

$V_o$ = is the maximum voltage and

$I_o$ = is the maximum current.

$\theta$, $V_o$ and $I_o$ changes with frequency. The magnitude of the complex impedance, $Z = V_o / I_o$. For a set of frequencies $\{f_1, f_2, \ldots, f_n\}$, there will be a corresponding set of phase angles $\{\theta_1, \theta_2, \ldots, \theta_n\}$ and a set of impedance values $\{Z_1, Z_2, \ldots, Z_n\}$.

From these set of values, the set of real impedance $Z'$ and the set of imaginary impedance, $Z''$ can be obtained i.e.,

$$Z' = \{Z_1 \cos\theta_1, Z_2 \cos\theta_2, \ldots, Z_n \cos\theta_n\}$$

and

$$Z'' = \{Z_1 \sin\theta_1, Z_2 \sin\theta_2, \ldots, Z_n \sin\theta_n\}$$

After obtaining the impedance data, the parameters of interest can be extracted. Two types of plotting (Nyquist and Bode) can be considered depending whether the model is known priori or not. The Nyquist plot or complex impedance plot is a plot of $Z''$ versus $Z'$ and may have the shape of perfect semicircle or a 'flattened' semicircle (Fig. 2.2). In both the cases the bulk impedance, $R_b$ can be determined. This value is then used to calculate the electrical conductivity of the material from the equation,

$$\sigma = l/R_b A$$

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2.1
Here

\[ \sigma = \text{is the total ionic conductivity} \]

\[ l = \text{is the thickness of the sample} \]

\[ A = \text{is the area of the sample and} \]

\[ R_b = \text{is the bulk resistance of the sample} \]

Impedance spectroscopy can also be carried out at different temperatures. The conductivities obtained at different temperatures are plotted in the form of \( \log \sigma T \) versus \( 10^3/T \). If the regression value, \( R^2 \) of all the points in the plot is almost unity, the plot represents a straight line and the conductivity can be represented by the equation

\[ \sigma = (\sigma_0/T) \exp. (-E_a/kT) \]

where

\[ \sigma_0 = \text{is the pre-exponential factor and} \]

\[ E_a = \text{is the activation energy and} \]

\[ k = \text{is the Boltzman constant} \]

If this is so, the conductivity mechanism can be described by a thermally activated hopping mechanism. In such a mechanism, the vibration of the salt that has complexed with the heteroatom increases with temperature. This vibration will cause the salt to "cling" into another free heteroatom when they come into close proximity. If the plot of \( \log \sigma T \) versus \( 10^3/T \) is a curve then the conductivity can be described by the equation

\[ \sigma = A \exp. (-B/k (T-T_0)) \]

\[ \text{(VTF equation)} \]

\[ 2.3 \]
Fig. 2.2. Nyquist plot having perfect (a) and depressed (b) semicircle [ref: 128]

Usually the conductivity and temperature of a material obey equation (2.3) if its \( T_g \) is well below room temperature and its melting point is quite low e.g. PEO. In this case, the ionic conductivity is enhanced by segmental motion of the polymer backbone.

Typical example of complex impedance plots for polymer electrolytes are illustrated in Fig. 2.3, which shows the ac-impedance spectrum for the PEO based polymer electrolyte. The ac-impedance was taken at room temperature and the spectrum clearly shows the semicircular nature. The ac-impedance spectrum for the PEO-LiClO\(_4\)-DOP shows a depressed semicircle and for PEO-LiClO\(_4\)-DOP: \( \gamma \)-Al\(_2\)O\(_3\) shows an almost perfect semicircle. From these two graphs, the bulk resistance value can be calculated. The bulk resistance \( R_b \) can be calculated by finding out the
intercept at the x-axis value. The bulk resistance can be used to calculate the ionic conductivity as per the equation (2.1).

![Figure 2.3 ac-impedance spectrum for (a) PEO-LiClO$_4$ : DOP and (b) PEO-LiClO$_4$ - DOP : γ-Al$_2$O$_3$ [ref: 129]](image_url)

The impedance measurements were carried out using *HIOKI 3531-01 LCR* tester that has been interfaced with computer for data collection in the frequency range from 50 Hz to 5 MHz. The polymer film was placed in between two stainless steel plates in the conductivity cell and measurements were carried out. The conductivity measurements at different temperature (room temperature to 100° C) were carried out for the polymer electrolyte samples.
2.3 X-ray Diffraction

After determining the highest electrical conductivity in the polymer electrolyte film, it is necessary to show that complexation has taken place between the salt and the heteroatom of the polymer i.e., the polymer has the lone pair of electron. This is the one of the criteria for a polymer host [32]. The X-ray diffraction technique can be used for this purpose although it has been shown in the case of PEO-AgSCN complex [130] no new peaks or shift was observed when the diffractogram of the complex and the salt were compared.

In using this technique, the X-ray diffractogram of the salt, pure polymer and the complex are taken. The shift in the peaks of the diffractograms of pure salt and polymer compared to the peaks of the complex and the existence of new peaks confirm the occurrence of complexation. Also, the disruption of the crystalline peaks as in the case of PEO complexes and upon comparison with conductivity studies prove that the ionic conductivity takes place in the amorphous region and not in the crystalline region as was initially proposed by Armand [32]. The X-ray diffraction measurements for the polymer electrolyte samples were measured using PHILIPS PW 1840 diffractometer. The X-ray diffraction pattern for the pure salt LiClO₄, PAN and their complexes with the plasticizers are shown in the Fig 2.4 [131].

The X-ray diffractogram for pure salt shows sharp crystalline peaks. The X-ray diffractogram of PAN shows a single peak. The X-ray diffractogram of a complex shows very clearly a shift in PAN peak and the complete absence of the peaks
corresponding to the salt. The broadening, shifting of a PAN peak and the complete absence of sharp crystalline peaks of the salt confirms the complexation between the polymer, salt and the plasticizer. In the case of polymer electrolyte, fully amorphous morphology produces greater polymer flow and ionic diffusivity. That is to say that high ionic conductivity can be obtained in amorphous polymers having high flexible backbones and low glass transition temperature.

Fig 2.4. X-ray Diffractogram of (a) LiClO$_4$, (b) PAN, (c) PAN + EC + BL+SL+ LiClO$_4$ and (d) PAN + EC + PC+DMF+ LiClO$_4$ [ref: 131]
2.4 Thermal Analysis

In order to investigate other characteristics of these PVDF-based polymer electrolytes in particular thermal characteristics, several techniques have been chosen. These include Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA).

2.4.1 Differential Scanning Calorimetry

Calorimetry involves the measurement of heat. Heat is the amount of energy exchanged between two systems that are in thermal contact within a period of time. The DSC uses the same principles applied in DTA. DTA is a dynamic method in which a record is made of the temperature difference between the sample and a reference material against time or temperature, as the two specimens are subjected to identical temperature regimes in an environment heated or cooled at a controlled rate.

The apparatus consists of two identical calorimeters (with thermocouples connected in opposite direction) placed inside a large copper block bath. This copper block bath is placed inside a thermostatically controlled bath. The galvanometer measures only the differences in temperature between the calorimeters. This method records phase transitions of the first order (e.g. enthalpy change, whether accompanied by change in weight or not, change of crystalline structure, boiling, sublimation, evaporation, melting, chemical reactions such as redox reactions, decompositions,
dehydration and dissociation) and phase transition of the second order (e.g. glass transition temperature).

The DSC was carried out using Rheometric Scientific DSC (LN) available at the Chemistry Department, University of Malaya. Fig 2.5 shows the DSC traces for the conditions given as shown below [132].

(a) Freshly prepared films were heated to 150°C, cooled down to 25°C and immediately reheated.

(b) Freshly prepared films were heated to 250°C, cooled down to 25°C and reheated after 2 days

(c) Films that were 2 months old when heated to 250°C, cooled down to 25°C and immediately reheated

(d) Films that were 2 months old were heated to 250°C, cooled down to 25°C and reheated after 2 days.

In all the cases, two endothermic peaks occur indicating that two crystalline phases coexist at room temperature: a pure PEO peak, which melts between 58-60°C, and an intermediate salt rich crystalline compound that dissolves in the elastomeric phase. Fig. 2.5 (a) shows that very little change in the peak areas occurs during the first heating and the second heating immediately after cooling. Fig. 2.5 (b) was also on a freshly prepared film and the first heating cycle was the same as in Fig. 2.5 (a), but after cooling the sample was allowed to remain at room temperature for 2 days. On further heating, the DSC trace was indifferent. The peak temperatures were the same, but the peak areas has decreased during the melting of the PEO and increased
during the melting of the intermediate compound. This suggests that during the lapsed time there occur a considerable redistribution of the lithium salt within the polymer and recrystallization of the crystalline intermediate.

Fig 2.5. DSC traces for (PEO)$_4$ : LiCF$_3$SO$_3$ complex [ref: 132]
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Fig. 2.5 (c) shows a DSC trace of an electrolyte material that had been allowed to stand for 2 months in the dry room. During the first heating cycle a considerably smaller melting peak was obtained for PEO than that observed in the Fig. 2.5 (a) and 2.5 (b), followed by a correspondingly larger peak for the intermediate complex. However, heating the sample immediately after cooling resulted in an increased PEO peak area whereas that for the complex decreased. This suggests that during the cooling, crystallization of the complex was incomplete. Fig. 2.5 (d) shows a trace where a sample was heated and allowed to cool at room temperature for 2 days. Further heating results in a trace similar to the first heating. From these results it can be concluded that crystallization to be complete, the sample must be

(1) Heated and cooled to room temperature and allowed to stand for sufficient length of time (~2 days) or

(2) Allowed to age.

The above results indicate that recrystallization can be increased if the sample is first heated to 150°C. However, the time of recrystallization can vary considerably in samples containing larger salt content or in samples that may have two or more intermediate compounds. The preferred route would be allowing the samples to age. This was the procedure adopted in determining the subsequent phase diagrams.

2.4.2. Thermogravimetric Analysis.

Thermogravimetry, the weight or change in weight of the sample is recorded as the sample is heated. The Thermogravimetric analysis provides the information
regarding the weight loss at different stages. From this weight loss measurement, we can identify the change in the property of the polymer electrolytes. The TGA was carried out using *Rheometric Scientific TGA 1000* at Department of Chemistry, University of Malaya. Typical thermogravimetric analysis graph for PEO and PEO$_n$ NaCF$_3$SO$_3$ for different salt concentrations are shown in Fig 2.6 [133].

No weight loss has been observed for all compositions in the temperature range 25°C to 250°C, suggesting the dryness of the prepared films. At high temperature, i.e., beyond 250°C, all the samples begin to lose weight. $T_d$, the temperature at which first derivative of weight loss with respect to temperature maximizes, is about 389.0°C for PEO and for all salt concentrations from $n=128$ to $n=8$. However, $T_d$ was found to be higher by about 15°C for $n=4$. These results indicate that adding salt to PEO does not significantly affect the thermal stability of PEO up to a salt concentration of $n=4$.

![TGA traces for PEO:NaCF$_3$SO$_3$ with n = 128, 64, 32, 16, 8 and 4](ref: 133)
2.5 Infrared Spectroscopy

As another means to confirm that complexation has taken place between the salt and the polymer or between the plasticizer and the polymer or even between the plasticizer and salt, infrared spectroscopy was performed. The basic principle in understanding infrared spectroscopy is shown in the literature [134-135].

As an example, in PEO the heteroatom is the ether oxygen that has a lone pair electron. A lithium salt e.g. LiClO₄ will be solvated with PEO to form a PEO-LiClO₄ complex where the lithium cation interacts with the oxygen atom. The C-O-C stretching vibration in the infrared spectrum of PEO is in the region between 800-1100 cm⁻¹ [136]. When complexation occurs the bands in the region, which is so close to one another, will overlap and broaden. The broadening due to overlap of such bands indicates that the bands have shifted and implies that LiClO₄ has complexed with the PEO. As another example, consider chitosan. Chitosan has an amide group in which the nitrogen atom has a lone pair electron. Apart from these there could also be present the NH₃⁺, NH₂ and C-NHR bands which are leftovers due to the incomplete deacetylation of chitin during the process of chitosan production. The NH₂ band occurs at 1590 cm⁻¹, NH₃⁺ band at 1560 cm⁻¹ and the C-NHR band at 1650 cm⁻¹. Upon complexation, the NH₂ band shifts to 1575 cm⁻¹ the NH₃⁺ band to 1510 cm⁻¹ and C-NHR band to 1620 cm⁻¹ [137].

Several workers using infrared spectroscopy have studied the interaction between polymer, salt and plasticizers [138-143]. In all these work the interaction is determined by the shift in the IR spectrum. The FTIR spectra for the polymer
electrolyte sample were recorded using *Perkin Elmer FTIR 1600* series. A drop of a polymer electrolyte sample was placed in between the NaCl pellets and the spectrum was recorded. It can be observed that, when the oxygen of the polyethers is coordinated with LiCF$_3$SO$_3$ (E4-8 and E6-8), the absorption band at 1108 cm$^{-1}$ becomes much wider and new bands appear in its environment, at 1083, 1090, 1138 and 1144 cm$^{-1}$. By the same token, a new and fairly broad absorption band is generated at 1265 cm$^{-1}$, which agglutinates other new and significant bands (1245, 1295, 1310 cm$^{-1}$, etc) [144]. The spectrum is shown in Fig 2.7.

Fig 2.7. IR spectra for E1-0 [PEO/PPO (100/0)], E4-8 [PEO/PPO (80:20)] and E6-8 [PEO/PPz (80/20)] [ref : 144]
2.6 X-ray Photoelectron Spectroscopy (XPS)

The initial studies on PVDF based polymer electrolytes suggests clearly the problem in association of the lithium salt with PVDF. As mentioned in the previous section, X-ray diffraction and FTIR studies can confirm the co-ordination between the polymer host and the lithium salt. In order to substantiate the results further, XPS study was carried out. The basic principle of XPS requires high energy X-rays (>1 keV) to release a core level electron of an element from the atom. This X-ray energy, $h\nu$ must satisfy Einstein’s equation

$$h\nu = \phi + E_b + E_k$$

where $\phi$ is the work function of the material, $E_b$ is the energy absorbed by the core electron to overcome its binding energy with the surface atom and $E_k$ is the kinetic energy of the ejected photoelectron.

The XPS study in this work was carried out using a *Kratos XSAMHS* surface analysis spectrometer with a Mg Kα X-ray source (1253.6 eV) (which is available at the Faculty of Physical and Applied Sciences, University of Kebangsaan Malaysia). The spectrum was taken at an operating current of 10 mA and an operating voltage of 14 kV. The spectrometer was calibrated using a clean Ag plat and the Ag₃d₃/₂ line was set at 368.25 eV. The C1s binding energy at 284.5 eV was used as a second reference. The solid polymer samples were mounted onto a standard stub holder using double-sided adhesive tape. The survey scan was recorded in the energy range between 10 eV to 110 eV. The pass and step size energy was 160 eV and 1 eV/step respectively. Sweep time was set at 300 seconds per sweep. For the narrow scan, smaller pass energy 20 eV with lower step size, 0.1 eV/step were utilized. The
sweep time was 59.898 seconds per sweep. Narrow scans were obtained for the C1s, O1s, N1s, F1s and Li1s regions. The sample analysis chamber was kept at \(5 \times 10^{-9}\) torr or less during the scans.

The vision software provided by Kratos deconvoluted all core level spectra into gaussian component peaks. As an example, the lithium 1s signal from a chitosan-LiCF\(_3\)SO\(_3\) sample (Fig 2.8) was deconvoluted into two Gaussian component peaks [145]. One of these peaks at binding energy of 52.1 eV is assigned to Li-N interaction, which provides evidence of interaction between the lithium cation of the salt and the nitrogen heteroatom of the amide group characteristic of chitosan. In this study, evidence for the occurrence of complexation will also be presented in the same manner. Charging effects were corrected for using the C1s binding energy at 284.5 eV. Samples were etched with Ar in order to remove impurity layers and make the signals more prominent.

![Graph](image)

Fig 2.8. Narrow scan Li 1s signal for chitosan-LiCF\(_3\)SO\(_3\) sample [ref : 145]
2.7 Scanning Electron Microscopy (SEM)

The nature and the morphology of a polymer electrolyte film surface is an important property for the polymer electrolyte. In order to understand the surface morphology of the polymer electrolyte film, SEM study was carried out using Philips 5100 series. The morphology of the polymer electrolyte is analyzed for the polymer films. Some typical examples are shown below. Fig. 2.9 shows the SEM images of the electrolyte films prepared by casting, in which the incorporated plasticizers were evaporated by freeze-drying. The electrolyte film containing no PMMA revealed the homogeneously dispersed pores the size of which was about 1-2 μm as shown in the Fig. 2.9 (a). The larger pores were revealed in the films containing both PMMA and PVC as typically shown in Fig 2.9 (b) and 2.9 (c).

The pores in the SEM images of pure PVC is due to the coagulation of PVC during casting. However, in the case of films containing PMMA, the driving force for the phase separation is reduced, since the PMMA has a compatibility with both the PVC and the plasticizer. This lowering driving force for the phase separation would give rise to the slower coagulation of the PVC and thus led to the better development of the phase mainly composed of the plasticizer and salt due to the longer growth time. Therefore, the addition of PMMA into the casting solution will lead to the larger plasticizer rich phase, which appears as the large pores in the SEM micrograph. Thus, SEM can be used to analyze the phase separation also.
Fig 2.9. SEM images of (a) PVC:PMMA (10:0), (b) PVC:PMMA (7:3) and (c) PVC:PMMA (5:5) [146]
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2.8 Battery Charge and Discharge

A battery is an energy storage device. It stores chemical energy and releases it on demand as electrical energy. The unique feature of batteries is that in them electrical energy is produced directly from chemical energy, by-passing the need to construct a so-called heat engine of one type or another, which is limited by the efficiency of the Carnot cycle.

The specifications of batteries are many and varied. First, one considers the energy density and the power density. These are usually given per unit weight, but in certain applications, the volume may be more important than the weight. This is the case for very small batteries used for wristwatches, electronic calculators, hearing aids and implantable devices. Weight is the critical factor for portable electronic devices for both military and civilian applications. The future of electric vehicles depends predominantly on the energy and the power densities of secondary batteries per unit weight. The current voltage characteristics are very important for all batteries. Ideally one would like to have a flat discharge curve namely a potential that is almost constant throughout the discharge and falls fairly sharp to zero when the voltage of the battery falls below its working voltage.

In order to find out the charge/discharge characteristics of a battery, galvanostatic charge/discharge method has been used. An experiment in electrode kinetics usually consists of determining the current potential relationship under a given set of fixed conditions. The measurement may then be repeated under a set of gradual conditions to obtain the I/E plots as a function of temperature or concentration. In
many cases the experiment can be performed either by controlling the current externally and measuring the resulting changes in potential at the working electrodes (i.e., between the working electrode and a suitable reference) or by controlling the potential and measuring the resulting current. The former is referred to as a galvanostatic measurement and the latter is called a potentiostatic measurement. Usually the battery charge/discharge characteristics were performed using the galvanostatic method. In the present investigation, the galvanostatic charge/discharge characteristic was performed using the BAS LG 50 galvanostatic instrument.

![Diagram](image)

Fig 2.10. Charge / Discharge characteristics of cell (CH)₆ / PVDF:LiClO₄ : PC / (CH)₆ [ref: 122]
Typical charge/discharge characteristics of a battery consists of (CH)$_x$ / PVDF:LiClO$_4$: PC / (CH)$_x$ was shown in the Fig 2.10 [122]. The battery was charged at a constant current of 0.4 mA (100 Ah/kg based on the weight of (CH)$_x$ film) for 10 min and discharged at a constant current of 0.4 mA to 2.5 V immediately after charging.

From these charge/discharge characteristics, a variety of parameters can be calculated. The voltage versus capacity curve for the battery from the charge/discharge characteristics is shown in the Fig. 2.11 [67]. This capacity versus voltage curve is for Li-V$_x$O$_{13}$ cells incorporating a PEO: LiCF$_3$SO$_3$ electrolyte operating at different current densities.

![Fig 2.11. Capacity versus voltage curve for the Li-V$_x$O$_{13}$ cell. [ref: 67]]
The electrode materials for the battery were prepared as follows. For the cathode, graphite is mixed with petroleum coke in the ratio of 70:30 and heated at 450°C in argon atmosphere for 6 hours. This mixture was then mixed with PVDF in the weight ratio of 95:5 with the lower weight ratio for PVDF. The new mixture was then dissolved in 15 ml of N-methyl pyrrolidone casted on the copper mesh. The mixture is allowed to dry inside a desiccator before it is cut into pieces of smaller sizes. The batteries were assembled inside an argon filled glove box specially designed battery casings made from Teflon. The lithium metal (Alfa product) is used as the anode.