EXPERIMENTAL METHODS

2.1 Materials and Methods:

2.1.1 Starting Materials

Polyethylene oxide (PEO) of average molecular weight 900,000 and polyvinyl chloride (PVC) of very high molecular weight were obtained from Aldrich. Triphenyltin chloride was purchased from Merck; the other organotin salts, namely, dibutyltin bis{p-[N-(3,4-dinitro phenyl)]amino benzoate} and dioctyltin bis{p-[N-(3,4-dinitro phenyl)]amino benzoate} were gift samples obtained from the Organotin Laboratory at the Institute of Postgraduate studies and Research(IPSR) in the University of Malaya. Other materials like ethylene carbonate (EC), propylene carbonate (PC), manganese dioxide (MnO_2) and the tin metal sheet (99.9%) were purchased from Fluka.

2.1.2 Preparation of Polymer Electrolyte Films

Samples of starting polymer materials and the dopant salts were dried in vaccum prior to use. The polymer electrolytes films were prepared by the solution casting technique.

Preparation of PEO-Ph_3SnCl films

In a typical preparation, 1.408 gm of PEO were dissolved in 40 mL acetonitrile and to this was added 0.385 gm of triphenyltin chloride dissolved in 20 mL tetrahydrofuran. The resulting solution contained in an open beaker was stirred for 24 hours to facilitate solvent evaporation. At the end of this period, the contents of the beaker were poured into a glass petri dish and left to stand until a distinct intact film was obtained that could be peeled off. Following further drying off this film in open air, it was placed in a desiccator pending studies on its characterization and properties.

Other PEO-Ph_3SnCl films with different ratios of dopant to polymer were similarly prepared. The above procedure was duplicated for the preparation of the corresponding dibutyltin bis{p-[N-(3,4-dinitro phenyl)]amino benzoate} and dioctyltin bis{p-[N-(3,4-dinitro phenyl)]amino benzoate} -doped films.

Preparation of PEO-Ph_3SnCl-EC-PC films

This was prepared in a similar manner to that described above, except for the addition of a mixture of 0.3598 mL of ethylene carbonate (EC) and 0.061 mL of propylene carbonate (PC) to the solution of PEO-Ph_3SnCl. This finally yields a film in which the total plasticiser ratio to polymer was 15:85, by weight. Films with other weight ratios as well as containing different relative amounts of EC and PC were similarly prepared (see table 2.1).

Table 2.1: Different weight compositions of PEO-Ph_3SnCl : EC : PC

Ratio	PEO (gm)	Sn (gm)	EC (gm)	PC (gm)
85 : 3 : 12	1.1968	0.385	0.1097	0.4388
85 : 5 : 10	1.1968	0.385	0.183	0.3657
85 : 7 : 8	1.1968	0.385	0.2559	0.2926
85 : 12 : 3	1.1968	0.385	0.4754	0.061

Preparation of PVC-Ph_3SnCl films

Procedurally, the preparation of the above film followed the steps outlined for the PEO case, except that here the polymer and the organotin dopant were initially dissolved together in tetrahydrofuran. The PVC – organotin ratio was varied from 90:10 to 50:50. The co-addition of the EC-PC plasticizers was confined to the 90:10 composition as the latter was found to have comparatively higher conductivity at ambient temperatures (*vide infra*).

2.1.3 Preparation of Composite Cathodes

Composite cathodes of MnO_2 and I_2 were prepared for battery cell fabrication employing the organotin – doped polymer film as electrolyte.

The composite MnO_2 cathode was prepared as follows:

1.5 gm of MnO_2 (analytical grade) was dissolved in 30 mL tetrahydrofuran (THF) and to this was added with stirring 0.25 gm of PVC pre-dissolved in 20 mL THF. Next, a suitably cut portion from a previously prepared (dried to constant weight) organotin – doped polymer film, weighing 0.975 gm, was added to the above solution and the whole stirred for 2-3 hours. A film of the composite cathode on the copper mesh (0.25 micron) was thus obtained and used as such in the cell fabrication. Other compositional ratios were also tried but were found to be less effective.

A similar procedure with iodine replacing MnO_2 was followed for the preparation of composite iodine cathode, the amounts of materials used remaining essentially unaltered.

2.1.4 Cell Fabrication

The polymer-plasticizer-salt film with the highest electrical conductivity was used as the electrolyte in the solid state electrochemical cell fabrication. Manganese dioxide (MnO_2) was chosen as the cathode material and tin metal (99.9%) was used as the anode. The composite cathode film, comprising 60% by weight of MnO2, 1% by weight of PVC, and 39% by weight of the (PEO-Ph_3SnCl:EC:PC) blend electrolyte, was prepared as described in Section 2.1.3. A small amount of the resulting solution was poured into a glass petri dish and on the top of the liquid surface was placed a copper mesh (0.25 micron) . The remainder of the solution was poured onto the copper mesh and left to dry. The cell was assembled by sandwiching the electrolyte between the tin metal and the composite cathode film under a pressure of approximately 20MPa. The fabricated cells have the galvanic chain of Sn metal | Electrolyte | MnO_2 ; Sn metal | Electrolyte | Iodine.

2.2 Characterization Techniques

Various techniques have been used to study the structure of these polymer electrolytes, including XRD and other spectroscopic techniques [43]. For the purpose of this study, the following spectroscopic experiments as given in table 2.2 were carried out.

All the samples were measured for their conductivity by sandwiching the films between two stainless steel electrodes of diameter 2 cm; impedance on the specimens were obtained using a Hioki 3520-01 LCR Hi-tester from which the best conducting sample was found and used for cell fabrication and study of discharge characteristics.

Table 2.2: List of experiments that were carried out in doing this work.

EXPERIMENT	Purpose of Study
• UV-Visible Spectroscopy	To confirm the presence of the added dopant.
• Infrared Spectroscopy	To confirm the presence of the added dopant.
• Differential Thermal Analysis	To check formation of polymer-dopant complexes.
• X-ray diffraction Analysis	To check the degree of crystallinity.
• Impedance Spectroscopy	To check the ac conductivity and identify the best conducting electrolyte.
• Scanning Electron Microscopy	To study the morphology of the samples.

2.2.1 UV-Visible Spectroscopy

Optical transmission and absorbance data in the wavelength range 200 - 800 nm were recorded using a Shimadzu UV - 3010 PC spectrophotometer. Spectrophotometers for measurement of absorption in the ultraviolet, visible and infrared regions of the spectrum are similar in that they consist of the same basic units, such as source of radiation, monochromator unit, and sample compartment and detector system. In this arrangement only a small percentage of the radiation from the source traverses the sample at any one time and photodecomposition of the sample is minimized.

In an ultraviolet/visible spectrophotometer, radiation from the source is passed via a mirror system to the monochromator unit where the radiation is dispersed into different wavelengths while passing through the exit slit. The wavelength of the radiation passing through the exit slit is varied by rotating the prism. In double beam operation the monochromatic split into two beams by means of a rotating sector. After passing through the sample and reference cells the light beams are focused onto a detector. By having two cells, the absorbance of the sample holder's material is deducted and only sample absorbance is recorded. A computer is interfaced to this system and thus the absorbance or transmittance of the sample is recorded as a function of the wavelength. By using UV-Visible spectroscopy, the result of complexation between PEO and Ph_3SnCl can be observed by a change in wavelength of maximum absorption as well as in molar absorptivity [44].

2.2.2 Infrared Spectroscopy (IR)

Infrared spectroscopy is a technique of identifying certain molecular species in a sample through interaction of infrared radiation with the various vibration modes of the molecules of the species leading to absorption of the infrared radiation [45]. Infrared absorption by the molecules will only take place if there is a change of dipole moment during vibration of the molecules. Thus infrared absorption takes place only in heteronuclear molecules and does not take place in homonuclear molecules. The infrared spectra of PEO and PEO doped organotin compounds were recorded in the 4000-500 cm^{-1} wavelength span which embraces most stretching, bending, twisting, and wagging vibrations are locared in the region 4000-500 cm^{-1}. The frequency which is of particular interest here is the Sn–O stretch which occours in the 500-700 cm^{-1} region, whose unequivocal identification can serve as evidence for PEO-organotin complexation [46-49].

2.2.3 Differential Thermal Analysis

In this technique, a few milligrams of the sample and a reference material such as Al_2O_3 are heated in the same heating block in hermetically sealed containers. The heat input into the sample and the reference is then the same, but when a thermal event such as melting temperature is reached, the temperature of the sample will differ from that of the reference. This temperature difference is plotted on the Y-axis. A linear heating rate is normally used so that what is plotted on the X axis can be regarded either as temperature or time .

A glass transition temperature is indicated by a steep change in the specific heat, whereas the infinite specific heat expected on melting appears as a DSC or DTA peak due to gradual melting over a small temperature range.

A Perkin Elmer DTA 7 Differential Thermal Analyzer was used to determine the glass transition temperatures, melting temperatures and other thermal characteristics of the electrolytes. A broad DTA spectrum is to be anticipated when the polymer salt forms a complex with the dopant [50,51].

2.2.4 X - Ray Diffraction

In any crystalline compound (most solids are crystalline), the atoms are arranged in a regular, three-dimensional pattern unique to that compound. X- rays striking a crystal interact with the atoms creating waves of scattered X-rays that intensify each other in certain directions. Intensification occurs when the rays diffracted from parallel atomic planes are in phase (when the path difference is an integral number of wavelength). This situation is represented by the well known Bragg equation

$$n\lambda = 2d \sin\theta \qquad (2.1)$$

where λ is the wavelength, d the interplanar spacing, θ the angle of incidence (and diffraction) and n is the integer .

An X- ray diffractometer works on the principle that when a sample is irradiated, the X-rays are diffracted in directions characteristic of the compounds present in the sample under analysis. By measuring the angles at which diffraction peaks occur and their intensities, the type and the amount respectively of the sample's constituent compounds can be determined. The incident beam of X-ray used is monochromatic; typically the copper K_α line at 0.154nm is used. A motor is attached to the sample holder which is used to rotate the sample during the measurement. Rotation is particularly important when the particle size in the sample is relatively large. The detector made from semiconductor is mounted in the goniometer and slowly rotated around the sample while the intensity of the radiation is recorded as a function of angle [52].

2.2.5 Scanning Electron Microscopy (SEM)

SEM was carried out with Philips 515 scanning electron microscope. Since its invention in the early sixties, SEM has been utilised in many surface science studies. An electron microscope is an electron accelerator that focuses the electron beam with the aid of electromagnetic lenses. The accelerating voltage is typically in the range of 60-100 keV. The illumination source is a tungsten filament, also known as the electron gun, which is enclosed in a metal cylinder called the Wehnelt cylinder or cathode and heated to a high temperature (2700^0K) causing electrons to be released from the tip of the filament. Lenses focus the electron beam and magnify the image after the electrons pass through the specimen. The lenses and the specimen stage are mounted in a vertical, lead-lined cylindrical column that allows the interior to be maintained under vacuum. The vacuum is needed so that the electrons do not collide with air molecules and get knocked off before they reach the specimen. A good vacuum is required (10^{-7} torr) since the mean free path of an electron is 125 cm in a vacuum of 10^{-4} torr.

In the scanning electron microscope (SEM), a beam of accelerated electrons is used to image surface features of specimens. The surface topography of a specimen is generated by the electrons reflected (back scattered) or given off (secondary electrons) by a metal-coated (gold or gold-palladium) specimen struck by electron beam. This is accomplished by foccussing a narrow, intense beam of electrons to form a very small spot of illumination (between $2A^0$ & $200A^0$ diameter) on the specimen. This fine spot is then moved side ways by deflecting the beam so that a narrow ribbon of specimen, whose width corresponds to the diameter of the spot, is traversed by the electron probe spot. The probe spot is then returned very rapidly to a point on the specimen one spot diameter above or below the original starting point, and the adjacent ribbon of the specimen is then traversed. The process is repeated until the whole area of the specimen has been covered by this "scanning" probe spot of electrons. The pattern of lines is called a raster, and is just like the ones seen on the screen of a television set. A visual image corresponding to the signal produced by the interaction between the beam spot and the specimen at each point along each scan line is simultaneously built up on the face of a cathode ray tube (CRT) in the same way as a television picture is generated. The specimen image then appears in a similar way to the pictures seen on a black & white television screen [53].

2.2.6 Energy Dispersive Analysis of X-rays (EDAX)

EDAX was performed with a Philips 9800 equipment coupled with LEICA S440 scanning electron microscope to analyse the chemical composition of the sample surface. X-ray microanalysis can be considered as a quantitative and non-destructive technique that allows *in situ* detection of elements as low as 10^{-19}g. Its limitations are that it cannot distinguish between ionic, non-ionic and isotopic species and EDAX in particular cannot detect the low atomic number elements. EDAX fitted with beryllium window detectors can detect elements with $Z>11$ while EDAX with windowless detection can detect elements with $Z>5$.

In the present study EDAX was used to confirm the presence of tin. The sample for observation was mounted on a stub using conductive carbon cement which provided the necessary electrical connections between the sample and holder. The sample was also carbon coated to prevent surface charging which may cause defects.

2.2.7 Impedance Spectroscopy (IS)

Although relatively new, IS has emerged as a powerful tool for the characterization of many electrical properties of materials and their interfaces with electron conducting electrodes [54]. With IS, it is possible to differentiate processes occurring at the electrode-electrolyte junction and at the grain boundaries with those occurring in the bulk.

In this work, the evaluation by IS of electrode and/or electrolyte behavior is made with cells having two identical electrodes applied to the faces of a sample. The cell is then subjected to an electrical stimulus in the form of a single frequency voltage and its impedance and the phase shift responses are measured at that frequency. The frequency is then changed and impedance and phase shift measurements continued until the whole frequency range is completed.

When a monochromatic signal $v(t) = V_m \sin(\omega t)$ is applied to a sample, the resulting steady state current through the material is given by $i(t) = I_m \sin(\omega t + \theta)$. Here V_m is the voltage amplitude, $\omega = 2\pi f$, f being the single frequency (which is changed until the frequency range is completed) and θ is the phase difference between the voltage and the current. For a purely resistive behavior, θ is zero. The impedance can now be defined as $Z(\omega) = v(t)\, i(t)$; its magnitude, $|Z(\omega)| = V_m/I_m$. Impedance is a more general concept than resistance because it takes phase differences into account. Impedance is a vector quantity and may be represented as $Z(\omega) = Z_R + jZ_I$, where Z_R is the real impedance and Z_I is the magnitude of the imaginary impedance. Z_R and Z_I are related to the magnitude of the complex impedance via the equations;

$$Z_R = |Z(\omega)| \cos\theta \tag{2.2}$$

and

$$Z_I = |Z(\omega)| \sin\theta \tag{2.3}$$

The response of a circuit, such as sketched in Fig 2.1, consisting of a parallel resistor-capacitor combination in series with another capacitor is as shown by the dotted lines in Fig.2.2. This is often called a Cole-Cole plot. In Fig.2.1, R is the bulk electrolyte resistance, C_1 is the geometric capacitance and C_2 is the charge transfer capacitance. The geometric capacitance is the capacitance that would arise if only air were present in the electrode gap. However, this term remains even in the presence of the electrolyte. The circuit of Fig.2.1 is the simplest arrangement that will give the impedance plot shown [55-57]. The type of Cole-Cole plots often encountered in solid electrolyte studies are the inclined spur or spike and the depressed semicircle with an inclined spike as shown by the bold lines in Fig.2.2. No manipulation of series and parallel combinations of resistors and capacitors can give these 'non-ideal' spectra [58].

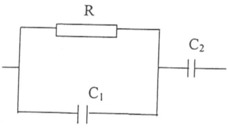

Fig 2.1

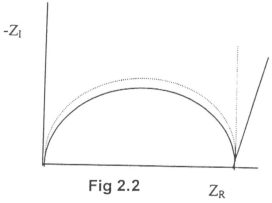

Fig 2.2

Figure: 2.1. Equivalent circuit containing R, C1 and C2

Figure: 2.2 Impedance response of circuit containing R, C1 and C2

To account for the depressed semicircle and spike inclination, a type of circuit element called the constant phase element (CPE) is required. The impedance of a CPE, Z_{CPE} is given by [55, 58]

$$Z_{CPE} = k\,(j\,(\omega)^{-\alpha} \qquad (2.4)$$

where $0 \leq \alpha \leq 1$, Z is independent of frequency and k is just the bulkresistance , R_B. When $\alpha = 1$, $Z = k\,(j\omega)^{-1} = -j\,/(\omega k)^{-1}$. Here $(\omega k)^{-1}$ is capacitive reactance with k^{-1} corresponding to a capacitance C. The CPE exhibits mixed resistor – capacitor behavior when α is between 0 and 1. Incorporating the expression for Z_{CPE} , an equivalent circuit can be modelled and the complex plane plots be interpreted. Knowing the bulk resistance, the electrical conductivity of the sample can be calculated using the equation

$$\sigma = L\,/R_bA \qquad (2.5) \qquad [59]$$

where σ is the electrical conductivity, L the sample thickness and A is the surface area of contact.

In all the impedance measurements the sample is sandwiched between two stainless steel electrodes. The thickness of the polymer film is measured using a micrometer screw gauge and the diameter of the electrode is measured with a vernier caliper. The impedance was measured with a HIOKI 3520-01 LCR Hi - Tester which has been interfaced to a computer. This bridge was set to measure the impedance and phase angle from 40Hz to 100 kHz. The software controlling the measurement also calculates the real and imaginary impedance. The imaginary impedance is usually negative indicating the sample to be capacitive. A plot of negative imaginary impedance versus real impedance on a graph with horizontal and vertical axes having the same scale will give a semicircle if the sample has a Debye nature. The conductivity measurements for each sample was also carried out at different temperatures up to 100^0C. If the plot of In (T) versus $10^3/T$ obeys the Arrhenius rule, the activation energy, E_A, can be calculated for each sample using the equation

$$\sigma = \frac{\sigma_0}{T} \exp (-E_A / kT) \qquad (2.6)$$

where σ_0 is the conductivity pre-factor, k and T are the Boltzman constant and absolute temperature, respectively [28].

2.2.8 Cell Characterization and Discharge Characteristics

The open circuit voltage is the voltage of the cell when there is no current flow through the external circuit. It is different from the potential difference of the cell i.e. the voltage of the cell when a certain current has been drawn out of it. These voltages are the result of the half-cell reactions between the anode and the cathode species at equilibrium via which the ions travel through the solid electrolytes of PEO-Ph_3SnCl complexes.

The discharge characteristics of an electrochemical cell can be defined as the variation of the terminal voltage against discharge time at a constant load from which the lifetime or operating time of the cell can be determined. Discharge characteristics and open circuit potential for these cells were obtained using a computer controlled galvanostat (BAS LG - 50) at the Institute of Postgraduate Studies and Research [60].