

## CHAPTER FOUR

### CHARACTERISTICS OF PEO-TETRAMETHYLAMMONIUM

#### DICHLOROTRIPHENYL –STANNATE (1V)

##### 4.1 Introduction

Different weight ratios [Salt/Polymer 0.25/0.75, 0.20/0.80, 0.15/0.85, 0.10/0.90, 0.05/0.95] of the PEO–tetramethylammonium dichloro triphenylstannate polymer electrolyte films were prepared using the technique as mentioned in section 2.1.2. As discussed earlier in section 3.1 small quantities of propylene carbonate (PC) and ethylene carbonate (EC) were added in order to enhance the conductivity. The composition that afforded the best conductivity for PEO- tetramethyl ammonium dichloro triphenyl stannate:EC:PC was (0.90:0.10) : (50:50), i.e. 0.90g PEO 0.10g tetramethylammonium dichlorotriphenyl stannate and 0.125g of EC 0.125g of PC.

##### 4.2 XRD Analysis

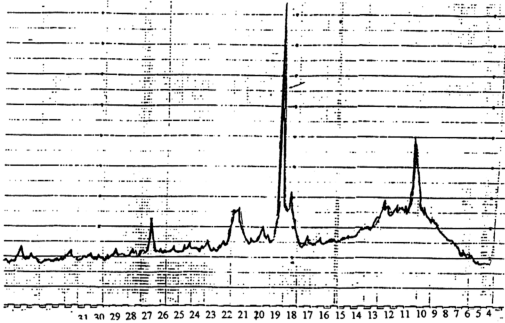
The X-ray diffraction pattern of PEO tetramethyl ammonium dichloro triphenyl stannate systems are as shown in Fig 4.1(a-d) and the PEO and salt with different concentration of plasticizers are shown in Fig 4.2 (a-c). Sharp and intense peaks occur at  $2\theta = 19^\circ$  and  $23^\circ$ , are indicative of some degree of crystallinity in the polymer. These peaks, although still present in the organotin-doped PEO, show slight shifts in their position and strong reduction in relative intensity.

This suggests that the added organotin intruding into the crystalline regions of the polymer cause the transformation of these regions to the amorphous state, in conformity with observations on other PEO-systems doped with inorganic salts at below saturation levels(103-104). This probably accounts for the higher

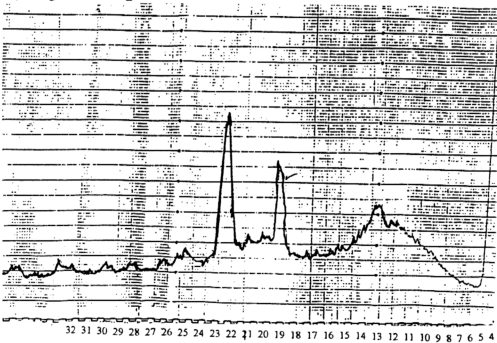
conductivity values for PEO doped tetramethyl ammonium dichloro triphenyl stannate relative to undoped PEO (vide infra).

Fig4.2.1 PEO + different concentrations of  $[\text{Ph}_3\text{SnSCN}]^+ [\text{Me}_4\text{N}]$

a) 0.75 gPEO+ 0.25g salt



b) 0.90g PEO+ 0.10g salt



c) 0.85gm PEO + 0.15gm salt

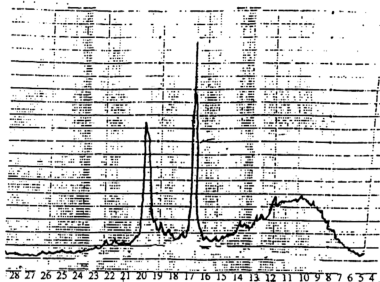
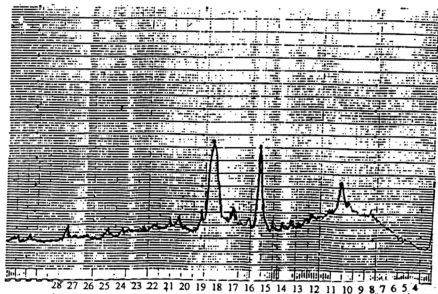
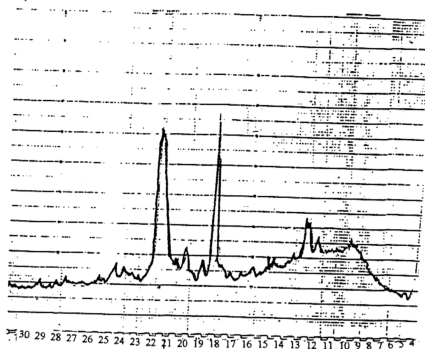


Fig 4.2.2 (a-c) PEO+  $[\text{Ph}_3\text{SnSCN}]^+ [\text{Me}_4\text{N}]^-$  + ECPC

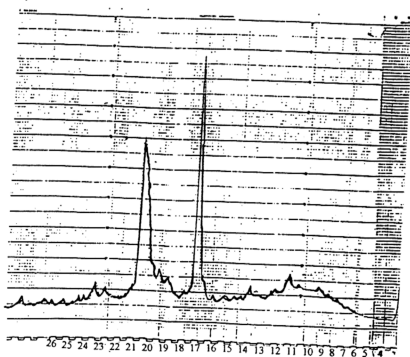
a) 50EC 50PC



b) 90%PC



c) 90% EC





### 4.3 IR- Spectral Analysis

The IR spectrum of pure PEO is depicted in Fig 4.3 the IR spectrum for pure tetramethyl ammonium dichloro triphenyl stannate and the compound with different concentration of EC PC are compared in Fig 4.4 (a), 4.5, 4.6, 4.7, and 4.8 respectively. As can be seen, the salt free PEO polymer has distinct bands at 844 and 948  $\text{cm}^{-1}$  which are assigned to  $\text{CH}_2$  rocking modes in a gauche conformation [105]. The infrared spectrum was taken from 4000  $\text{cm}^{-1}$  to 70  $\text{cm}^{-1}$  in the case of tetramethyl ammonium dichloro triphenyl stannate. The observed vibrational modes of the  $\text{SnC}_3\text{Cl}_2$  skeleton are 148, 192 and 136  $\text{cm}^{-1}$ . If the  $\text{Ph}_3\text{SnCl}_2^-$  anion is considered to be monomeric, the tin atom must be Penta coordinate and various structures based on the trigonal bipyramid and the square based pyranid are possible. The band at 192  $\text{cm}^{-1}$  assigned to  $\text{SnCl}_2$  antisymmetrical stretch. These bands are characteristic bands of tetramethylammonium dichloro triphenyl stannate [106] appearing with slight shifts in the band position may be indicative of complex formation between PEO and respective triorganotin dopants.

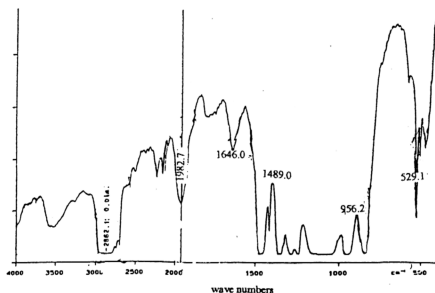


Fig4.3 (a) IR spectrum of pure PEO

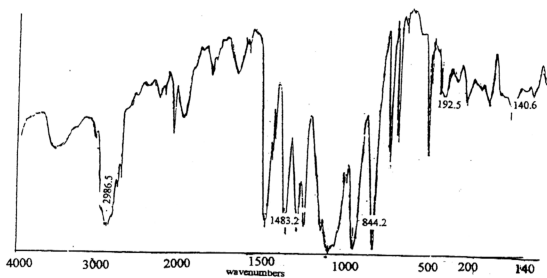


Fig 4.4 0.90gm PEO + 0.10gm Salt

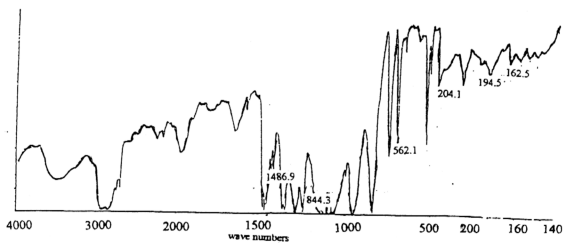


Fig 4.5 salt + PEO + 50 EC 50 PC

Fig 4.6 0.90 gPEO + 0.10g salt + EC

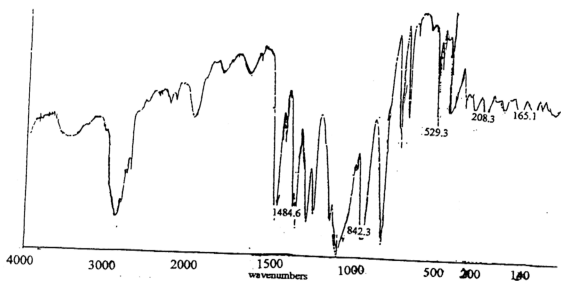
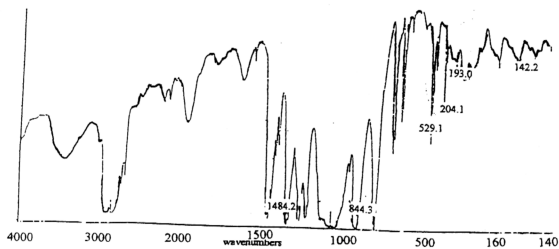
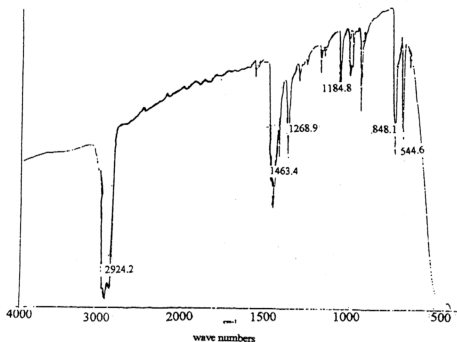


Fig 4.7 0.90 gPEO + 0.10g salt + PC



**Fig 4.8 IR spectrum of tetramethylammonium dichlorotriphenyl stannate**



#### 4.4 Impedance Spectroscopy Analysis

It is necessary to know the electrical conductivity of the samples so that the sample with composition giving the highest electrical conductivity can be identified and used for the fabrication of electrochemical cells.

##### 4.4.1 Room Temperature Dependence Of Electrical Conductivity

From the data of impedance spectroscopy, the cole-cole plot is constructed by plotting the imaginary impedance magnitude ( $Z_i = Z \sin \theta$ ) against the real impedance magnitude ( $Z_r = Z \cos \theta$ ). The cole-cole plots obtained on films of different compositions of PEO- tetramethyl ammonium dichlorotriphenyl stannate depicted in Fig 4.9 (a-c) and PEO salt with different concentrations of ECPC are shown in Fig 4.10 (a-c) respectively. The electrical conductivity was calculated as explained in the previous chapter section 3.4.1 the values are tabulated in Table

4.1

Weight ratio of Sn/EO	Bulk resistance in Ohms	Thickness of the the film in cms	Conductivity S/cm
0.25/0.75	4223461.3	0.0112	$1.72 \times 10^{-9}$
0.20/0.80	4332853.3	0.0125	$1.8 \times 10^{-9}$
0.15/0.85	4666662.1	0.0103	$1.4 \times 10^{-8}$
0.10/0.90	375242.2	0.0105	$1.8 \times 10^{-8}$
0.05/0.95	3834020.1	0.0114	$1.93 \times 10^{-9}$

Table 4.1 .Conductivity values

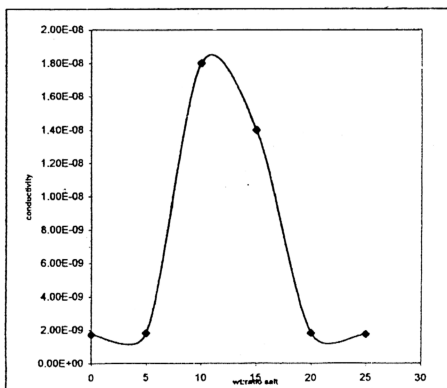


Fig 4.11.Compositional dependence of conductivity of PEO-Tetramethyl ammonium dichlorotriphenyl stannate

With an increase in the Sn/EO ratio, the conductivity reaches a maximum of  $1.8 \times 10^{-8} \text{ S/cm}$  for PEO with the salt at Sn/EO 0.10/0.90. In PEO electrolytes, it is generally accepted that the conduction phases are amorphous phases containing dopants [107]. Therefore, the initial rise in conductivity can be attributed to the increasing salt concentration [108]. On the other hand, the decrease in the conductivity of PEO- tetramethyl ammonium dichloro tri phenyl stannate electrolytes observed at higher dopant concentrations can be related to the decrease in ionic mobility [109] as well as to the increase in the degree of crystallinity of PEO. The decrease in mobility is related to the increase in viscosity of the polymers on addition of dopant [110-112].

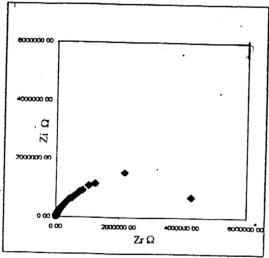
As these polymer electrolytes cannot be used as electrolytes for all solid state batteries at ambient temperature for the reasons already stated in chapter 3, the plasticizers (EC & PC) were therefore added to the polymer electrolytes at different ratios to secure the best conducting samples. These were obtained for the composition (PEO-tetra methyl ammo: dichlorotriphenyl stannate: EC:PC (90:10) : (50:50) see in Table 4.2

Sample Composition				Thickness	Bulk	Electrical
PEO	Sn	EC	PC	t cm	conductivity	
0.90	0.10	0	0	0.104	375244.2	$1.8 \times 10^{-7}$
0.90	0.10	0	100	0.11	4666.6	$1.7 \times 10^{-5}$
0.90	0.10	100	0	0.012	3853211.2	$2.0 \times 10^{-9}$
0.90	0.10	50	50	0.115	4232.2	$1.5 \times 10^{-5}$
0.90	0.10	70	30	0.0125	4332853.1	$1.8 \times 10^{-9}$
0.90	0.10	30	70	0.012	4253.6	$2.1 \times 10^{-6}$

Table 4.2 conductivity values for dichlorotriphenyl tin stannate with different concentrations of ECPC

Fig 4.9 (a-c) PEO+ tetramethyl ammoniumdichlorotriphenyl stannate different concentration

Fig 4.9 a, 0.90 gm PEO+ 0.10 gm salt



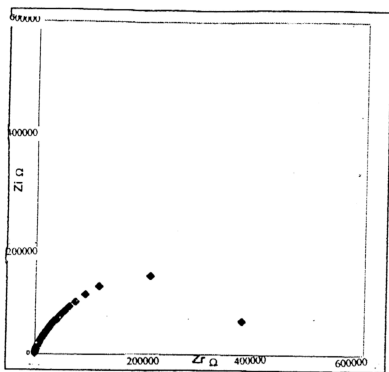


Fig 4.9. b, 0.85gm PEO+0.15gm salt

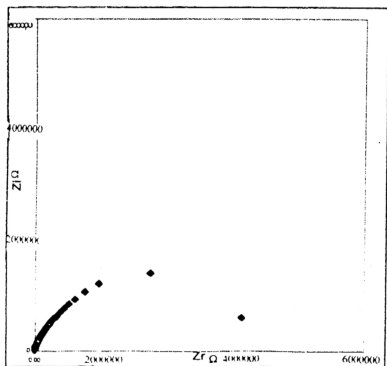
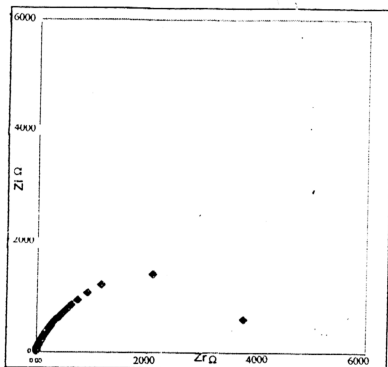


Fig 4.9. c, 0.75gm PEO +0.025gm salt

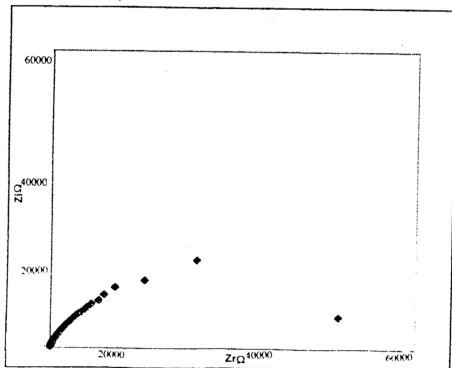


Fig 4.10 (a-c) PEO+  $[\text{Ph}_3\text{SnCl}_2]^- [\text{Me}_4\text{N}]^+ + \text{ECPC}$ 

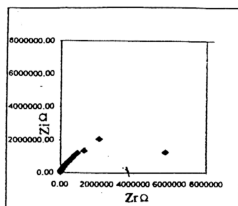
a) 50EC 50PC



b) 90% PC



c) 90% EC



#### 4.4.2 Temperature Dependence of Electrical Conductivity

The temperature dependence of the electrical conductivity of PEO- tetramethyl ammonium dichlorotriphenyl stannate is shown in the Fig 4.12. As discussed earlier in section 3.4.4 this compound also shows VTF behaviour.

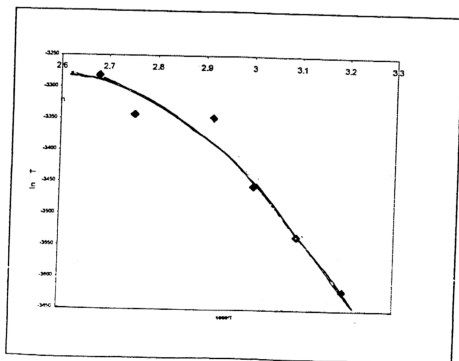


Fig 4.4.2 VTF behaviour of the tetramethylammonium dichlorotriphenyl stannate

#### 4.4.2 Complex Permittivity

As discussed earlier in Sec 3.4.2 here also we can observe Fig4.13 the dielectric constant varies with salt ratio.

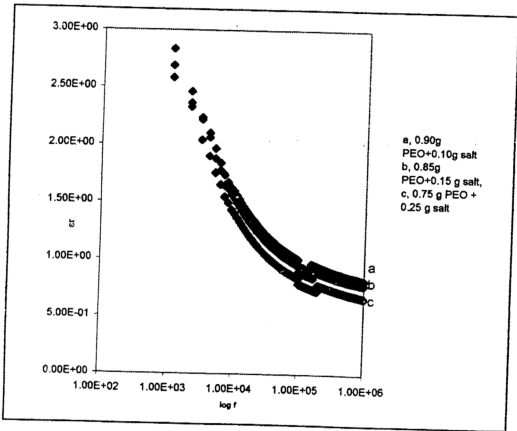


Fig 4.13 Dielectric constant versus frequency for the PEO with the salt at different concentrations

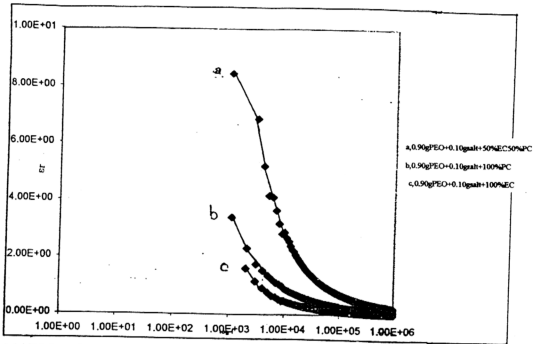


Fig 4.14 Dielectric constant versus frequency for PEO +salt+different con. of ECPC

Fig 4.15 and Fig 4.16 shows the dielectric loss versus frequency. Dielectric loss also increases at low frequency due to the free charge motion with in the material.

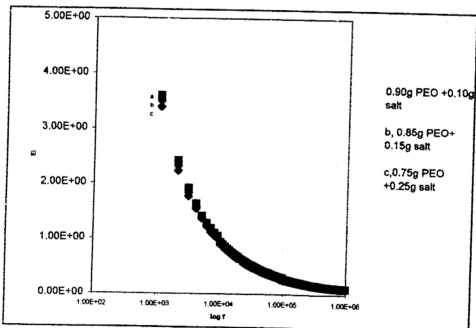


Fig 4.15 Dielectric loss versus frequency for PEO with the salt at different concentration

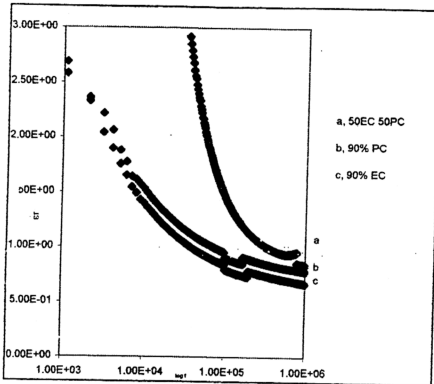


Fig 4.16 Dielectric loss versus frequency for PEO+salt with different concentrations of ECPC

#### 4.4.3 Electrical Modulus

Fig 4.17 and 4.18 show the modulus patterns for the dichlorotriphenyltin stannate with different concentrations of EC and PC. The real part  $M_r$  is shown in Fig 4.17 and 4.18, the imaginary part is shown in Fig 4.19 and 4.20. Hence modulus is the reciprocal of resistivity, the highest conducting sample is at the bottom most line.

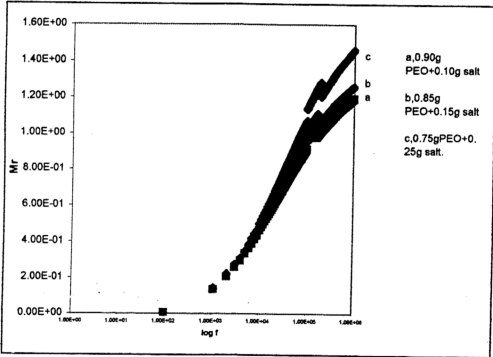


Fig 4.17 Real part of modulus versus frequency at different salt concentrations

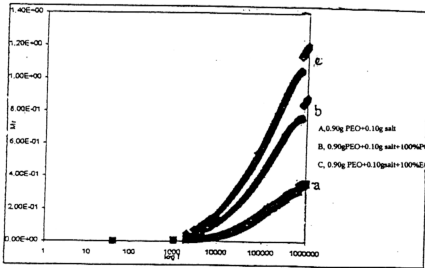


Fig 4.18 Real part of electrical modulus versus frequency of salt with different concentrations of ECPC

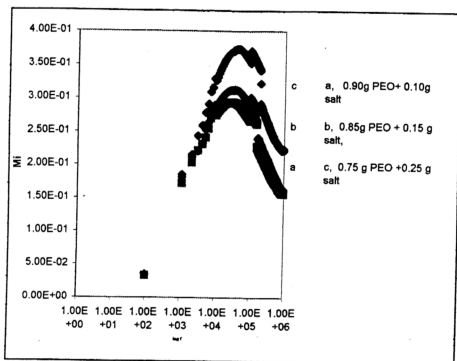


Fig 4.19 Imaginary part of electrical modulus versus frequency at different salt concentrations

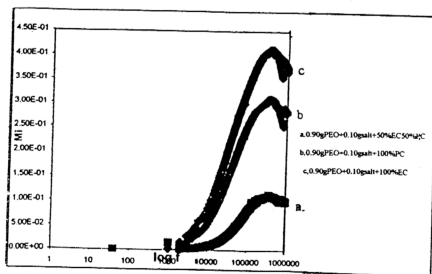


Fig 4.20 Imaginary part of electrical modulus versus frequency of salt with different concentrations of ECPC.

#### 4.5 Transference number Measurement

The transference number studies were performed to enable the major conducting species in the polymer electrolytes to be identified. The polymerization current was collected until it gets saturated. The value of transference number was obtained by normalizing the polarization current was obtained by normalizing the polarization current with the initial current at  $t=0$ . The experiment is conducted as described in previous section 3.6. From the studies it shows the presence of electronic conduction in the compound Fig 4.21

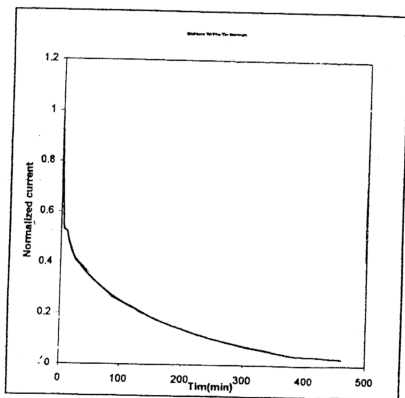


Fig 4.21 shows electronic conduction in tetramethylammonium dichlorotriphenyl stannate



The presence of a quite substantial electronic conduction is not favourable for good battery performance. This is because internal short circuiting can cause the lost of mobile ions due to the reduction of the ionic species to its metallic form.