

## Characteristics of PVC- $\text{Ph}_3\text{SnCl}$

### 5.1 Introduction

Different compositions based on weight percentages of the polymer electrolyte systems were prepared using the technique described earlier in section 2.1.2. The resulting films were further dried and used for analysis. The films showed low room temperature conductivity of  $10^{-8}$  S/cm. Therefore their use as electrolytes in solid state batteries would enable attainment of only moderate to high power in the 50-100 $\mu\text{C}$  range [93-97]. This prompted the use of plasticizers such as ethylene carbonate (EC) and propylene carbonate (PC) as additives in the preparation of the above films, since as with the case for the PEO –  $\text{Ph}_3\text{SnCl}$  system it was envisaged that their presence would enhance conductivity.

The following compositions with and without plasticizers were prepared

- 1) 75%PVC+25% $\text{Ph}_3\text{SnCl}$
- 2) 50%PVC+50% $\text{Ph}_3\text{SnCl}$
- 3) 80%PVC+20% $\text{Ph}_3\text{SnCl}$
- 4) 90%PVC+10% $\text{Ph}_3\text{SnCl}$

The composition with 75% PVC + 25%  $\text{Ph}_3\text{SnCl}$  yielded a relative higher conductivity value (*vide infra*), and hence was chosen to prepare the following plasticized polymer electrolyte films:

- 5) 15 wt% PVC + 5 wt%  $\text{Ph}_3\text{SnCl}$  + 20 wt% PC + 60 wt% EC
- 6) 15 wt% PVC + 5 wt%  $\text{Ph}_3\text{SnCl}$  + 30 wt%PC + 50 wt%EC
- 7) 15 wt% PVC + 5 wt%  $\text{Ph}_3\text{SnCl}$  + 40 wt% PC + 40 wt% EC
- 8) 15 wt% PVC + 5 wt%  $\text{Ph}_3\text{SnCl}$  + 60 wt% PC + 20 wt% EC.

The best conducting sample among these compositions (5) - (8) was then used for the cell fabrication and study of discharge characteristics.

## 5.2 XRD Analysis

The XRD patterns for PVC, and PVC -  $\text{Ph}_3\text{SnCl}$  were procured as depicted in Figures 3.1 through 5.3. A broad peak is shown in the XRD pattern for Pure PVC which indicates that the material is not fully amorphous as seen in Figure 5.1.

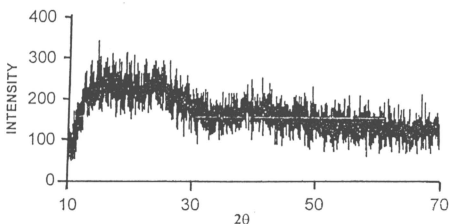


Figure 5.1: XRD pattern for pure PVC

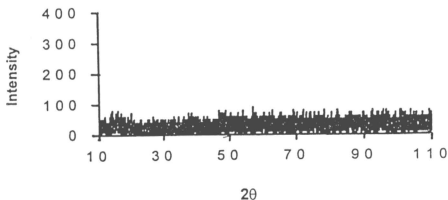
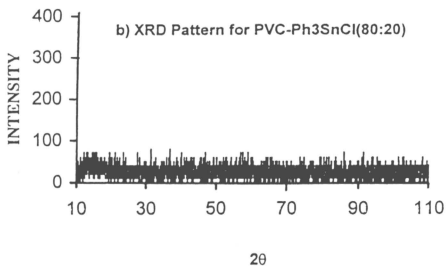
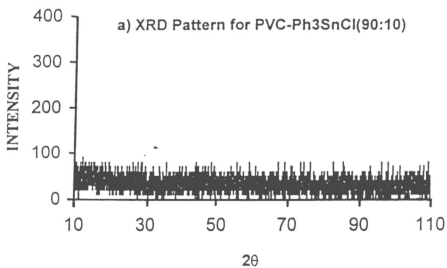


Figure 5.2: XRD pattern for pure  $\text{Ph}_3\text{SnCl}$



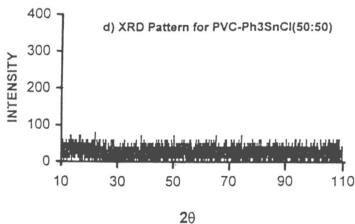
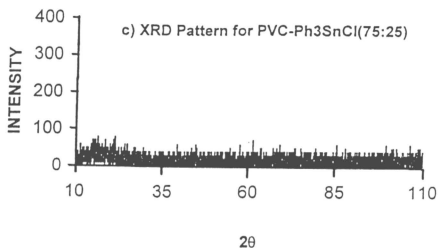
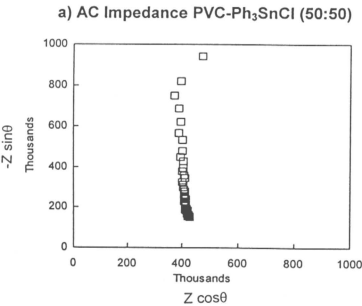


Figure 5.3: XRD patterns (a – d) for different compositions of PVC-Ph<sub>3</sub>SnCl

Pure  $\text{Ph}_3\text{SnCl}$ , however, shows no peaks in the XRD (Fig. 5.2). A similar result was also obtained for the PVC -  $\text{Ph}_3\text{SnCl}$  systems as shown in Figures 5.3 (a - d). This suggests that the  $\text{Ph}_3\text{SnCl}$  when added to the PVC matrix leads to a diminution in the crystalline character of the polymer.

5.3 Impedance Spectroscopy Analysis

Impedance of the specimen was taken in the frequency range 40 - 100kHz and Cole-Cole plots were constructed in the manner described in Chapter 3 (Section 3.6.1). The Cole - Cole plots for different composition of PVC -  $\text{Ph}_3\text{SnCl}$  and also PVC -  $\text{Ph}_3\text{SnCl}$ :EC:PC are exhibited in Figures 5.4 (a & b) and 5.5 (a - d) from which the bulk resistance of each sample was determined and the conductivities were calculated using the equation 3.1 and these are tabulated in Table 5.1 and 5.2.



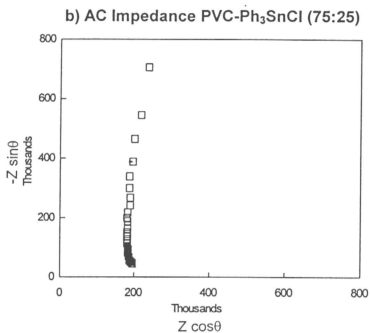
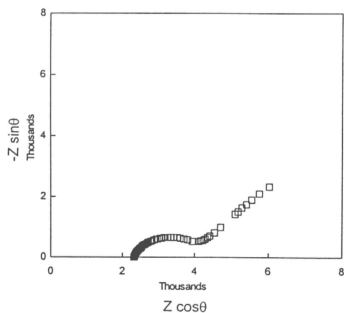
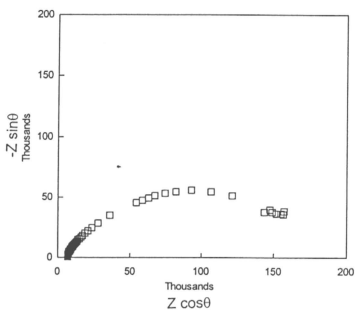
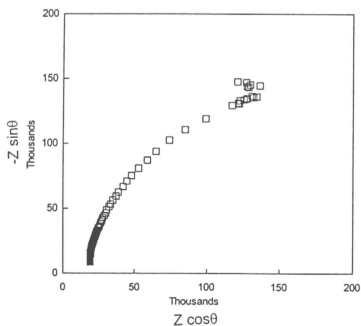


Figure 5.4: Cole - Cole plots (a & b) for PVC -  $\text{Ph}_3\text{SnCl}$  polymer electrolyte systems with different composition ratios.

a) AC Impedance PVC -  $\text{Ph}_3\text{SnCl}$ :EC:PC (15:5:20:60)



**b) AC Impedance PVC -  $\text{Ph}_3\text{SnCl}$ :EC:PC (15:5:30:50)****c) AC Impedance PVC -  $\text{Ph}_3\text{SnCl}$ :EC:PC (15:5:40:40)**

d) AC Impedance PVC-Ph<sub>3</sub>SnCl:EC:PC (15:5:60:20)

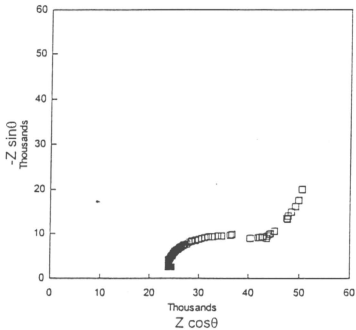


Figure 5.5: Cole - Cole plots (a - d) for PVC-Ph<sub>3</sub>SnCl plasticized polymer electrolyte System.

Table 5.1: Ionic conductivity values of PVC - Ph<sub>3</sub>SnCl from the Cole-Cole plots.

Sample Composition	Conductivity S/cm
90:10	$2.66 \times 10^{-8}$
80:20	$2.6 \times 10^{-8}$
75:25	$3.8 \times 10^{-8}$
50:50	$1.73 \times 10^{-8}$

Table 5.2: Ionic conductivity values from the Cole-Cole plots of PVC-Ph<sub>3</sub>SnCl:EC:PC

Sample Composition	Conductivity S/cm
15%PVC+5%Ph <sub>3</sub> SnCl:20%PC:60%EC	$3.3 \times 10^{-6}$
15%PVC+5%Ph <sub>3</sub> SnCl:30%PC:50%EC	$1.19 \times 10^{-6}$
15%PVC+5%Ph <sub>3</sub> SnCl:40%PC:40%EC	$4 \times 10^{-7}$
15%PVC+5%Ph <sub>3</sub> SnCl:60%PC:20%EC	$3.05 \times 10^{-7}$

From tables 5.1 and 5.2 it can be seen that the plasticized polymer electrolytes shows better conductivity than the simple polymer -dopant



system. Initially in the polymer electrolyte systems the conductivity was found to be the highest when the wt% ratio between the polymer to dopant was 75:25. This ratio was kept constant in the follow-up preparations involving added plasticizers. From table 5.2 it can be seen that the plasticizer polymer electrolyte system with composition 15 wt% PVC + 5 wt%  $\text{Ph}_3\text{SnCl}$  + 20 wt% PC + 60 wt% EC gives the best conductivity of  $3.3 \times 10^{-6} \text{ S cm}^{-1}$ . In plasticized polymer electrolytes, the role of the host polymer is secondary in the conducting matrix. The dopant solvating power and the sufficient mobility of ion necessary for ionic conduction are imparted by the incorporated plasticizer. Hence the plasticised polymer electrolyte has high conductivity as compared with the polymer electrolyte system without the plasticizer.

#### 5.4 EDAX Analysis

Figures 5.6 and 5.7 shows EDAX pictures for pure PVC and PVC- $\text{Ph}_3\text{SnCl}$ :EC:PC which clearly shows the presence of Sn and Cl.

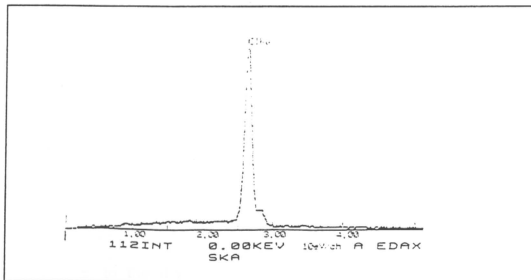
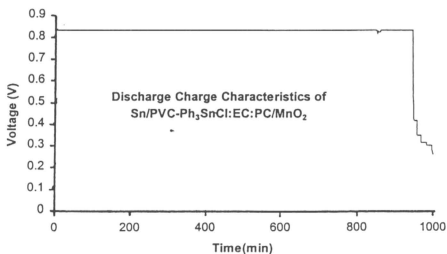


Figure 5.6: EDAX data for pure PVC

fabricated cell was measured and the OCV was found to be 0.87 volts.

This voltage is the result of the half-cell reactions between the anode and



**Figure 5.8: Discharge characteristics of fabricated cell**

the cathode species at equilibrium via which the ions travel through the solid electrolytes of PVC-Ph<sub>3</sub>SnCl system.

Figure 5.8 shows the discharge characteristics for the fabricated cell at a constant load current of 10  $\mu$ A. It is found that the voltage of the cell drops at the beginning of the discharge and as the discharge proceeds the voltage appears to remain quite stable for several minutes in the plateau region before it starts to decrease. As mentioned in Chapter 3 (Section 3.8) the theoretical OCV value of the above cells is also 1.36V and the experimentally obtained OCV values are 60% - 70% of the theoretical value.

## ***Summary and Conclusions***

UV – visible spectral analysis of the  $\text{Ph}_3\text{SnCl}$  - doped PEO revealed slight perturbations of the tin environment in the polymer. FTIR spectroscopy indicated that there was a weak interaction between PEO and  $\text{Ph}_3\text{SnCl}$ , which was observed from the band shifts of the  $\text{Ph}_3\text{SnCl}$ . X – ray diffraction study showed that the polymer electrolyte was semi – amorphous in nature and confirmed the disruption of the crystalline nature of PEO upon interaction with the organotin dopants. The plasticized PEO -  $\text{Ph}_3\text{SnCl}$  showed higher conductivity than the unplasticized PEO -  $\text{Ph}_3\text{SnCl}$  from the impedance spectroscopy analysis . The probable reason for the high ionic conductivity in the plasticized polymer electrolyte is that the plasticizer decreases the viscosity of the polymer electrolyte and thereby increases ionic mobility. The temperature dependent studies for the conductivity showed an Arrhenius pattern, with an activation energy of 0.21 eV, which is strongly indicative of ionic conductivity, based on similar values reported in the literature for other PEO – doped systems. SEM studies showed that the incorporation of the dopant in the polymer changed its spherulitic morphology altogether, implying a conversion to essentially amorphous characteristics. EDAX analysis of the doped polymer served to corroborate further the presence of Sn in the PEO – matrix. The discharge characteristics of the fabricated cells show an open circuit potential (OCV) of 0.8 V for  $\text{Sn/PEO-Ph}_3\text{SnCl:EC:PC/ MnO}_2$  and 0.65 V for  $\text{Sn/PEO-Ph}_3\text{SnCl:EC:PC/ I}_2$  which are in the range of 60% -

70% of their theoretical OCV values.

A similar pattern of results was also obtained for PEO doped with dibutyltin - bis{p-[N-(3,4-dinitro phenyl)]amino benzoate} and dioctyltin - bis{p-[N-(3,4-dinitro phenyl)]amino benzoate} . However, the conductivity was found to be lower than the PEO – Ph<sub>3</sub>SnCl system. Another study was done by preparing the electrolytes with a different host polymer, namely PVC. X-ray diffraction analysis showed the disruption of the crystalline nature of the PVC upon the addition of Ph<sub>3</sub>SnCl. Impedance spectroscopic analysis showed that the conductivity of the PVC – Ph<sub>3</sub>SnCl is of the order 10<sup>-7</sup>S/cm which is lower than those obtained with the PEO - organotin systems. However, from the discharge characteristics of PVC - Ph<sub>3</sub>SnCl, it is seen that the OCV of 0.87V for PVC – Ph<sub>3</sub>SnCl is quite good when compared with the OCV values of the other PEO – organotin systems.

Overall, it is seen from the discharge characteristics of batteries fabricated using the polymer electrolytes developed in the present study that their cell capacities are rather low when compared with some current commercial systems. This poor capacity may be due to the low ionic conductivity of the polymer electrolyte, high interfacial resistance and the formation of surface layer between the electrode - electrolyte interface. Nevertheless we have successfully shown that PEO or PVC doped organotin films can be employed as an electrolyte to make solid state polymer batteries. However, further studies are needed to improve the

ionic conductivity, and contact at the electrode - electrolyte interface to have a better battery performance.