Chapter 4

Results & Discussion
PVC doped with Li^{+} salts and plasticizers

4.0 RESULTS AND DISCUSSION OF PVC DOPED WITH Li^+ SALTS AND PLASTICIZERS

In order to improve upon the existing conductivity of PVC doped with $LiClO_4$, which is of the order of 10^{-7}, plasticizers were added to the above. The plasticizers used in our study are a combination of EC (ethylene carbonate) and PC (propylene carbonate). It was first started with a small concentration and later on, steadily increased.

4.1 AC Conductivity Analysis

Table[4.1] to table [4.5] gives us the details of the concentration that was added to the polymer-salt mixture. With the increase in the concentration of plasticizers, it can be seen that conductivity also increases slowly and steadily. And finally in the table [4.5], it can be seen that with the polymer salt ratio of 70 : 30, a good conductivity of the order of 10^{-4} is achieved. Although this value is obtained in an earlier concentration in table [4.4], the value is higher in the next table, i.e., table [4.5]

Table – 4.1: Conductivity at PVC – $LiClO_4$ ratio at 40 : 10

Sl. No.	PVC Wt% (g)	$LiClO_4$ Wt% (g)	EC Wt%	PC Wt%	Thickness (cms)	Conductivity (S/cms)
1	40	10	50	-	0.0105	5.77×10^{-7}
2	**40**	**10**	**25**	**25**	**0.0150**	**1.08×10^{-6}**
3	40	10	-	50	0.0115	4.41×10^{-7}

Table – 4.2: Conductivity at PVC – $LiClO_4$ ratio at 30 : 10

Sl. No.	PVC Wt% (g)	$LiClO_4$ Wt% (g)	EC Wt%	PC Wt%	Thickness (cms)	Conductivity (S/cms)
1	30	10	40	20	0.0035	1.26×10^{-7}
2	**30**	**10**	**30**	**30**	**0.0056**	**7.13×10^{-6}**
3	30	10	50	10	0.0045	2.38×10^{-6}

Table – 4.3: Conductivity at PVC – $LiClO_4$ ratio at 20 : 10

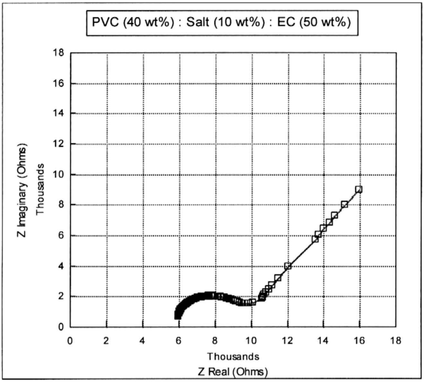
Sl. No.	PVC Wt% (g)	$LiClO_4$ Wt% (g)	EC Wt%	PC Wt%	Thickness (cms)	Conductivity (S/cms)
1	20	10	35	35	0.0080	1.02×10^{-6}
2	20	10	30	40	0.0080	1.95×10^{-7}
3	**20**	**10**	**25**	**45**	**0.0070**	**8.44×10^{-6}**
4	20	10	20	50	0.0070	4.69×10^{-6}

Table – 4.4: Conductivity at PVC – $LiClO_4$ ratio at 15 : 5

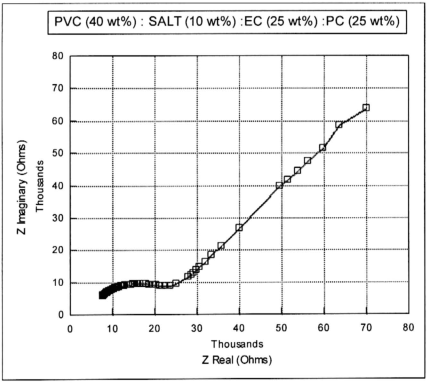
Sl. No.	PVC Wt% (g)	$LiClO_4$ Wt% (g)	EC Wt%	PC Wt%	Thickness (cms)	Conductivity (S/cms)
1	15	5	80	-	0.0080	6.56×10^{-7}
2	**15**	**5**	**40**	**40**	**0.0060**	**1.73×10^{-4}**
3	15	5	-	80	0.0080	2.23×10^{-5}

Table – 4.5: Conductivity at PVC – $LiClO_4$ ratio at 11.7 : 5

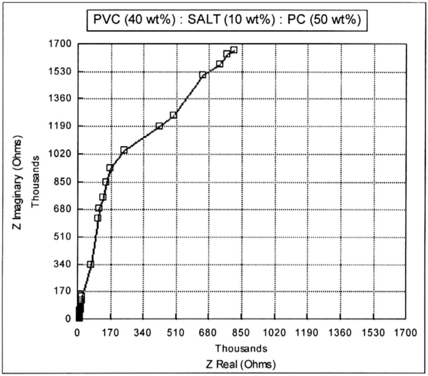
Sl. No.	PVC Wt% (g)	$LiClO_4$ Wt% (g)	EC Wt%	PC Wt%	Thickness (cms)	Conductivity (S/cms)
1	11.7	5	3.3	80	0.0085	6.50×10^{-5}
2	**11.7**	**5**	**13.3**	70	**0.0075**	**3.34×10^{-4}**
3	11.7	5	23.3	60	0.0090	3.47×10^{-6}
4	11.7	5	33.3	50	0.0065	1.81×10^{-5}
5	11.7	5	43.3	40	0.0185	5.40×10^{-5}
6	11.7	5	53.3	30	0.0090	1.21×10^{-5}
7	11.7	5	63.3	20	0.0125	2.15×10^{-5}
8	11.7	5	73.3	10	0.0190	3.41×10^{-5}



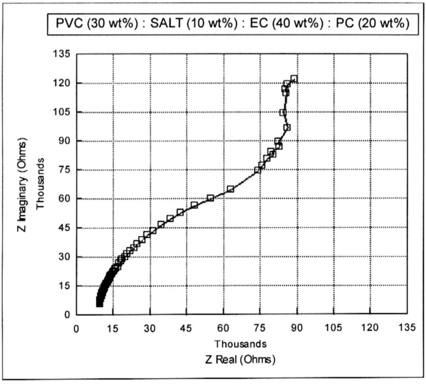
Fig[4.1]: Impedance spectrum of PVC-$LiClO_4$ with plasticizers (R_b=5787Ω)



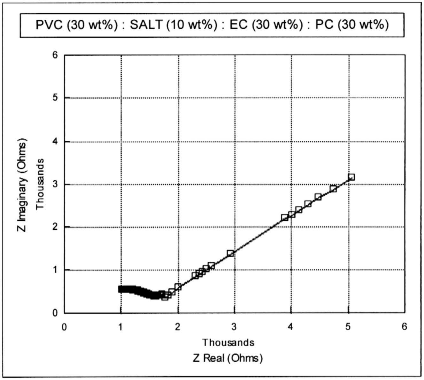
Fig[4.2]: Impedance spectrum of PVC-$LiClO_4$ with plasticizers (R_b=4423Ω)



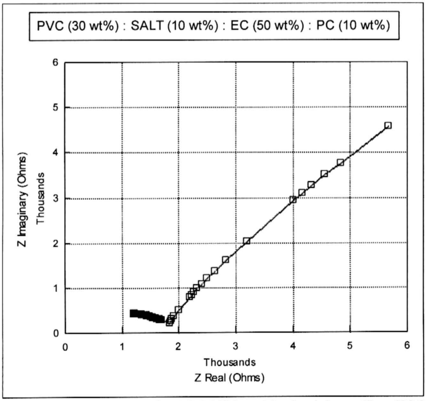
Fig[4.3]: Impedance spectrum of PVC-$LiClO_4$ with plasticizers (R_b=8292Ω)



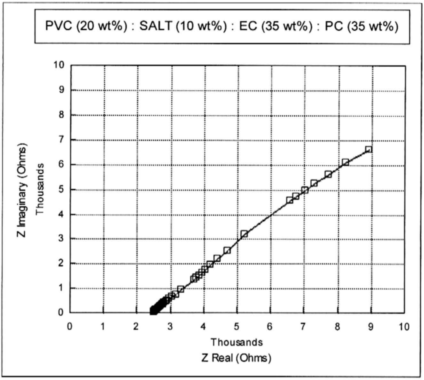
Fig[4.4]: Impedance spectrum of PVC-$LiClO_4$ with plasticizers (R_b=8804Ω)



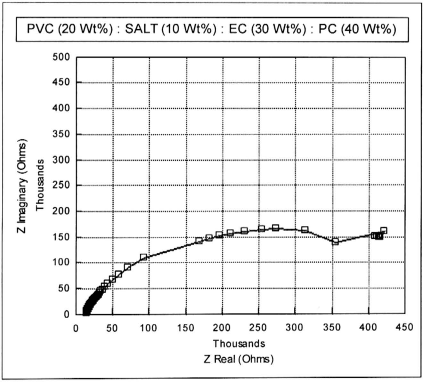
Fig[4.5]: Impedance spectrum of PVC-$LiClO_4$ with plasticizers (R_b=457Ω)



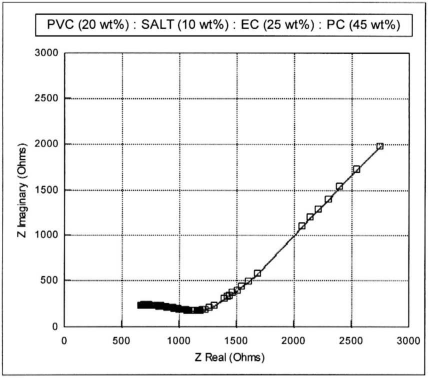
Fig[4.6]: Impedance spectrum of PVC-$LiClO_4$ with plasticizers (R_b=633Ω)



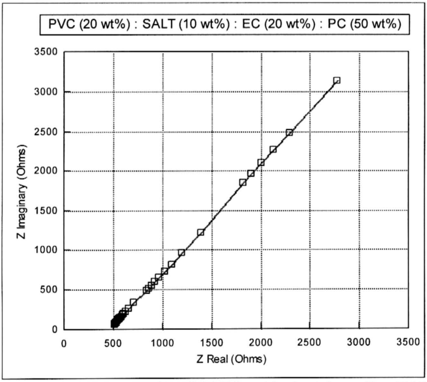
Fig[4.7]: Impedance spectrum of PVC-$LiClO_4$ with plasticizers (R_b=2476Ω)



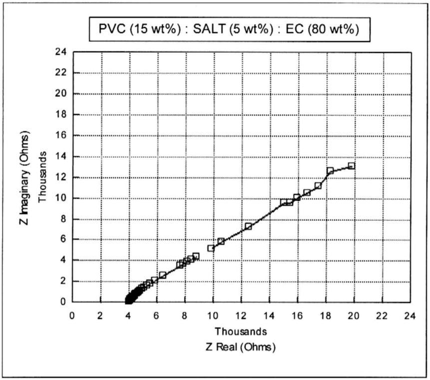
Fig[4.8]: Impedance spectrum of PVC-$LiClO_4$ with plasticizers (R_b=13043Ω)



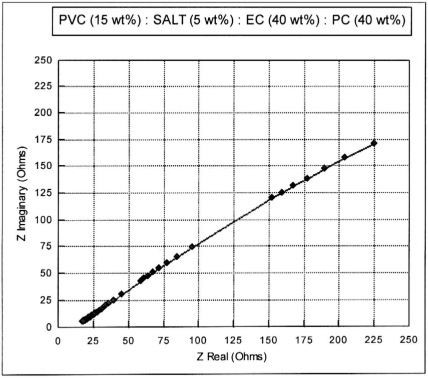
Fig[4.9]: Impedance spectrum of PVC-$LiClO_4$ with plasticizers (R_b=264Ω)



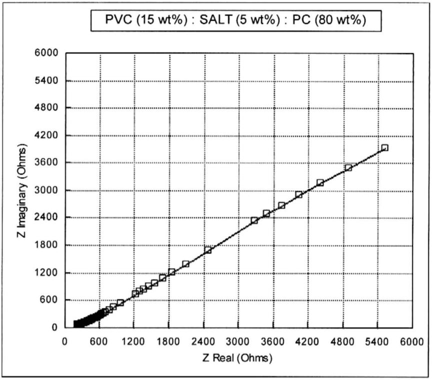
Fig[4.10]: Impedance spectrum of PVC-$LiClO_4$ with plasticizers (R_b=475Ω)



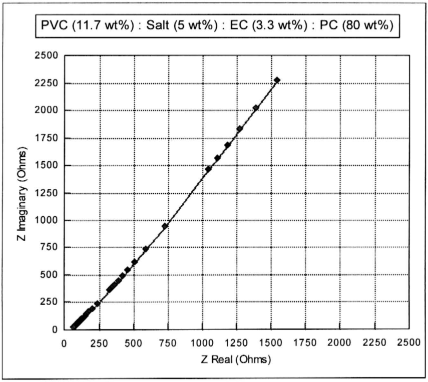
Fig[4.11]: Impedance spectrum of PVC-$LiClO_4$ with plasticizers (R_b=3882Ω)



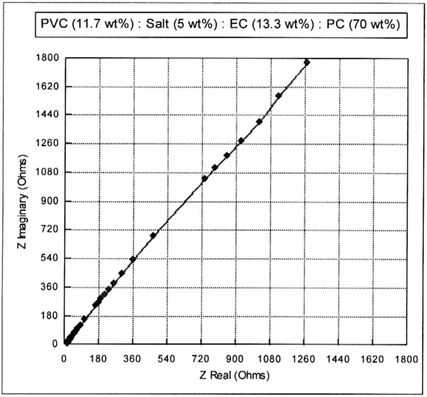
Fig[4.12]: Impedance spectrum of PVC-$LiClO_4$ with plasticizers (R_b=11.6Ω)



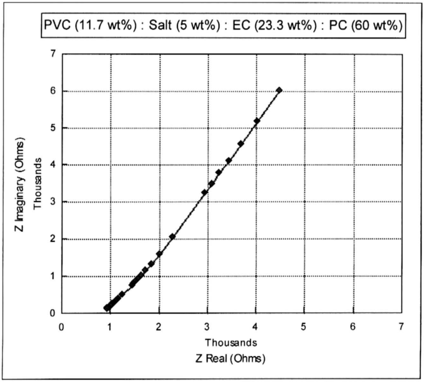
Fig[4.13]: Impedance spectrum of PVC-$LiClO_4$ with plasticizers (R_b=114Ω)



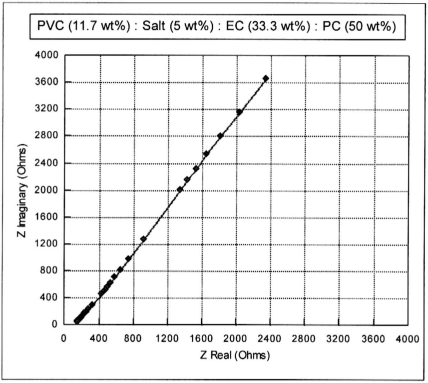
Fig[4.14]: Impedance spectrum of PVC-$LiClO_4$ with plasticizers (R_b=41.6Ω)



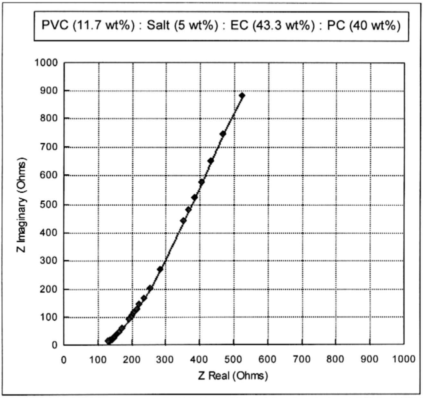
Fig[4.15]: Impedance spectrum of PVC-$LiClO_4$ with plasticizers (R_b=7.14Ω)



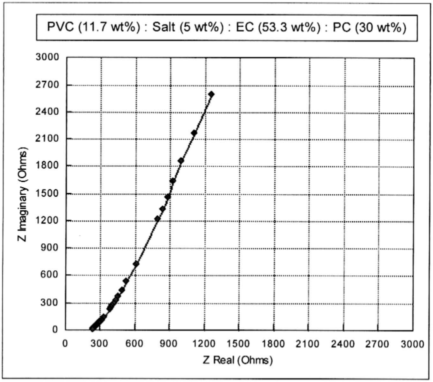
Fig[4.16]: Impedance spectrum of PVC-$LiClO_4$ with plasticizers (R_b=825Ω)



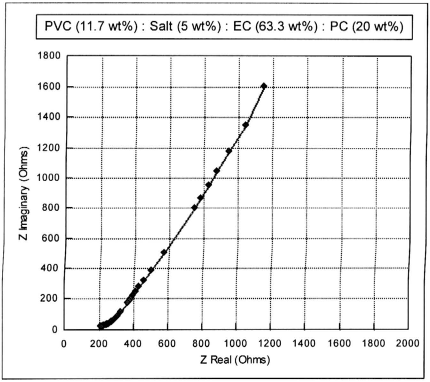
Fig[4.17]: Impedance spectrum of PVC-$LiClO_4$ with plasticizers (R_b=114Ω)



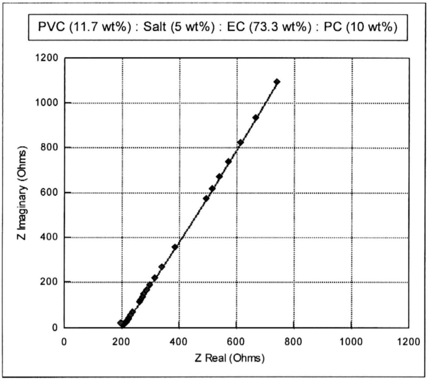
Fig[4.18]: Impedance spectrum of PVC-$LiClO_4$ with plasticizers (R_b=109Ω)



Fig[4.19]: Impedance spectrum of PVC-$LiClO_4$ with plasticizers (R_b=235Ω)



Fig[4.20]: Impedance spectrum of PVC-$LiClO_4$ with plasticizers (R_b=185Ω)



Fig[4.21]: Impedance spectrum of PVC-$LiClO_4$ with plasticizers (R_b=177Ω)

The key to the development of polymer electrolytes with ionic conductivities approaching those of their liquid electrolyte counterparts (i.e., $\sigma=10^{-3}$ S/cm) at room temperature) is to incorporate structural features in the electrolyte that increase the mobility and concentration of the ionic charge carriers. Traditionally, this has been done by adding plasticizers to the polymer electrolyte. The main effect of the plasticizer is higher conductivity [75]. The mobility of the charge carriers is apparently increased as a result of addition of plasticizers. The addition of a suitable amount of PC or a mixture of PC and EC to the polymer-salt complex does increase the room temperature conductivity of the electrolyte closed to 10^{-3} S/cm as seen from the tables given above. The high dielectric constants of the organic liquids promote the dissociation of ion pairs, enhancing the concentration of ionic charge carriers [76,77]. The smaller activation energies for the motion of small molecules compare with those for the sequential motion of polymer backbones promote enhanced ionic mobility at low temperature. Since EC, PC or EC/PC have a higher permittivity solvent they help in increasing room temperature conductivity

Table [4.6] gives the dielectric constants and viscosities of of several plasticizers.

Sl.No.	Plasticizers	Dielectric Constant	Viscosity (cp)
1	Dimethylformamide	36.7	0.80
2	γ-Butyrolactone	39.1	1.75
3	Propylene Carbonate	64.4	2.51
4	Ethylene Carbonate	89.0	1.90
5	Poly(ethylene glycol)$_{400}$	-	6.47

Thus the apparent role of the plasticizer is to assist in dissolution of and dissociation of the salt. One might then expect the conductivity to be related to the polarity of the plasticizer. Whilst this may be one contributing factor, it is not the sole reason for enhanced values of conductivity. The trend follows the viscosity of the medium rather than the dielectric constant, thereby following Walden's rule that the ionic mobility is inversely proportional to the viscosity of the medium. This implies that in hybrid films the plasticizer acts as a polar medium providing a pathway for conduction by ion transport. The polymer is then merely a convenient supporting system which affords structural stability to the film while assisting in the dissolution of the salt in the matrix. Conduction then depends on the saturation amounts of the salt dissolved in the plasticizer and the viscosity of the medium, which will control the ease with which the dissociated ion can migrate [78].

The scheme below illustrates the formation of the new solid electrolytes. Li^+ salt-solvates (I-as shown below) form when the Li^+ salt dissolved in the EC/PC solvent mixture is immobilised in the PVC polymer host by the electrostatic forces between the solvate and the polymer (as shown in II). [49]

$LiX + EC/PC \rightarrow Li + [(PC)_x(EC)_y]X$

I

PVC

$\rightarrow (CH_2CHCl)_n$

$Li + [(PC)_x(EC)_y]X$

II

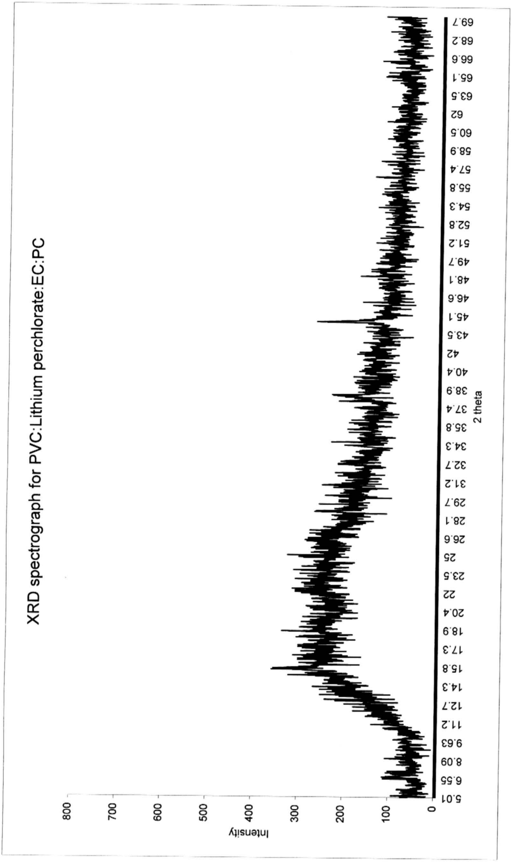
The complex impedance diagram which is the plot of $-Z'$ versus Z'' can show the characteristics of the interface, where $-Z'$ and Z'' are real and imaginary part of the complex impedance respectively. Since the blocking electrode was used in the impedance measurements, the film/electrode interface can be regarded as a capacitance. When this capacitance is ideal, it should give rise to a vertical spike in complex impedance diagram. However, the spike inclined at an angle less than 90^o to Z'axis is generally observed instead of the vertical spike. This is known to rise from the roughness of the flim/electrode interface [79-82]. In such cases, the impedance corresponding to the film/electrode interface can be given by the following equation.

$$Z^*=Z_0\omega^{-\alpha}[Cos(\alpha\pi/2) - isin(\alpha\pi/2)] \quad (1)$$

Where Z_0 is the proportionality constant and ω is the frequency of the ac electric field. From the figure [4.15], it can be seen that θ is 50^0 and using this value, we get value of α=0.5555, which is greater than 0 and less than 1. This implies that the material is more capacitative in nature.

4.2 XRD Analysis

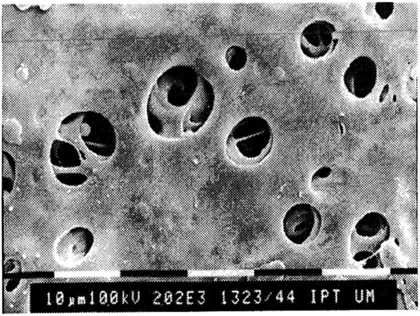
Figure[4.22] shows the XRD graph of the polymer electrolyte with the highest conductivity of **3.34 x 10^{-4}S/cm** from the table[4.5]. It can seen from this graph that it is completely amorphous and complexation has taken place between the polymer, salt and plasticizers. There are absolutely no peaks in the graph, i.e., the degree of crystallanity is very low which accounts for the high conductivity. Comparing the figures [4.22] and [3.13], we can clearly see that complexation is more and the degree of crystallanity is low in the former than the latter. It can be infered that conductivity is high in the amorphous phase.



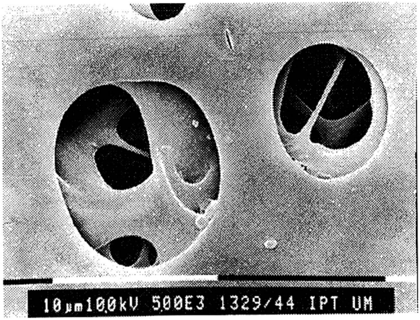
Fig[4.22]: XRD of polymer-salt complex with plasticizers giving a conductivity of 3.34 x 10^{-4} S/cm.

4.3 SEM Analysis

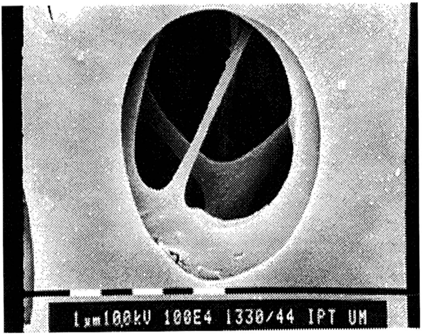
SEM micrographs for the polymer-salt complex with plasticizers giving a conductivity of 3.34 x 10^{-4} S/cm are shown below in figures [4.23] to [4.25] in different levels of magnification. From these pictures, it is very clear that the surface appears to be more smooth, because of which the ions move more steadily and more in number thus increasing the conductivity of the film. It can also be seen that, the surface area is high and more continuous when compared to the SEM micrograph of polymer-salt complex without plasticizers, which satisfies an important prerequisite for a good electrolyte. From the picture, it is evident that there is a more even distribution of Li salts. All these lead to an increase in the conductivity of the film. Plasticizers seem to have played an important role. Upon their addition, the film has gained more smoothness and continuity.



Fig[4.23]: SEM micrograph of PVC-$LiClO_4$ with plasticizer (2000 magnification)



Fig[4.24]: SEM micrograph of PVC-$LiClO_4$ with plasticizer (5000 magnification)



Fig[4.25]: SEM micrograph of PVC-$LiClO_4$ with plasticizer (10000 magnification)

4.4 EDAX Analysis

Similar to our earlier attempt, EDAX was carried out again on the film containing plasticizer with highest conductivity to find out whether there are any other elements which contribute to the increase in σ value. But no peak was obtained other than that of chlorine beloning to the PVC chain. EDAX was also performed on the mouth of the large holes seen from the SEM micrographs. There was no change in the result obtained. Lithium, once again, cannot be detected because of its low atomic weight. Figures [4.26] and [4.27] give the EDAX graphs taken on the surface and from the mouth of the hole.

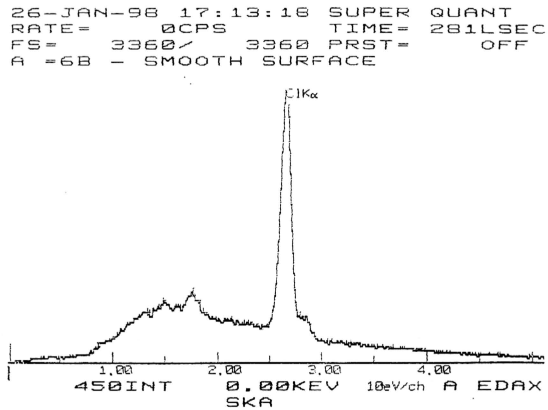


Fig [4.26]: EDAX of the polymer film on a smooth surface

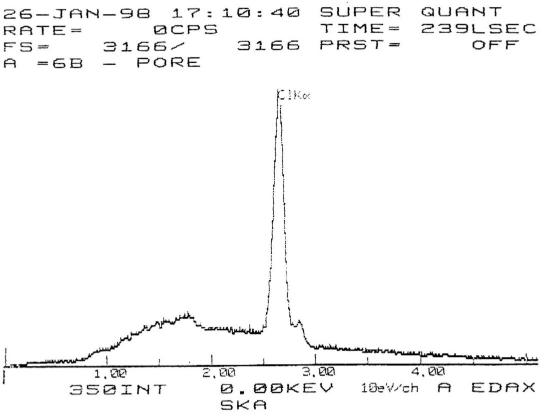


Fig [4.27]: EDAX of the polymer film from the mouth of the hole

4.5 Electrochemical Cell Fabrication

From the above results, it is clear that the sample PVC-$LiClO_4$: EC:PC with composition of 11.7:5:13.3:70 has the highest electrical conductivity and therefore was used as an electrolyte in the electrochemical cell fabrication. The anode consists of graphite while the cathode material consists of intercalation compound, $LiCoO_2$ to assure adequate electronic conductivity in the cathode. The anode and the cathode were hotpressed and laminated with the electrolyte in between them and then connected to the galvanostat for characterization.

4.6 Electrochemical Cell Characterization

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. This voltage is 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 PVC-$LiClO_4$ complex. It was found to be 0.13V for the above sample in the as-assembled stage. The cell was charged with a constant load of 1000μA for 2 minutes. The cell charged upto a value of 3.6 volts and then discharged. Lithium cells normally charge upto a voltage of 4.0 volts. This cell also charged upto a voltage nearing to that of 4.0 volts, since lithium cobalt oxide and graphite were being used as anode and cathode materials respectively.