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INVESTIGATION OF THE ROLE OF DIFFERENT PLASTICIZERS IN PVdC-co-AN BASED GEL POLYMER ELECTROLYTES

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Abstract - *In recent years, large scientific and technical interest in lithium polymer secondary batteries leads to the development of electrolytes with high electrochemical windows. Several researches deliberate the performance of polymer electrolytes owing to its high energy density, ease of preparation, compatibility between the electrodes etc. Numerous strategies are followed to match the ionic conductivity and mechanical stability of polymer electrolytes. This work describes the clear effect of plasticizer on the performance of lithium ion batteries with four different plasticizer such as ethylene carbonate (EC), propylene carbonate (PC), γ-Butyrolactone (γBL) and diethyl carbonate (DEC) were used. Gel polymer electrolytes comprising of PVdC- AN (52wt%) – $LiClO_4$ (8wt.%)–ZrO_2 (6wt%)- X(40) (X- EC,PC, γBL, DEC) were prepared by solution casting technique. The structural and complexation formation of the prepared electrolytes have been confirmed by XRD and FTIR analysis. The effect of plasticizer on ionic conductivity is depicted using a.c impedance studies in the temperature range 303 -363 K. The highest ionic conductivity value 1.2×10^{-3} S/ cm was measured for the sample incorporating EC, owing to its high dielectric constant (89.6). Thermal stability of the samples has been examined using TG/DTA. The maximum conducting sample, with plasticizer EC can be operated up to 160 ℃. The morphology is analyzed by SEM.*

Keywords- *polymer electrolytes, ionic conductivity, ethylene carbonate, propylene carbonate, Thermal stability*.

I. INTRODUCTION

Presently, due to the rapid usage of electronic gadgets, there is a wide energy gap between the energy sources and the need. The worldwide attention is directed towards the development of advanced battery technologies. Lithium ion battery seems to be an eminently suitable choice for the high energy density and reliability. The inevitable studies of Wright and Armand et al. on ionic conducting polymer initiated a new field of materials research with potential application in the power industry**.** Wright and Armand [1,2] found that poly(ethyleneoxide) (PEO) dissolved salts had ionic conductivity of 10^{-8} –10^{-7} Scm^{-1} at ambient temperature. A series of experimental investigations began with Wright and Armand in order to enhance the room temperature ionic conductivity of the polymer. The realization that the low mobility of lithium ions in solid polymer electrolyte may be difficult to overcome has led the researchers to develop a polymer electrolyte film that incorporating a plasticizer. In 1975, Feuillade and Perche proposed the concept of plasticizing polymer containing an alkali metal salt in which the organic solution of the alkali metal salt was retained and trapped within the matrix of the polymer [3]. There have been numerous reports on polymer electrolytes encompassing plasticizers [4-7]. Therefore, a particular attention has been given to identify and optimize the best choice of electrolyte based on plasticized film.

Plasticizer is a low molecular weight organic liquid with high dielectric constant, which reduces the crystallinity of the polymer thereby reducing the glass transition temperature (t_g) value even for the addition of small quantities. The plasticizer molecules penetrate into the polymer matrix and establish forces between the polymer chains, which results in the segmental mobility and the decrease in t_g value by generating free volume. Therefore, the ions can easily tunnel through the free volume resulting in the enhancement of ionic conductivity.

After finding the optimum salt composition for P(VdC-co-AN)/$LiBF_4$(94:6) from previous chapter 3, by considering both the ionic conductivity and mechanical stability the appropriate quantities of polymer, salt and plasticizer are fixed in this chapter. As detected from earlier analyses the optimized composition of polymer, salt and plasticizers are PVdC-co-AN (94 wt.%), $LiBF_4$ (6 wt.%) and plasticizer X (80%) respectively. In the present work, polymer, salt and plasticizer ratio has been fixed with different plasticizers to optimize the choice of plasticizer in view of getting maximum ionic conductivity. Polymer electrolytes composed of Poly (vinylidene chloride-co-acrylonitrile)/$LiBF_4$ with different plasticizer was prepared by solvent casting technique.

II. EXPERIMENTAL ASPECTS

A. Sample preparation

The polymer PVdC-co-AN(M_w ≈150,000) employed in this study were obtained from Aldrich, USA. Plasticizers such as ethylene carbonate (EC), propylene carbonate (PC), gamma Butyrolactone (γBL) and diethyl carbonate (DEC), were also received from the Aldrich. Lithium tetrafluoro borate ($LiBF_4$) was dried under vacuum at 80 °C for 24 h using a digitally controlled vacuum oven. Polymer electrolytes were prepared by dissolving appropriate quantity of the corresponding constituents in anhydrous tetrahydrofuran (THF). The polymer and the salt were dissolved separately in THF and then mixed together; then the resultant solution was mixed with various plasticizers followed by continuous stirring for 12h. The resulting homogenous solution was casted onto the well cleaned flat bottom petri plate. The films were allowed to evaporate THF at room temperature for 24 h. Then, the films were further dried in the vacuum oven at 50 °C for 12 h to remove the traces of residual solvent, if any. Thus prepared samples were carefully peeled off from petri plates. The films were stored in the desiccators for further drying before the measurement and characterization studies to be carried out.

B. Characterization studies

The structural and complex formations of the prepared electrolytes were confirmed by X-ray diffractometer (X'pert PRO PANalytical) using Cu-Kα radiation as source and operated at 20KV. The sample was scanned in the range $2\theta = 10\text{-}80°$. Fourier transform infrared (FT-IR) spectroscopy studies were performed using Perkin Elmer 577-IR spectrophotometer in the range 4000-400 cm^{-1} in the transmittance mode. The variation of ionic conductivity with respect to temperature for various plasticizer based electrolytes was recorded through AC impedance analyzer at the temperature range (303K to 363K). The AC impedance studies of the complexes were carried out using Keithley LCZ 3330 meter. Thermal studies were conducted on all the polymer electrolyte samples using Perkin Elmer STA-6000 thermogravimetry/differential thermal analysis (TG/DTA) analyzer. The thermogravimetric analysis (TGA) and DTA curves were recorded in nitrogen atmosphere from room temperature to 800 °C at heat rate 10 °C/min. The surface morphology of the sample that possesses maximum conductivity was studied via SEM.

III. RESULTS AND DISCUSSION

A. X-ray diffraction studies

In order to investigate the crystallinity of the prepared electrolytes, the X-ray diffraction studies were carried out. Fig. 1 displays the XRD patterns of the pure polymer, salt and their complexes containing different plasticizers. Based on the diffractograms, the following observations are made. The sharp peak at 2θ= 40.25, 46.76, 67.94° in Fig.4.1, shows the crystalline nature of the pure polymer. The characteristic peaks of lithium tetrafluoroborate salt at 2θ=18, 26.7, 28.1, 37.7 44.6, 52.8 and 57.93° [JCPDS- 40-1431] reveals the crystalline nature of the salt. From [JCPDS- 40-1431], it is clear that it possesses orthorhombic crystal structure. No peaks in respect to polymer and salt have been found in the diffraction patterns of complexes that indicates the complete dissociation of lithium salt in the polymer matrices in the presence of organic plasticizers. As correlated by Hodge et al. [8], the degree of crystallinity with the height of the peak, all the complexes containing different plasticizers show the reduction in the peak intensity. This confirms the amorphous nature of the prepared electrolytes. The addition of plasticizers reorganizes the structure of the polymer and enhances the amorphous nature [9]. This confirms that there is a good interaction between polymer and salt in the plasticizer background.

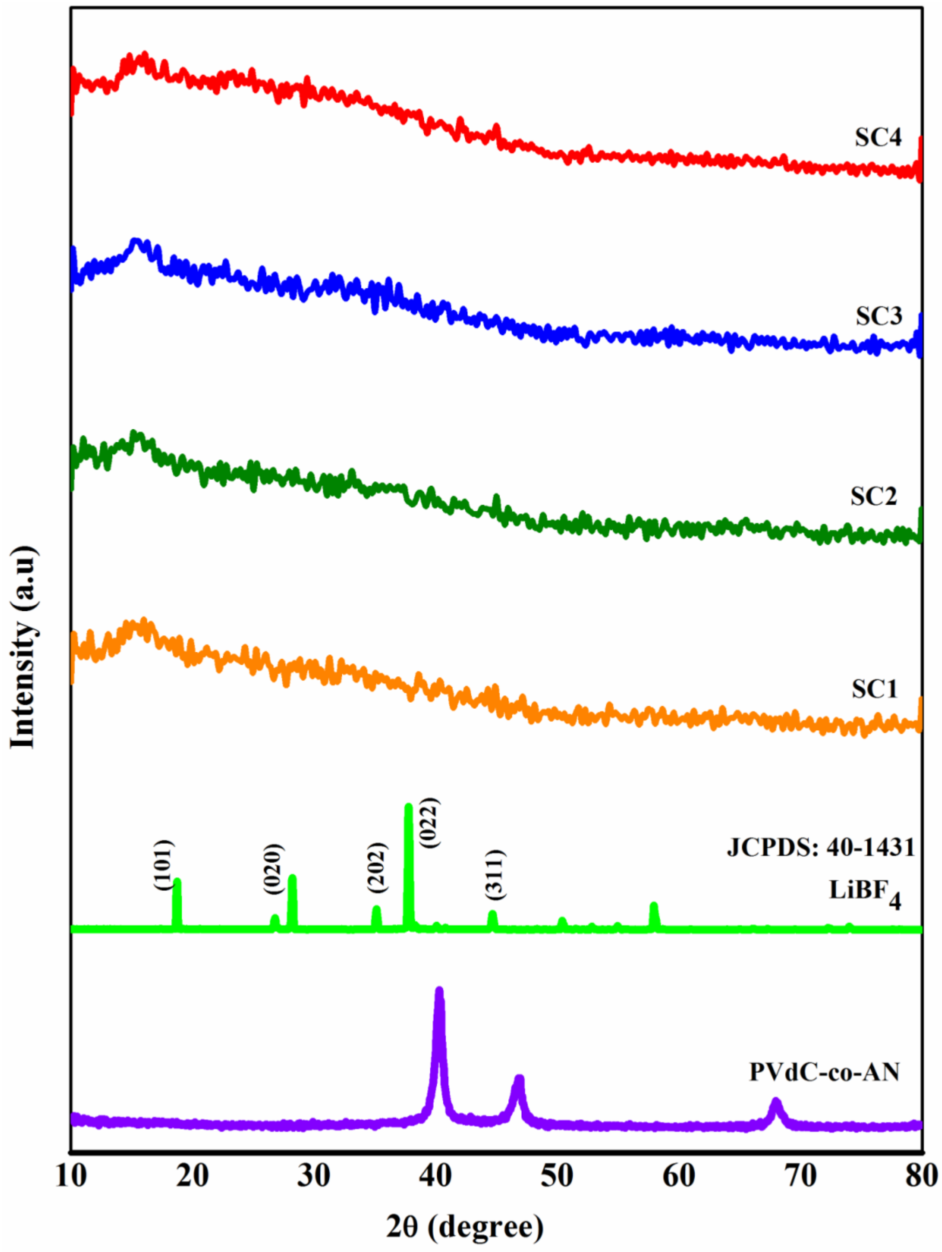

Figure 1. XRD pattern of pure and the prepared complexes

B. FT-IR Studies

FTIR spectroscopy is an important tool for the investigation of nature of the bond and for studying different functional groups in the polymer matrices. FT-IR spectra of pure and the prepared complexes are displayed in Fig.2. The pure IR spectra of PVdC-co-AN shows the vibrational band at 2245 and 1642 cm^{-1} that correspond to the stretching vibration of nitrile group (C≡N) [10].

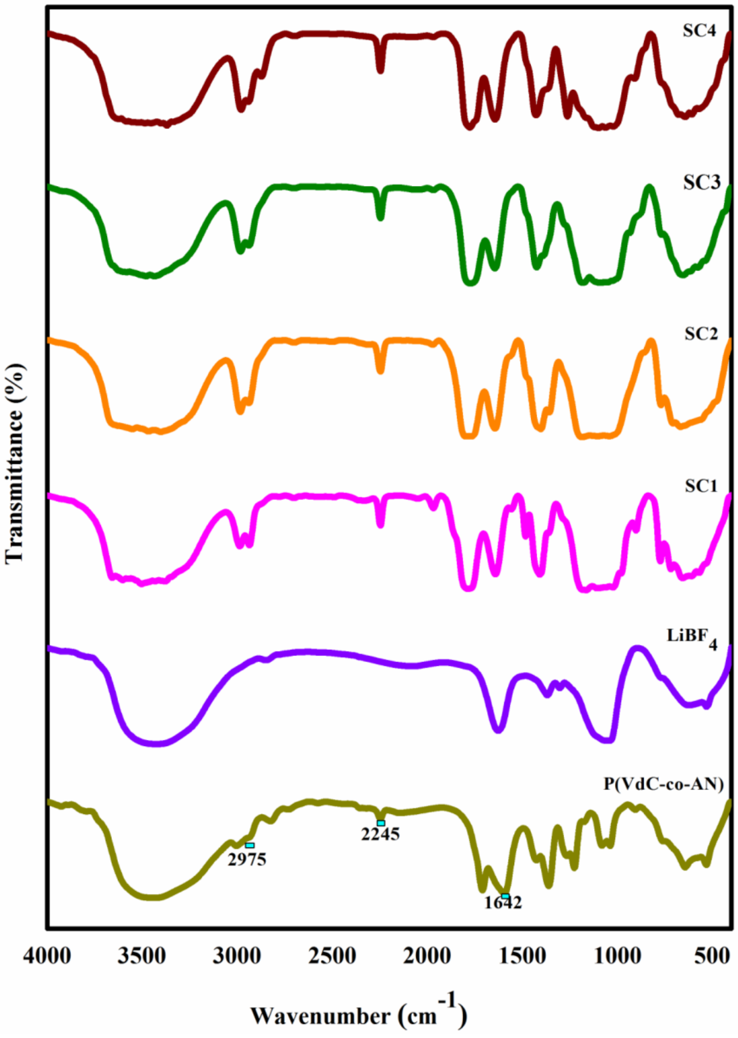

Figure 2. FTIR spectra of pure and the prepared complexes

In the complexes, the intensity of vibrational band at 2245 cm^{-1} increases. This indicates that when the salt is incorporated in the polymer host, the cation of the metal co-ordinate with polar group in the host polymer matrix and exhibit complexation. This type of interaction will influence the local structure of the polymer and therefore certain infrared active modes of vibration get altered which will be the evidence of complex formation Fig.4.2. The C=CH$_2$ symmetric stretching at 2975 cm^{-1} [11-12] of the polymer PVdC-co-AN has broadened and shifted to 2964, 2962, 2960 and 2962 cm^{-1} in the complexes. The broadened peak at 1073 cm^{-1} related to vibrational band of LiBF$_4$ appeared in all complexes. The broad band of BF$_4^-$ band appearing at 510 cm^{-1} is shifted to 521 cm^{-1} in the complexes, which indicates that the salt is comlplexed with the polymer matrix. The vibrational peak of LiBF$_4$ at 1633 cm^{-1} is shifted to 1637, 1637, 1626, 1626 cm^{-1} respectively in SC1- SC4. It shows the dissociation of salt in all plasticizer responsible for the complex formation. A significant band occurring in $\gamma_{c=0}$ region is due to fermi resonance of skeletal breathing around 1788 cm^{-1}. This is shifted to 1792, 1779, 1784 cm^{-1} in the prepared electrolytes. Thus the FTIR studies ensure the ionic co-ordination of the polymer and their complexes.

C. Conductivity studies

The variation of ionic conductivity with temperature and type of plasticizer was recorded with AC impedance analyzer in the temperature range 303 to 363 K. The prepared polymer film were cut into circular shape and was kept in between two stainless steel (SS) electrodes of the cell and then signal voltage was applied. The impedance was measured by varying the frequency from 40 Hz to 100 KHz. The ionic conductivities of the gel polymer electrolytes were calculated from the relation

$$\sigma = t / R_b A,$$

where, t - thickness of the sample,
A - area of the electrolyte sample,
R_b - bulk resistance of the polymer electrolyte membrane

From the complex impedance plot, the ionic conductivity of poly (vinylidenechloride-co-acrylonitrile)/$LiBF_4$/X complex with different plasticizer (where X= EC, PC, γBL and DEC) has been calculated and furnished in Table 1. It is evident that the conductivity value increases upon the temperature for all prepared gel polymer electrolyte containing various plasticizers such as EC, PC, γBL and DEC.

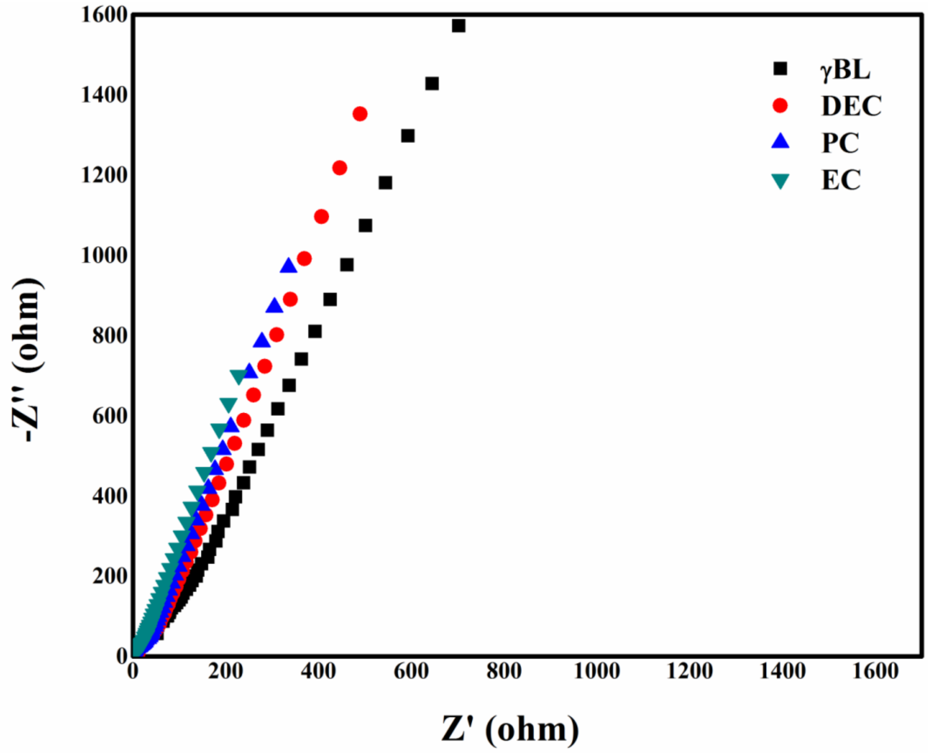

Figure 3(a). Complex Impedance plot of PVdC-co-AN(94)-$LiBF_4$(6)-X(80) at ambient temperature (where X=EC, PC, γBL and DEC)

The disappearance of the semicircular portion in the complex impedance plot (Fig.3(a)) corresponding to the high frequency region confirms that the current carriers are ions [13]. This depicts that the total conductivity is mainly due to the result of ion conduction. A spike at the low frequency region corresponds to the interfacial impedance of the electrodes. R_b is the bulk resistance of the gel electrolyte obtained from complex impedance plots of the samples. It is widely followed that R_b could be obtained from the intercept on the real axis at the high frequency end of the Nyquist plot of complex impedance [14].

From Table 1, it is seen that the maximum conductivity value 1.2×10^{-3} Scm^{-1} at ambient temperature is for PVdC-AN(94)–$LiBF_4$(6)–EC(80) complex and the conductivity values descent as EC, PC, γBL and DEC. It is higher than the value reported by Subbu et.al., for the PEO (64) / PVdC-co-AN (16) / $LiClO_4$ (8) / EC (12) system which has a conductivity of 3.0 x 10^{-4} S/cm [15]. From the Table 1, it is learnt that the specific nature of the plasticizer such as dielectric constant, viscosity, polymer plasticizer interaction and polymer ion interaction influences the segmental and ionic mobility. The plasticizer with high dielectric constant is able to dissociate more concentration of charge carriers [16]. The plasticizers EC, PC, γBL and DEC used in this investigation have dielectric constants viz, 89.6, 64.4, 39.1 and 2.82 respectively [17]. The high conductivity has been obtained for the sample possessing EC as plasticizer, which has high dielectric constant among the plasticizers used. The correlation of ionic conductivity and the dielectric constant is good in agreement with earlier report [18].

Table 1. Ionic conductivity values of PVdC-co-AN(94wt.%) – $LiBF_4$(6wt.%) – Plasticizer X (80 wt.%) (where X = EC, PC, γBL, DEC) polymer electrolyte systems

Sample	Plasticizer	Ionic conductivity × 10^{-3} S cm^{-1}							
		303K	313K	323K	333K	343K	353K	363K	E_a(eV)
SC1	EC	1.2	2.23	3.80	5.01	6.33	7.98	10.07	0.142
SC2	PC	0.70	0.94	1.34	1.93	2.94	3.45	5.98	0.143
SC3	γBL	0.28	0.50	.604	0.763	1.17	2.12	2.78	0.158
SC4	DEC	0.067	0.084	0.134	.298	.425	.670	0.856	0.194

Fig.4 (b) shows the variation of ionic conductivity versus reciprocal of temperature. From the Fig.3 (b), it is evident that the temperature dependent ionic conductivity plot obeys Arrhenius relation and confirms that the movement of ions takes place in plasticizer rich phase [18-20].

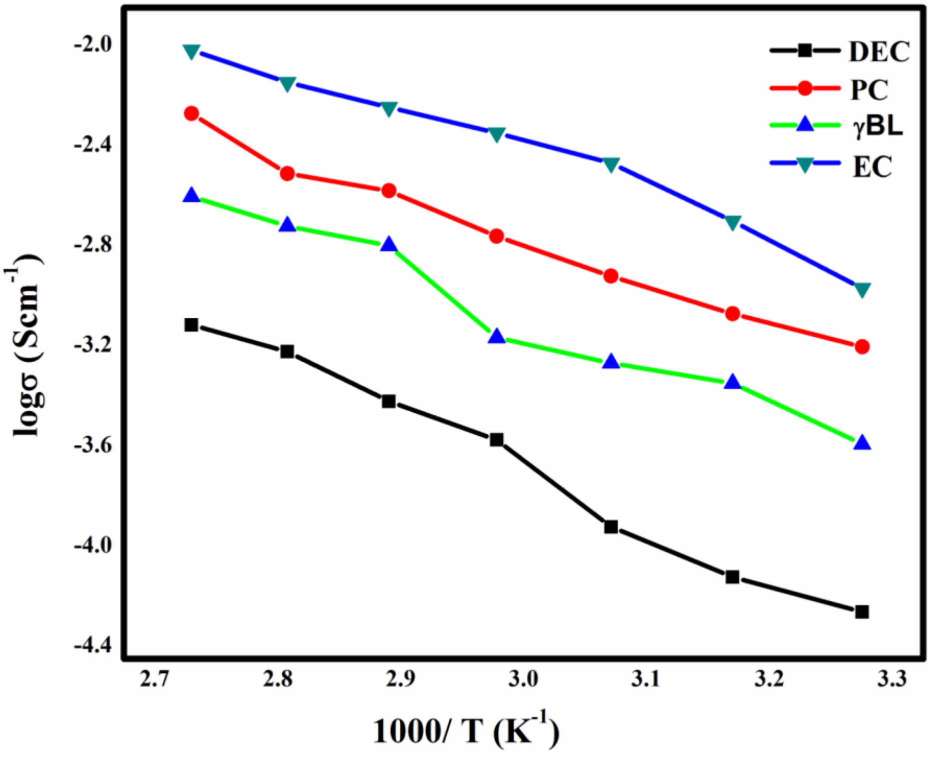

Figure 3(b). Arrhenius of PVdC-co-AN (94)-$LiBF_4$ (6)-X (80) (where X=EC, PC, γBL and DEC)

The increase in conductivity with temperature may be effectively explained with the help of free volume model. According to it, when the temperature increases the polymer can expand easily and produce free volume [21]. The ion solvated polymer molecules or the polymer segment can swift through the free volume. As a result, the increase in conductivity is assisted with segmental mobility. Addition of plasticizer also increases the free volume and thus it enhances the conductivity further.

D. TG/DTA Analysis

TG/DTA study is used to investigate the weight changes, thermal degradation, phase transition and crystallization of the material prepared. Fig. 4(a-d) shows the TG/DTA curves of EC, PC, DEC and γBL and DEC) based PVdC – AN(94) – $LiBF_4$(8) – Plasticizer(X) system.

Table 2. TG/DTA results of the prepared samples

Code	Transition range (°C)			% wt. loss (± 1% at various temperatures (°C))			Endothermic peaks (°C) in DTA		Exothermic peaks (°C) in DTA
	I	II	III	I	II	III	I	II	
SC1	66	159	276	2	86	37	70	100	268
SC2	74	171	274	3	88	42	-	213	264
SC3	77	191	271	2	83	45	-	211	259
SC4	61	190	273	3	84	44	112	218	263

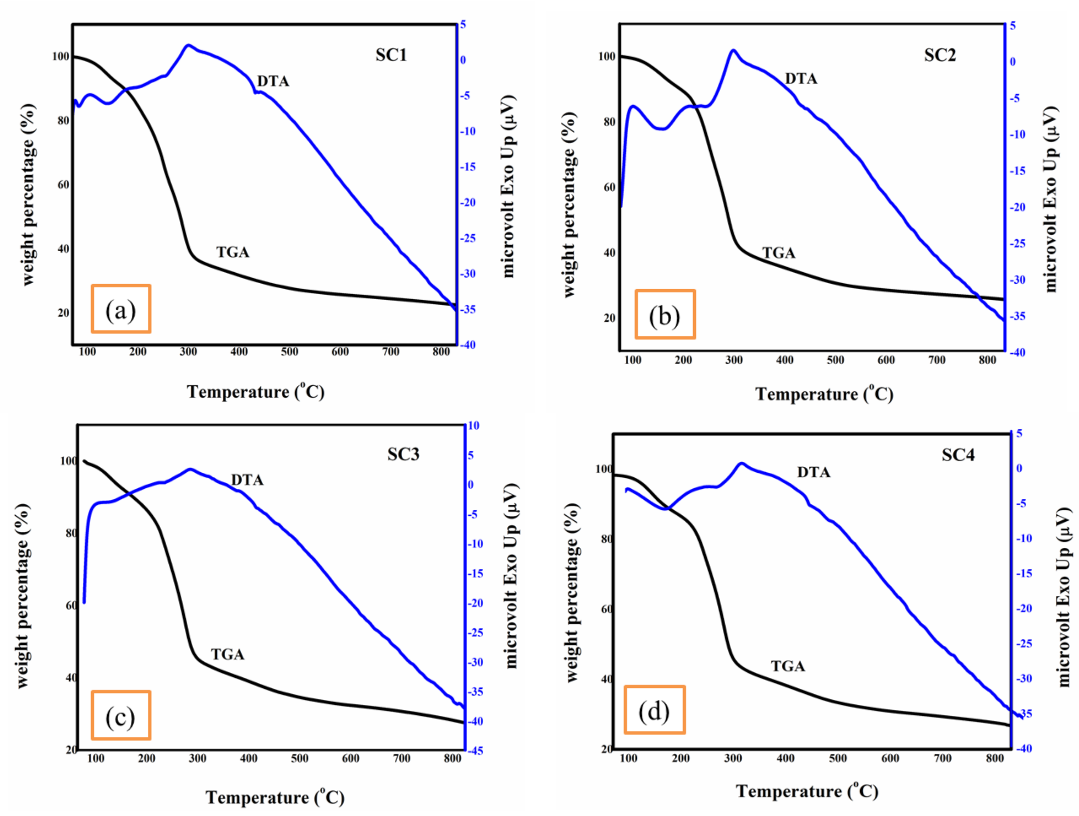

Fig. 4(a-d) TG/DTA trace of prepared samples with different plasticizers

Table 2 shows the initial weight loss upto 3% around 70 °C which may be due to the moisture content while loading the sample for measurement. The film SC1 undergoes the major transition in between 159 and 275 °C with the corresponding weight loss of 13 and 70%. The same major transition has been observed between 171 and 274 °C 191 and 271 °C and 190 and 273 °C for the samples SC2, SC3, and SC4 respectively with the weight losses of 12 to 58 %, 17 to 55% and 16 to 56%. An exothermic peak at 268, 264, 259 and 263 °C is appeared in the DTA curves of SC1-SC4 electrolytes respectively and it is in accordance with the TG curves.

E. SEM Analysis

In order to investigate the surface morphology of the maximum conducting sample, SEM has been carried out for the sample SC1 with the magnification of 5K. The smooth surface morphology of the sample (Fig.5) reveals the complete dissociation of the salt in polymer matrix. Also some pores on the surface have been observed and it may be due the addition of EC whose dielectric constant is higher than the rest of the organic solvents studied. This higher dielectric value provides more dipoles in the polymer matrix and leads to ion hopping and subsequent free volume. This gives rise to more flexible smoothened pores in the surface of polymer which results in more ionic conduction.

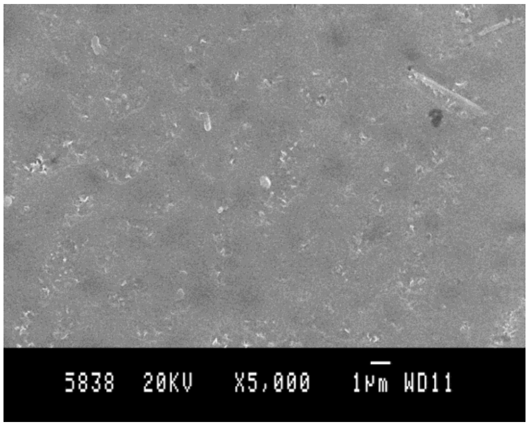

Figure 5. SEM image of PVdC-AN(94)–LiBF$_4$ (6)- EC(80) polymer electrolyte

IV. CONCLUSION

Polymer electrolytes P(VdC-AN)(94) – LiBF$_4$(6) – Plasticizer (X) (80%) systems X= EC, PC, DEC and γBL were prepared by solvent casting method. The maximum ionic conductivity value has been observed in EC based polymeric film since the plasticizer EC has high dielectric constant compared to other plasticizers. Complexation of the polymer constituents are confirmed by XRD and FTIR studies. Ionic conductivity of the polymer electrolytes has been measured in the range 303–363K. The temperature-dependent ionic conductivity plot of the electrolyte films seems to obey the Arrhenius relation. The ionic transport of the electrolytes has been discussed on the basis of free volume model. TG/DTA analysis reveals that the maximum conducting sample, which encompasses EC as plasticizer can be operated up to 160 °C which is in the safer operating range of Lithium batteries. The ionic conductivity of the electrolyte for EC based system is well supported by the surface morphology investigation.

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