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Augmentation of conductivity in PVdF-HFP/PMMA polymer electrolytes

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ABSTRACT

Solid polymer electrolyte films consisting of poly (vinylidene fluoride-co-hexa fluoro propylene) (PVdF-HFP), poly (methylmethacrylate) (PMMA) with varying concentration of LiClO₄ are prepared by solvent-casting technique. The structural elucidation, complex formation and morphological properties are studied by X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy and Scanning electron microscopy (SEM). The temperature dependent ionic conductivity of the polymer films seems to obey WLF equation. The conductivities of PVdF-HFP-PMMA-LiClO₄ complexes are determined at different salt concentrations. The highest ionic conductivity of $1.659 \times 10^{-5} \text{ S cm}^{-1}$ is obtained for 8 wt.% LiClO₄ in the polymer complex at 302K. The thermal stability of the electrolyte is ascertained from Differential Scanning Calorimetry (DSC).

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KEYWORDS

Polymer electrolyte;
Poly (vinylidene fluoride-co-hexafluoro propylene) /
Poly (methylmethacrylate)
blend;
Ionic conductivity;
Thermal stability;
Lithium perchlorate.

INTRODUCTION

The exponential growth in portable electronic devices such as cellular phones and laptop computers during the past decade has created enormous interest in compact, light weight batteries which could provide high energy density compared to its contemporary. Such quests lead to the fabrication of solid polymer electrolytes which could also be used efficiently in electrochromic devices and chemical sensors. Solid polymer electrolytes (SPE) are advantageous over its contemporary in terms of shape, geometry, mechanical strength and the capability of strong electrode electro-

lyte contact^[1]. Since then, substantial research activities have been carried out to develop polymer electrolytes with all required qualities^[2-6].

Despite extensive research on lithium polymer conductors, the conductivity of pure solid electrolytes were insufficient for practical applications at room temperature^[7-9]. The investigations on solid polymer electrolytes have shown that the improved conductivity can be achieved by the increase in the volume fraction of amorphous phase. Therefore investigations were carried out to disrupt the crystalline phase by, synthesis of copolymers, comb branched polymers and cross-linked polymers, or addition of inert ceramic fillers and blending of

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polymers^[10-15].

Solid polymer electrolyte prepared by blending two polymers have several advantages over the other methods, such as easy control of composition, ease of preparation and a large variety of polymers can be used, more notably the improvement of electrical, mechanical and thermal properties of SPE can be achieved by blending of polymers^[16].

Of late studies has proved poly (vinylidene fluoride-co-hexafluoro propylene) (PVdF-HFP) as a potential component for the preparation of polymer electrolyte for rechargeable lithium batteries due its high solubility, and the low crystallinity and glass transition temperature. The success of PVdF-HFP polymer electrolyte is now broadly confirmed by the development in lithium polymer batteries^[17,18].

The use of poly (methylmethacrylate) (PMMA) as a host polymer was first reported by Iijima et al.^[19] and followed by others^[20-23]. PMMA based polymer electrolytes exhibit high ionic conductivity close to that of liquid electrolyte, but suffers from poor dimensional and physical properties^[24].

In the present investigation the effect of concentration of inorganic salt on the pre optimized blend ratio^[25] is being investigated and reported. Structural elucidations, complex formation, thermal stability, morphological properties and electrical studies were carried out using XRD, FTIR, DSC, SEM and ac impedance analysis and are discussed in detail.

EXPERIMENTAL

Poly (vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP) (average molecular weight 4×10^5) and poly (methylmethacrylate) (PMMA) (average molecular weight 12×10^4) bought from Aldrich, USA were dried at 373K under vacuum for 10 h; LiClO₄ (Aldrich) was dried at 343K under vacuum for 24 h and used.

The electrolytes were prepared by solution casting technique. Appropriate quantities of (PVdF-HFP), (PMMA), LiClO₄ (TABLE 1) were dissolved by adding in sequence to pre-distilled acetone (E. Merck, Germany). The solution was subjected to magnetic stirring for 24 hrs at room temperature for thorough mixing and at an elevated temperature (60 °C) for 2 hrs, before the electrolyte was cast on finely polished Teflon

supports or Teflon covered glass plates. The films were dried in vacuum oven at 333K at a pressure of 10^{-3} Torr for 24 h to evaporate the residual solvents if any, thus obtained films were dry and free-standing in nature. The phase analysis of the polymer was performed with X-ray diffractometer (XRD) [Bruker (D8 Advance)] and Fourier transform infrared (FTIR) spectrums were recorded in the range 4000–400 cm⁻¹ using Jasco FTIR 460 plus (Japan) spectrophotometer respectively at room temperature.

TABLE 1 : Conductivity values of PVDF-HFP-PMMA-LiClO₄ systems with different salt concentrations

Sample	Concentration PVdF-HFP – PMMA-LiClO ₄	Conductivity σ ($\times 10^{-5}$ S cm ⁻¹)				
		302 K	318 K	333 K	353 K	373 K
B ₁	72-24-4	0.028	0.037	0.096	0.148	0.709
B ₂	70.5-23.5-6	0.089	0.100	0.417	0.708	1.662
B ₃	69-23-8	1.659	2.236	9.121	11.200	25.081
B ₄	67.5-22.5-10	0.408	0.502	1.646	2.174	6.225

The conductivity measurements were carried out with specially designed conductivity jig, where the film is sandwiched between the stainless steel electrodes with a spring load arrangement to ensure proper electrode – electrolyte contact. For electrical conductivity measurement, Aurbin FRA2 μ AUTOLAB - III, was used with signal amplitude of 10mV in the frequency range 100Hz–500 kHz. Temperature dependence of ionic conductivity is recorded in the range 302–373 K. The films were subjected to Differential scanning calorimetric studies using Mettler Toledo DSC 822e with a heating rate of 10 °C / min.

X-ray diffraction analysis

X-ray diffraction (XRD) studies provide wide range of information on crystal structure, crystal orientation, crystallinity and phase changes of materials which are characterized by the presence of sharp diffraction rings or peaks. In amorphous materials, there is no long-range order present; however, the non-crystalline samples are characterized by one or two broad “halos”. In the present case, the X-ray diffraction method has been used to elucidate the change in crystallinity and increase of amorphous nature in the complex upon the increasing salt concentration, which would be amenable for the increase in conductivity.

XRD patterns of pure PVdF-HFP, PMMA, LiClO₄

and complexes are shown in Figure 1(a-g). Figure 1(a-c) shows the diffraction patterns of pure PVdF-HFP, PMMA and LiClO_4 . The sharp crystalline peaks at 18, 20° and broad diffraction peaks at 26 and 38° in Figure 1(a) are due to the presence of the crystalline PVdF in PVdF-HFP^[26-28]. Figure 1(b) exemplifies the amorphous nature of PMMA with one wide peak at about 15°. The sharp diffraction peaks indicates the crystalline phase of LiClO_4 (Figure 1(c)).

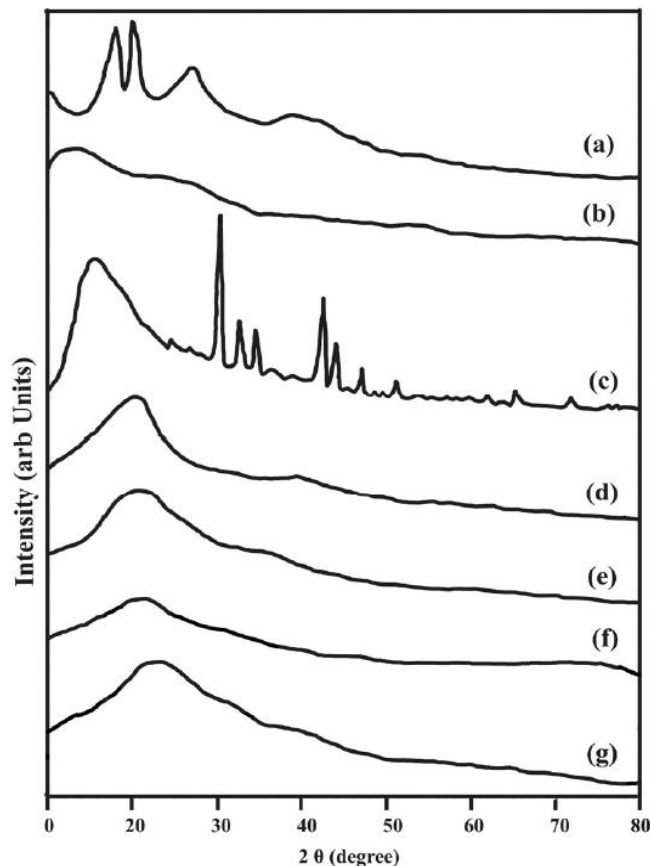


Figure 1 : XRD spectra of (a) PVdF-HFP; (b) PMMA; (c) LiClO_4 ; (d) PVdF-HFP(72)-PMMA(24)- LiClO_4 (4); (e) PVdF-HFP(70.5)-PMMA(23.5)- LiClO_4 (6); (f) PVdF-HFP(69)-PMMA(23)- LiClO_4 (8); (g) PVdF-HFP(67.5)-PMMA(22.5)- LiClO_4 (10)

It is evident from Figure 1(d-g) that the sharp crystalline peaks pertaining to LiClO_4 (Figure 1(c)) are found almost absent in the complexes, indicating the complete dissolution of lithium salts in the polymer matrices, which is in accordance with the statement that complexation between the salt and polymer takes place in the amorphous region^[29]. The presence of excess salts forms ion clouds (ion agglomeration) which could be the reason for the lower conductivity of the film B₄ which could

be ascertained from the reappearance of the rough morphology of the surface (Figure 6d).

FTIR studies

FTIR spectroscopy is a very sensitive method for studying the local physical and chemical environment of chemical groups and the changes associated due to complexation. The FTIR spectra of the pure PVdF-HFP, PMMA, LiClO_4 and polymer complexes are shown in Figure 2(a-g). Figure 2(a) indicates the characteristic group frequencies corresponding to virginal PVdF-HFP, for example -CF=CF-skeletal bending at 1688 cm^{-1} , -C-F stretching at 1408 cm^{-1} , -C-F and -CF₂- stretchings at 1267 & 1164 cm^{-1} respectively, C-C skeletal vibration at 1074 cm^{-1} , Vinylidene group at 880 cm^{-1} , CH₂ rocking at 839 cm^{-1} , CF₃ stretching at 772 cm^{-1} , CH₂ bending at 684 cm^{-1} , CF₂ bending at

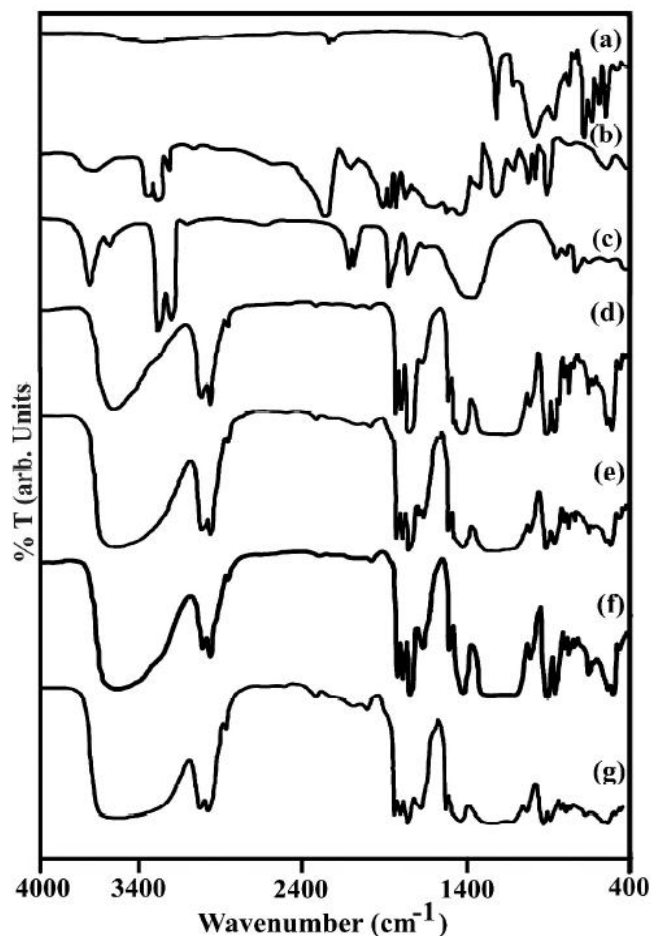


Figure 2 : FTIR spectra of (a) PVdF-HFP; (b) PMMA; (c) LiClO_4 ; (d) PVdF-HFP(72)-PMMA(24)- LiClO_4 (4); (e) PVdF-HFP(70.5)-PMMA(23.5)- LiClO_4 (6); (f) PVdF-HFP(69)-PMMA(23)- LiClO_4 (8); (g) PVdF-HFP(67.5)-PMMA(22.5)- LiClO_4 (10)

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511 cm^{-1} and CF_2 wagging at 484 cm^{-1} which is similar to those obtained by other researchers^[30-34].

The group frequencies at 1403 cm^{-1} is attributed to CH_2 deformation which has moved to higher frequency region in the complexes indicating the weakening of interaction between H atoms of CH_2 groups and F atoms of CF_2 groups. The group frequencies corresponding to $-\text{CF}=\text{CF}$ -skeletal bending (1688 cm^{-1}), CH_2 rocking (839 cm^{-1}), CF_3 stretching (772 cm^{-1}) and CF_2 wagging (484 cm^{-1}) frequencies of PVdF-HFP are found to be shifted to a lower side in all the complexes irrespective of the salt concentration which could be due to the interaction of polymer and lithium salt. The frequencies corresponding to carbonyl group $\text{C}=\text{O}$ (1733 cm^{-1}), CH_2 scissoring (1485 cm^{-1}), CH_2 wagging (988 cm^{-1}) and CH_2 rocking (752 cm^{-1}) vibrations of PMMA are found to be shifted in all the complexes.

The C-C skeletal vibration (1074 cm^{-1}) of PVdF-HFP is found to be shifted to a higher side in the complex containing 8 wt.% of LiClO_4 . The O- CH_3 deformation (1451 cm^{-1}), C-C-O bending vibrations (1242 cm^{-1}) of PMMA and C-F and $-\text{CF}_2$ - stretching vibrations (1267-1164 cm^{-1}) of PVdF-HFP are found absent in all the complexes. The CH_2 twisting (1388 cm^{-1}) of PMMA is found at 1393 cm^{-1} in the complex containing 4wt.% of LiClO_4 and absent in all the remaining complexes. The characteristic absorption vibrations of LiClO_4 (1150, 1080, 941 and 627 cm^{-1}) are assigned to symmetrical vibration of ionic pairs between Li^+ and ClO_4^- and stretching vibrations of ClO_4^- respectively. In addition to this some new peaks are observed at 2301, 2207, 2047, 1973, 1805, 442 cm^{-1} . Hence, the complex formation is confirmed from the above analysis^[35-40].

Conductivity studies

The electrochemical impedance spectroscopy is an excellent tool to characterize many of the electrical properties of the material and their interfaces with the electrodes. The conductivity studies were performed using ac impedance technique employing Aurbin FRA2 μ AUTOLAB - III. The conductivity of the polymer electrolyte was calculated using the relation $\sigma = L / (A \cdot R_b)$ where R_b is the bulk resistance, A is the area and L the thickness of the polymer membrane. TABLE 1 shows the conductivity values of the complex with different wt% of LiClO_4 in the range 302-373k. It is well known

that lithium ions migrate in two ways: (i) move along the molecular chains of polymer, and (ii) move in an amorphous phase of polymer electrolyte^[41]. The former is slow transport while the latter is fast.

From the table it is evident that as the salt concentration increases the conductivity is found to increase up to 8wt% and decreases for further increase of salt content (10wt %). This may be due to the combined effect of ion aggregation due to the presence of excess undissolved salt, which is evident from SEM studies and also the increasing values of T_g , as indicated in the DSC studies. The increasing value of T_g which could be due to the polymer clustering seems to nullify the increase in the number of carrier ions at higher salt concentrations due to the increase in cohesive forces between the molecules.

Among the various films prepared in this work, the conductivity value of PVdF-HFP(69) – PMMA(23)- LiClO_4 (8) has the maximum value of $1.659 \times 10^{-5} \text{ S cm}^{-1}$ at room temperature and corresponding impedance plot is shown in Figure 3. Figure 4 represents the Arrhenius plot of the ionic conductivity of the polymer electrolyte films. The temperature dependant ionic conductivity of the polymer electrolytes seems to obey Williams-Landel-Ferry (WLF) mechanism describing the ionic motion due to the polymer segmental motion. As the temperature increases, the ions tend to diffuse through the free volume produced due to the expansion of the polymer segments ensuing conductivity.

DSC studies

In order to investigate quantitatively the evolution of crystallinity of the polymer films and the complexation,

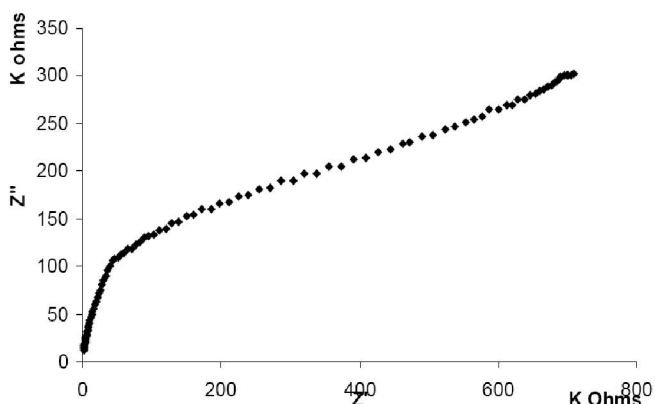


Figure 3 : Impedance diagram for PVdF-HFP –PMMA– LiClO_4 (69 – 23 – 8 wt.%) at 302 K

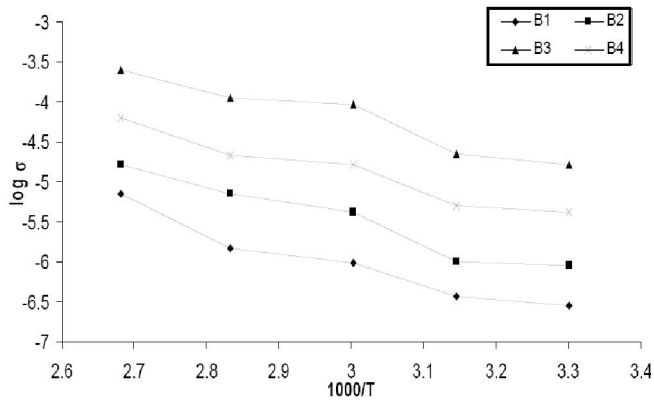


Figure 4 : Arrhenius plot of the conductivity for PVdF – HFP – PMMA – LiClO₄ polymer complexes for different salt concentrations

DSC studies were carried out with the samples prepared. The DSC data of the complex systems containing constant PVdF-HFP - PMMA ratio and different weight ratio of LiClO₄ (TABLE 1) are shown in Figure 5(a-d). It is evident that the T_g of the polymer electrolytes are found to increase as the concentration of LiClO₄ increases (from 71°C to 95°C) ascertaining the concept of increase

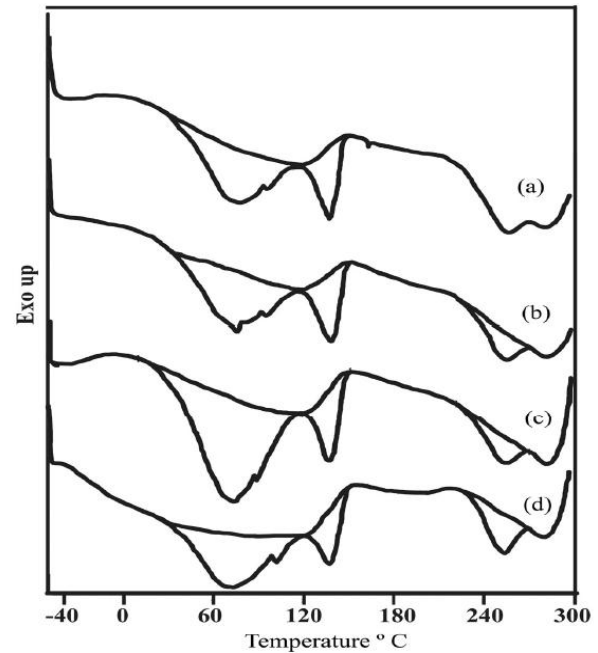
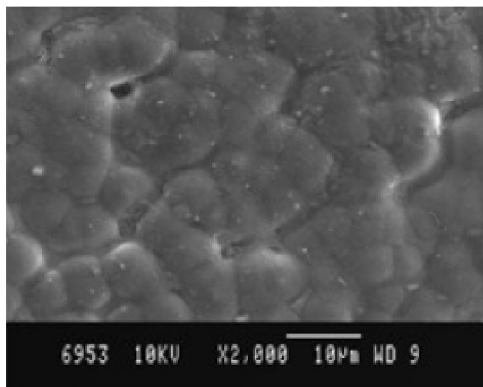
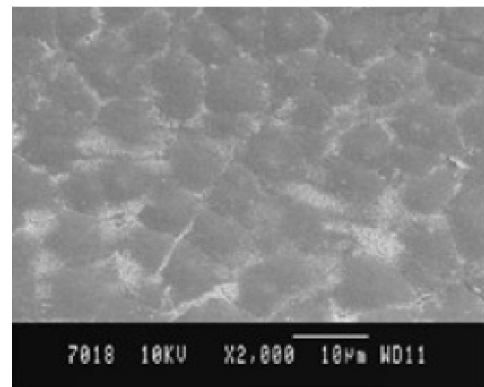


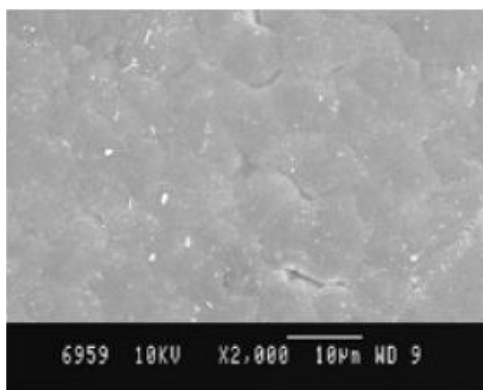
Figure 5 : DSC spectra of (a) PVdF-HFP(72)-PMMA(24)-LiClO₄(4); (b) PVdF-HFP(70.5)-PMMA(23.5)-LiClO₄(6); (c) PVdF-HFP(69)-PMMA(23)-LiClO₄(8); (d) PVdF-HFP(67.5)-PMMA(22.5)-LiClO₄(10)



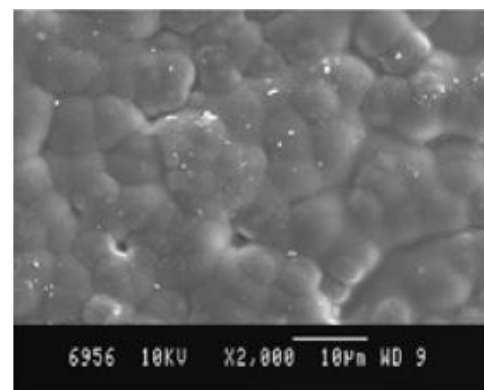
(a)



(b)



(c)



(d)

Figure 6 : SEM photographs of polymer electrolyte samples at 2000 magnification (a) PVdF-HFP(72)-PMMA(24)-LiClO₄(4); (b) PVdF-HFP(70.5)-PMMA(23.5)-LiClO₄(6); (c) PVdF-HFP(69)-PMMA(23)-LiClO₄(8); (d) PVdF-HFP(67.5)-PMMA(22.5)-LiClO₄(10)

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in T_g with the addition of lithium salt^[42]. The melting temperatures of the polymer matrices suffer an increase in melting temperature when the salt content is increased from 4 to 10wt% but the film suffers a receding in melting temperature for the film containing 8wt% indicating the higher amorphicity due to the interaction persisting between the salt and the polymer matrices, which could be ascertained for the higher conductivity at this concentration. Hence, the effect of salt concentration on the polymer matrices is brought out.

SEM studies

Scanning electron micrograph studies were carried out to elucidate the surface morphology of the polymer electrolytes prepared. The photographs of the samples with 2000 magnification are shown in figure 6(a-d). It is evident from the studies that as the concentration of salt is increased the roughness of the surface reduces which may be due to the increase in amorphicity of the polymer electrolytes. Further from Figure 6(d) it is evident that the white spots could be due to the excess salts present in the case of electrolyte with 10% of LiClO_4 . Thus, the presence of excess undissolved salt in the polymer electrolyte could be the reason for lower conductivity as discussed earlier.

CONCLUSION

The prepared polymer electrolytes are characterized by XRD for elucidating the amorphicity, FTIR for confirming the complex formation, DSC to find the thermal stability, ac impedance studies to find the conductivity and SEM to study the surface morphology. The ac impedance studies are carried out at different temperatures to find the temperature dependence of ionic conductivity, and are found to obey WLF relation. The highest ionic conductivity $1.659 \times 10^{-5} \text{ S cm}^{-1}$ is obtained for the polymer complex PVdF-HFP(69)-PMMA(23)- LiClO_4 (8) at 302K. Hence, from the aforesaid properties the polymer electrolyte based on PVdF-HFP - PMMA - LiClO_4 could be efficiently used in lithium battery applications.

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