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Elizabeth, R. Nimma; Kalyanasundaram, S.; Saito, Yuria; Stephan, A. Manuel
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Compatibility and Thermal Stability Studies on Plasticized PVC/PMMA Blend Polymer Electrolytes Complexed with Different Lithium Salts

R. Nimma Elizabeth

Lady Doak College, Madurai, India

S. Kalyanasundaram

Algappa University Karaikudi, India

Yuria Saito, A. Manuel Stephan

Osaka National Research Institute, Japan

Abstract: The lithium salt (x) ($X = \text{LiAsF}_6, \text{LiPF}_6, \text{LiN}(\text{C}_2\text{F}_5\text{SO}_2)_2, \text{LiN}(\text{CF}_3\text{SO}_2)_2, \text{LiBF}_4$) was complexed with a host of poly(vinyl chloride) (PVC)/ poly(methyl methacrylate) (PMMA) blend polymer and plasticized with a combination of ethylene carbonate (EC) and propylene carbonate (PC). The polymer electrolyte films were prepared for constant PVC/ PMMA blend ratio. The electrochemical stability and thermal stability of the solid polymer electrolytes were reported. The role of PMMA to the phenomena occurring at the interface between the electrolyte and the lithium metal electrode was explored.

Keywords: *Polymer electrolyte, plasticizer, lithium-polymer interface, electrochemical stability.*

Introduction

The development of polymer electrolytes has drawn the attention of many researchers in the last two decades as they find applications not only in lithium batteries, but also in other electrochemical devices such as super capacitors, electrochromic devices and sensors etc^[1,2]. Such systems based on conventional poly (ethylene oxide) (PEO) matrix offer room temperature conductivities generally of the order of $10^{-5} \text{ S cm}^{-1}$ which preclude their utility in practical devices. Others based on polymer systems such as poly(acrylonitrile) (PAN), for example possess advantages such as appreciable room temperature conductivities ($10^{-3} \text{ S cm}^{-1}$)^[2,3] electrochemical stability up to 4.5v and high Li^+ transference number. But their poor compatibility with lithium is of great concern^[4-6]. Poly (methyl methacrylate) PMMA, on the other hand, demonstrated to form highly conducting gel electrolytes ($10^{-3} \text{ S cm}^{-1}$) at room temperature^[7-9,11,13] and also they have been shown to possess higher Li^+ transference numbers than PEO and good compatibility with lithium^[13]. Recently, Appetecchi^[14] et.al., Lee et.al.,^[15,16] have reported the electrochemical studies on PMMA with different lithium salts and PMMA, PAN blend based electrolytes respectively. In spite of better conductivity and compatibility of PMMA electrolytes with lithium electrodes their practical application is offset due to their poor mechanical strength. The possibility of using PVC as

electrolytes in lithium batteries has been reported by Abraham and his co-worker^[21].

In the recent past, the importance of using PVC/ PMMA blend polymer electrolytes was emphasized by us^[21-25] and other researchers^[26]. In this continuation, so far to our knowledge, not much attention has been paid on the compatibility and thermal stability studies of PVC/ PMMA blend polymer electrolytes. The most important finding concluded from the present study is the effect of PMMA on the interfacial resistance, " R_i " between the lithium electrodes and PVC-PMMA blend electrolytes. An attempt has been made to evaluate the possibility of using plasticized PVC/PMMA blend polymer as an electrolyte in practical rechargeable lithium –polymer batteries. Also, the salts commonly used in lithium battery electrolytes such as LiPF_6 , LiAsF_6 and LiBF_4 have poor thermal stability and may have toxic by products. Among the salts commonly used, an attempt has been made to choose the best salt for lithium batteries in terms of thermal, electrochemical and compatibility points of view.

Experimental

PVC, (mol. wt 1.5×10^5) and PMMA, (mol. wt. of 3.5×10^5) (both Aldrich, USA) were used in the present study. As plasticizers, ethylene carbonate (EC) and propylene carbonate (PC) (both E.Merck, Germany), were

Table 1. The composition of polymer, plasticizer and lithium salt.

Sample	PVC g	PMMA g	EC g	PC g	Li salt g
S1	35	0	35	25	5
S2	8.5	26.5	35	25	5
S3	0	35	35	25	5

used without further purification. The lithium salts, $\text{LiN}(\text{C}_2\text{F}_5\text{SO}_2)_2$, $\text{LiN}(\text{CF}_3\text{SO}_2)_2$, LiAsF_6 , LiPF_6 and LiBF_4 were dried at 70 °C and kept under vacuum for 48 h before use. All the electrolytes were prepared by dissolving, appropriate amounts of polymer, plasticizer and salt in anhydrous tetrahydrofuran (THF) and cast as films with doctor blade as reported elsewhere^[16,21,22]. After evaporation of THF, the films were further dried in a temperature-controlled oven over 50 °C for 8 h to remove any traces of THF. The samples were prepared in a glove box under argon atmosphere and stored in desiccators inside the glove box to minimize water contamination. From our earlier studies^[23-26], the polymer film with the blend ratio of PVC: PMMA, 25:75 is found to be optimal in conductivity and mechanical property points of view. For the present study, the samples with pure 100% PMMA, 100% PVC and 25: 75 of PVC: PMMA and EC and PC as plasticizers were considered as in Table 1.

Results and Discussion

Compatibility studies

Lithium is an attractive anode material for a lithium secondary battery and provides a larger capacity of 3800 mAh g⁻¹. This capacity is about ten times higher than that of a carbon based anode (372m Ahg⁻¹) with a composition of LiC_6 . However, lithium metal is quite well known to react with both aprotic and protic solvents carrying reactions at its surface. The cycle life of lithium metal secondary cells is very short due to the low cycling efficiency of the lithium metal anode. Many reasons for the poor cycling of lithium metal anode have been reported. They include the electrochemical reactions between the anode and the electrolyte^[10] and loss of electronic contact between the electrode and dendritic lithium.

Although various solvents have been used as the lithium secondary cells electrolyte, the results obtained so far are still unsatisfactory. The ethylene carbonate and propylene carbonate are well known corrosive agents for lithium metal. Among the plasticizers the propylene carbonate is the most reactive compound^[12] which affects charge- discharge cycling efficiency of secondary batteries with lithium metal anode. Many attempts have been reported to increase the cycling efficiency, by using organic, inorganic and gaseous additives to the electrolytes for the rechargeable Li- batteries. Mostly the chemical properties of the Li-interface are known to affect the Li-cycling efficiency.

In polymer electrolyte systems, a resistive layer covers the lithium and the resistance of this layer grows with time, which can reach values over 10K Ωcm^{-2} . This resistive layer

hinders the lithium ion migration and leads the battery for poor cycling and safety hazards eventually.

The structure of this layer is not understood, but it is known, that uncontrolled passivation phenomena affect the cyclability of lithium electrodes and thereby entire lithium battery system. It is also suspected that the nature of this layer depends mainly on the purity and composition of the electrolyte. This solid electrolyte interface (SEI) plays a major role in determining their properties, which include shelf life, safety and lithium deposition- dissolution efficiency and cycle life.

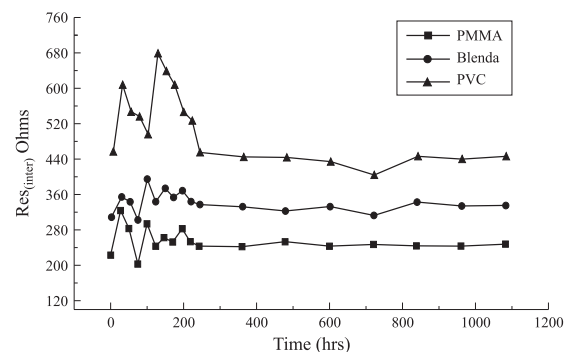
In intensive studies, it was found by many authors that this layer is formed by decomposition process of the solvent and anions of lithium salts used. For a well reversible lithium battery, one needs a fast formation of SEI with a homogenous chemical composition, a high transference number of lithium ion and desirably without electron transport inside this layer. Also that the rate of layer formation is in a time domain less than 100 micro seconds but the composition of the formed layer is very inhomogeneous^[32].

The reasons are: a) the solvent molecules and the electrolyte anions decompose at different potentials and with different velocities, b) the reaction products exhibit in homogeneity with respect to their chemical composition, c) solvated electron with a long life time trapped in the growing layer and d) the passive layer shows therefore, a lot of region with variation in the electronic and ionic conductivity causing a variation in the local layer thickness and local reactivity with respect to subsequent cycling^[32].

As it is well known, uncontrolled passivation phenomena affects the cyclability of the lithium electrode and thus of entire battery and may lead to serious safety hazards eventually. Therefore, the criteria for the selection of a proper battery electrolyte must be based not only on fast ion transport properties but also, and perhaps principally, on favorable interfacial properties.

In the present study, the interfacial studies on PVC, PMMA and PVC/PMMA blend electrolytes containing different lithium salts have been carried out. A symmetric cell of the type Li/ polymer electrolyte/ Li was assembled and tested under open circuit conditions at room temperature.

Figures 1-5 display the variation of interfacial resistance “ R_i ” as a function of time for the polymer electrolytes containing different lithium salts, namely $\text{LiN}(\text{C}_2\text{F}_5\text{SO}_2)_2$,

**Figure 1.** The time evolution of the interfacial resistance “ R_i ” of the lithium electrolyte- Li cells at 25 °C. salt: $\text{LiN}(\text{C}_2\text{F}_5\text{SO}_2)_2$.

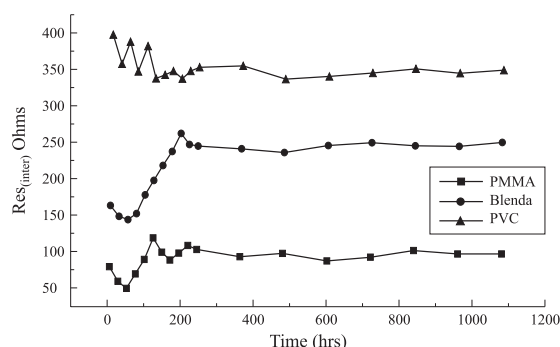


Figure 2. The time evolution of the interfacial resistance “ R_i ” of the lithium electrolyte- Li cells at 25 °C. salt: $\text{LiN}(\text{CF}_3\text{SO}_2)_2$.

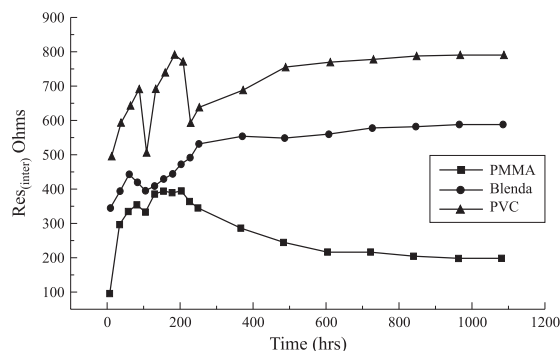


Figure 3. The time evolution of the interfacial resistance “ R_i ” of the lithium electrolyte- Li cells at 25 °C. salt: LiAsF_6 .

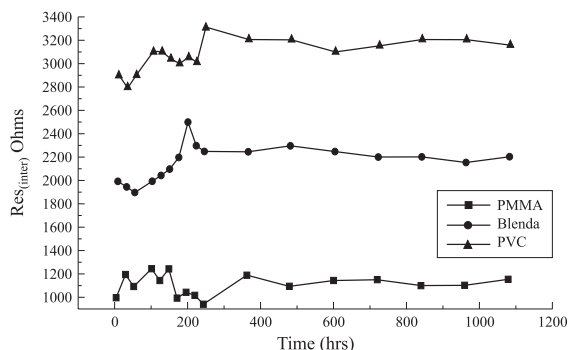


Figure 4. The time evolution of the interfacial resistance “ R_i ” of the lithium electrolyte- Li cells at 25 °C. salt: LiPF_6 .

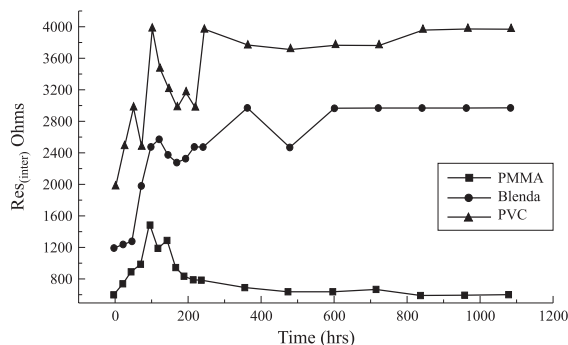


Figure 5. The time evolution of the interfacial resistance “ R_i ” of the lithium electrolyte- Li cells at 25 °C. salt: LiBF_4 .

$\text{LiN}(\text{CF}_3\text{SO}_2)_2$, LiAsF_6 , LiPF_6 and LiBF_4 respectively. It is observed, from Figures 1-5 that the polymer electrolyte containing $\text{LiN}(\text{C}_2\text{F}_5\text{SO}_2)_2$ is the most suitable for lithium metal anode. The interfacial resistance “ R_i ” is minimum for PMMA, PVC and PVC/PMMA blend electrolytes when compared with other salts. However, “ R_i ” values for the films with $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ are little higher than those films with $\text{LiN}(\text{C}_2\text{F}_5\text{SO}_2)_2$. On the other hand, films with LiAsF_6 , LiPF_6 and LiBF_4 undergo severe passivation when in contact with lithium metal i.e., the rate of growth of interfacial resistance is higher than that of the films with $\text{LiN}(\text{C}_2\text{F}_5\text{SO}_2)_2$ and $\text{LiN}(\text{CF}_3\text{SO}_2)_2$.

Although, most of the salts contain fluorine, $\text{LiN}(\text{C}_2\text{F}_5\text{SO}_2)_2$ and $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ offer excellent compatibility with lithium metal. These results are consistent with the earlier results^[14]. Obviously, the interfacial resistance value for the films containing LiBF_4 , is maximum as it is more reactive with lithium than any other salt^[32].

The poor compatibility of the polymer electrolytes containing fluorinated lithium salts with lithium metal anode may be attributed to the following reasons. As confirmed by XPS analysis^[17-20] the amount of fluorine substances on the lithium surface increases according to the storage time. An important reason for the increase in “ R_i ” is supposed to be the formation of fluorine compound on lithium surface.

In fact, the increase of interfacial resistance “ R_i ” may generally be ascribed due to a resistive layer continuously growing on lithium electrode surface. It indicates, that the lithium electrode is passivated when in contact with the polymer electrolytes. The increase of “ R_i ” is not surprising as some of the electrolyte components like propylene carbonate are corrosive of lithium metal. It is also evident from the Figures, that the growth of resistive layer does not follow a regular way^[14].

However, the growth of interfacial resistance does not follow a regular trend for all samples studied. After, 200 hours the resistance values remain unchanged. This may be attributed by assuming that the morphology of the passivated films changes with time to finally acquire a non-compact, possibly porous structure^[14].

It is seen from the Figures, 1-5 the values of “ R_i ” is minimum for the films with 100% PMMA and maximum for the films with 100% PVC irrespective of the salts used. As it has been seen from the Figures, similar trends were observed for all the salts studied. Interestingly, in the case of PVC/PMMA blend polymer electrolytes the value of “ R_i ” lies between these two i.e., the value of “ R_i ” has been considerably reduced upon the addition PMMA. The same trend was observed for all the systems studied. The possibility that can explain the reduction of the interfacial resistance R_i for the films containing PMMA is attributed due to the reaction of lithium cations with the ester groups of PMMA and the formation of a protective layer closed to the electrode-electrolyte interface. The effect of this layer may protect the Li from the impurities present in the electrolyte^[33]. A similar observation has also been reported by Wiecek et.al^[33].

As it has been, discussed earlier^[33], the formation of passive layer normally takes place in two steps. In the first step, the “primary film” is formed with initial resistance “ R_i ” and it is most probably due to the addition of the polymer end groups and metallic lithium. The second step involves the chemical properties of electrolytes and therefore the secondary films is normally called as solid electrolyte interface (SEI) in the case of lithium batteries and polymer electrolyte interface (PEI) in the case of polymer electrolyte. The properties of this film depend on electrolyte composition, salt and the transference number of the ions^[14].

More attention should be paid to suppress the formation of passivation films. The propylene carbonate may decompose in the presence of lithium and form propylene and Li_2CO_3 ^[14]. Poly propylene oxide and carbon dioxide may be formed as

a result of polymerization of propylene carbonate^[14]. The polymer macromolecules may be crosslinked through free radical couplings in the presence of lithium metal. Therefore, the passivation film may contain all the products of the unexpected reactions of lithium electrode with PC and the carbonyl groups on the polymer chains. This passivation consists of Li_2CO_3 and LiHCO_2 when carbonates are added in the electrolyte system. This passivation limits the charge transfer reaction at the electrolyte/ electrode interface.

Electrochemical Stability

An electrochemical window greater than 4.5v is an important parameter for a polymer electrolyte for applications in polymer based lithium batteries. The electrochemical stability studies for the PVC and PMMA films have already

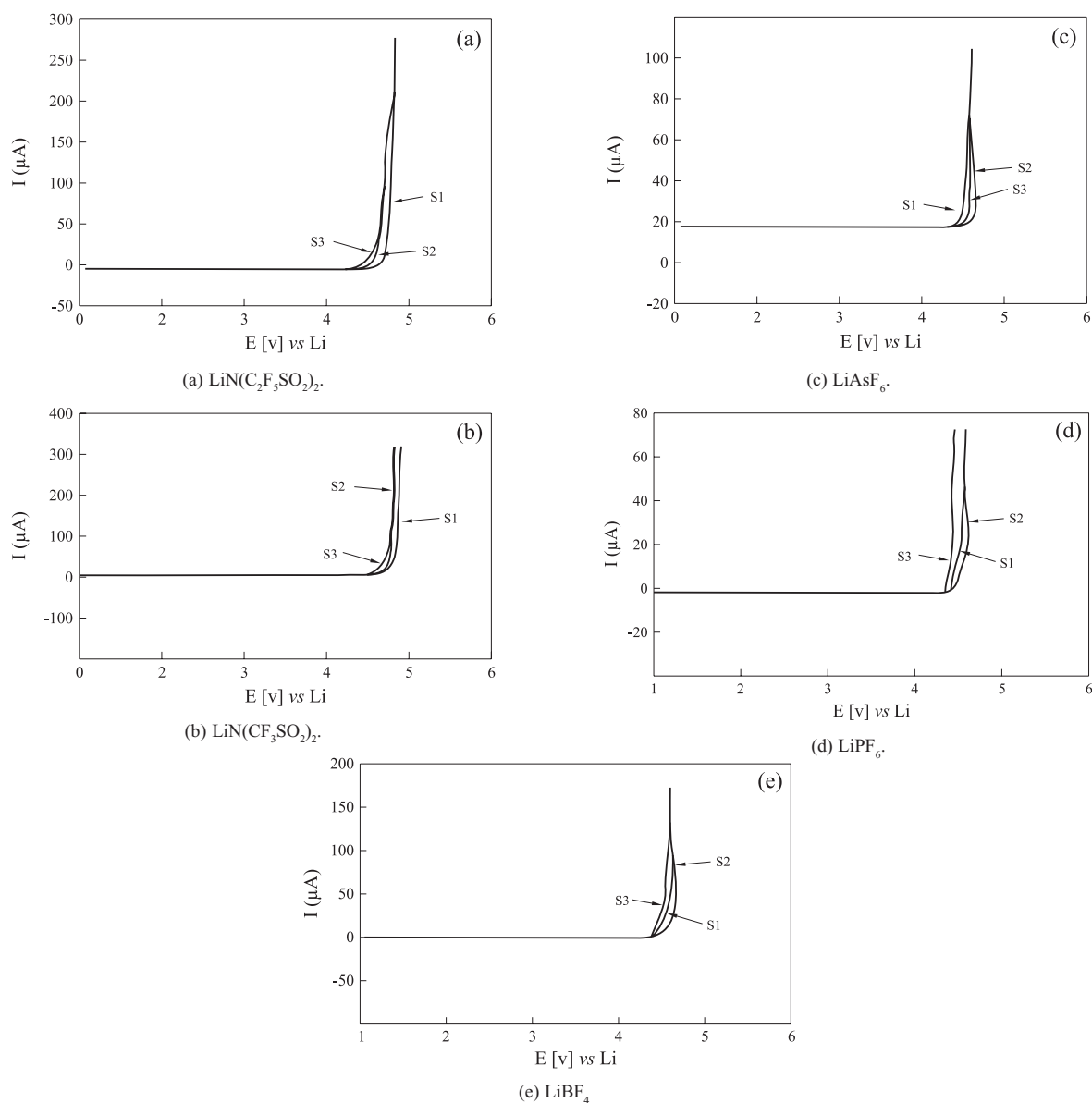


Figure 6. Current- voltage response at 25 °C of stainless- steel electrode for the samples S1, S2 and S3.

been reported^[14,37]. Figure 6 (a-e) depicts the current-voltage curves obtained by sweeping a stainless steel (SS) electrode and polymer electrolytes for different lithium salts, $\text{LiN}(\text{C}_2\text{F}_5\text{SO}_2)_2$, $\text{LiN}(\text{CF}_3\text{SO}_2)_2$, LiAsF_6 , LiPF_6 and LiBF_4 respectively at 25 °C. The anodic decomposition limit of the electrolyte can be considered as the voltage at which the current flows through the cell^[14,26,38]. It is evident from the figure, that electrolytes with $\text{LiN}(\text{C}_2\text{F}_5\text{SO}_2)_2$, $\text{LiN}(\text{CF}_3\text{SO}_2)_2$, salts have an anodic stability above 4.7v Vs Li and those with LiAsF_6 , LiPF_6 and LiBF_4 are above 4.3v. These electrolytes may be compatible with high voltage electrodic couples such as LiC_6 , LiMn_2O_4 , etc.

TG-DTA analysis

High ionic conductivity, high lithium transport number and wide electrochemical stability window, although desirable properties, are not sufficient to make an electrolyte completely useful in practical applications. The thermal stability of the polymer electrolyte is also an important parameter to guarantee acceptable performance in lithium batteries especially when it is operated at elevated temperatures and where safety is concerned.

In order to ascertain the thermal stability, PVC, PMMA, PVC/PMMA blend and plasticized PVC/PMMA blend electrolytes containing different lithium salts were subjected to TG/DTA analysis. In the present study, the sample S₂ (as given in Table 1) was chosen because it is found to be suitable in terms of ionic conductivity, mechanical strength and compatibility. Figures 7(a)-(d) depict the TG/DTA traces of PVC, PMMA, PVC-

PMMA blend films without plasticizers and films with PVC-PMMA-EC-PC respectively. It is seen from Figure 7(a) that for PVC no weight loss (endothermic peak) was observed until 270 °C at which an endothermic peak appears. This indicates that, PVC is stable up to 270 °C after which it decomposes. A similar trend was observed for the polymer PMMA, which is stable up to 250 °C (Figure 7(b)). This result is in accordance with those reported earlier^[25]. But for the blend film without plasticizers an exothermic peak is seen at 210 °C (Figure 7(c)), which implies, that the decomposition has been advanced to 210 °C. When EC and PC are added plasticizers in the blend the decomposition temperature has been further decreased to 120 °C as indicated in Figure 7(d). As described in^[26] when the plasticizers are added in the polymer electrolyte the glass transition temperature (T_g) is reduced and its decomposition temperature has also been reduced.

Figure 8(a) shows the TG/DTA curves for the films containing PVC-PMMA-EC-PC $\text{LiN}(\text{C}_2\text{F}_5\text{SO}_2)_2$. It is interesting to note that for the films containing $\text{LiN}(\text{C}_2\text{F}_5\text{SO}_2)_2$ an endothermic peak is observed with a weight loss <1% in the temperature range 45-50 °C presumably due to the evaporation of residual moisture absorbed when the sample was loaded^[25]. No subsequent weight loss was observed until irreversible decomposition began around 120 °C. When the salt $\text{LiN}(\text{C}_2\text{F}_5\text{SO}_2)_2$ was added the decomposition temperature further reduces to 120 °C. Figure 8(a) also demonstrates that the lithium ion reduces the decomposition temperature. A similar observation was seen by Xu et al.^[31] where they reported the decomposition of nylon with LiCl and LiBr systems^[41].

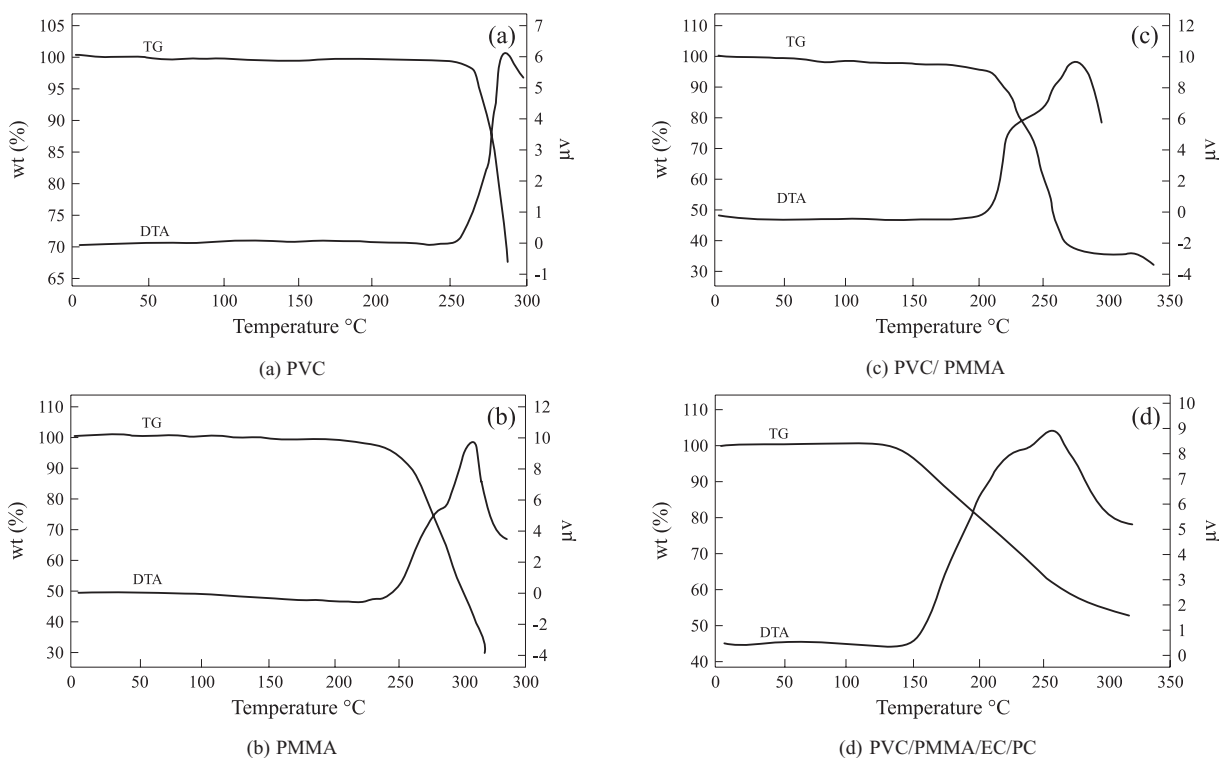


Figure 7. TG-DTA

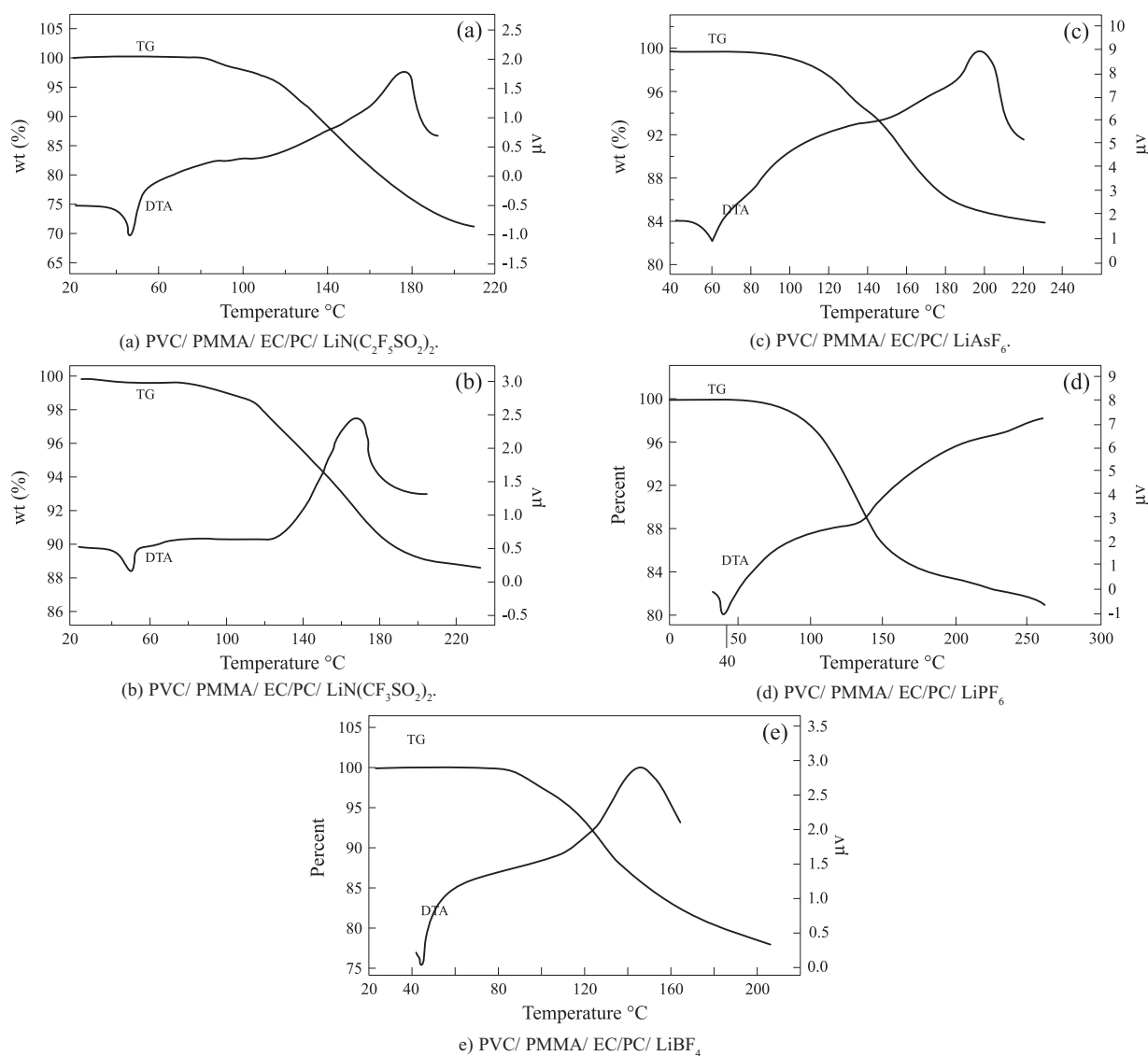


Figure 8. TG-DTA

Similarly, an endothermic peak was observed with a weight loss <1% in the temperature range 45-50 °C was observed for the films containing PVC-PMMA-EC-PC-LiN(CF₃SO₂)₂ as salt (Figure 8(b)). Further an endothermic peak was observed around 100 °C with the weight loss, which indicates the decomposition of the polymer electrolyte^[39,25].

On the other hand, an endothermic peak was observed at 42 °C with a weight loss < 0.5% for the sample containing PVC-PMMA-EC-PC-LiAsF₆ (Figure 8(c)). Above 100 °C, ie., after complete dehydration no further weight loss was observed until irreversible decomposition began around 110 °C. A similar trend in endothermic peaks for the samples containing lithium salts LiPF₆ and LiBF₄ at 43 °C and 45 °C respectively (Figure 8(d)-(e)). The same Figure also reveal that the irreversible decomposition starts at 82 °C and 100 °C, (ie., endothermic peak) for the samples containing LiPF₆ and LiBF₄ respectively. From these observations, it is clear that

the decomposition temperature of the polymer blend electrolytes has been advanced when the lithium salt is added in the blend.

Thus the plasticized blend electrolytes complexed with LiN(C₂F₅SO₂)₂, LiN(CF₃SO₂)₂ and LiAsF₆ are not suitable for battery operations above 100 °C which is fairly high when compared to the operating temperature of lithium cells viz., 50-60 °C. On the other hand films with LiPF₆ and LiBF₄ can be used as separators in lithium batteries when its operating temperature is below 80 °C.

Conclusions

It can be concluded from our studies,

(i) that the films containing LiN(C₂F₅SO₂)₂, LiN(CF₃SO₂)₂, LiPF₆ and LiBF₄ as salts are more compatible with lithium metal anode than the films with LiAsF₆.

(ii) The interfacial resistance “ R_i ” has been considerably reduced by adding PMMA in the blend.

(iii) The films prepared with $\text{LiN}(\text{C}_2\text{F}_5\text{SO}_2)_2$ and $\text{LiN}(\text{CF}_3\text{SO}_2)_2$, are anodically stable up to 4.7v and those with LiAsF_6 , LiPF_6 and LiBF_4 up to 4.3v.

(iv) The polymer electrolytes containing lithium salts, $\text{LiN}(\text{C}_2\text{F}_5\text{SO}_2)_2$ and $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ are thermally stable up to 90 °C whereas, films with LiAsF_6 , LiBF_4 and LiPF_6 are stable up to 80 °C.

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