

Characterization of poly(vinylidene fluoride–hexafluoropropylene) (PVdF–HFP) electrolytes complexed with different lithium salts

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Abstract

Poly(vinylidene fluoride–hexafluoropropylene) (PVdF–HFP) gel electrolytes comprising a combination of plasticizers, ethylene carbonate (EC) and propylene carbonate (PC) and lithium salt LiX ($X = \text{BF}_4^-, \text{CF}_3\text{SO}_3^-, \text{ClO}_4^-$) have been prepared using the solution casting technique in an argon atmosphere. The prepared electrolytes were subjected to ionic conductivity, compatibility with lithium metal anode and thermogravimetric (TG)/differential thermal analysis (DTA). The membranes, which possess lithium salt, LiBF_4 exhibited maximum conductivity and on contrary it undergoes severe passivation with lithium metal. All these membranes are found to be stable thermally about 70°C.

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1. Introduction

In the recent years, there has been a tremendous interest in the preparation of polymer electrolytes with high ionic conductivity, good mechanical strength and thermal stabilities because these polymer electrolytes play a major role not only in lithium polymer/lithium ion batteries but, also in other electrochemical devices such as super capacitors, electrochromic devices etc. [1,2]. Polymer electrolytes are expected to produce safe, high energy density and flexible lithium polymer batter-

ies. Although, poly(ethylene oxide) (PEO)-based electrolytes are the earliest and most extensively studied system, it offers conductivity, which ranges from 10^{-8} to 10^{-4}Scm^{-1} at temperatures between 40 and 100°C that excludes practical applications [3,4]. On the other hand, poly(acrylonitrile) (PAN)-based electrolytes offer high ionic conductivity at room temperature (10^{-3}Scm^{-1}), good electrochemical stability and appreciable transference number (0.6). However, these electrolytes undergo severe passivation when in contact with lithium metal anode [5,6]. The ionic conductivity of poly(methyl methacrylate) (PMMA) gel electrolytes remain very close to that of liquid electrolytes 10^{-3}Scm^{-1} at 25°C [7,8] and even at low temperature e.g., at -20°C the conductivity remains at quite high i.e., 10^{-4}Scm^{-1} . The transference number of PMMA-based electrolytes was higher than

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those obtained for conventional PEO-based polymer electrolyte systems [7,8]. Unfortunately, these polymer electrolytes lose their mechanical strength when they are plasticized. Abraham et. al [9] and Mary Suheshini et. al [10] have made studies on poly(vinyl chloride) (PVC)-based electrolytes. However, these electrolytes offered low ionic conductivity at ambient temperatures [9,10].

The possibility of using PVC/PMMA blend electrolytes for rechargeable lithium batteries has been explored by Rhoo and co-workers [11] and also by us [12–14]. Although the mechanical strength of PMMA has been enhanced by blending PMMA with PVC, it could not be employed in real polymer batteries because of its poor conductivity at ambient temperature [12–14].

Very recently, poly(vinylidene fluoride) (PVdF) as a host has drawn the attention of many researchers by virtue of its appealing properties. It has high anodic stability due to strong electron withdrawing functional group and has a high dielectric constant of $\epsilon = 8.4$ that helps for greater ionization of lithium salt [15,16]. Unfortunately, PVdF-based polymer electrolytes suffer due to its poor interfacial stability towards lithium metal on the fact that fluorinated polymers are not chemically stable towards lithium leading to an interfacial reaction between lithium and fluorine which results in the formation of LiF and makes the PVdF electrolytes unsuitable of battery using lithium metal as anode [16].

Generally, gel polymer electrolytes are obtained by dissolving a low molecular weight plasticizer, polymer host along with lithium salt in a low boiling solvent (e.g. tetrahydrofuran) and the resultant solution is cast as film after the evaporation of the solvent. However, these electrolytes lose their mechanical strength when the plasticizers are added [11–14,17]. These films have to be hardened by either chemical or physical curing, which leads high processing costs. In the present study, rather than choosing the commonly used gel electrolytes we have chosen a co-polymer of vinylidene fluoride and hexafluoropropylene (PVdF 88:HFP 12) which contains an amorphous phase capable of trapping large amount of electrolyte and a crystalline phase that acts as a

mechanical support for the formation of a free standing film [18,19]. Also of importance, an attempt has been made to find the role of different anion namely BF_4^- , CF_3SO_3^- and ClO_4^- on the ionic conductivity and compatibility with lithium metal anode points of view. The thermal stability of these polymer electrolytes has been reported.

2. Experimental procedure

2.1. Sample preparation

All the samples were prepared by solution casting technique [12–14]. The PVdF–HFP (Kynar Flux 2751, Elf Atochem, Japan), ethylene carbonate (EC) and propylene carbonate (PC) (Aldrich, USA) were used as received. Lithium perchlorate (LiClO_4), lithium tetrafluoroborate (LiBF_4) and lithium trifluoromethane sulfonate (LiCF_3SO_3) were dried by annealing them under vacuum at 120 °C, 70 °C and 80 °C, respectively for 24 h. All components, namely the selected lithium salt, polymer and plasticizers EC and PC were dissolved in an anhydrous tetrahydrofuran (THF). We set the total weight of polymer, EC, PC and lithium salt to be identical (100%) when preparing the films of various plasticizer content and polymer ratio. The polymer solution was cast as film and THF was allowed to evaporate at room temperature. After the evaporation of THF, mechanically stable films (free standing) of uniform thickness (100 μm) were obtained. The films were further dried in the temperature-controlled oven at 50 °C for 12 h to remove the traces of THF, if any. The electrolytes were prepared for different compositions as depicted in Table 1. All the electrolytes were prepared in an argon filled glove box (M braun, Germany) with less than 10 ppm of moisture content.

2.2. Ionic conductivity measurements

The ionic conductivity of the various electrolyte samples were determined by sandwiching the given sample

Table 1
Composition of polymer, plasticizer and lithium salt

Sample	Polymer PVdF–HFP (wt.%)	Plasticizers EC+PC (wt.%)	Lithium salt LiX (X = BF_4^- , CF_3SO_3^- , ClO_4^-) (wt.%)
S1	90	5.00	5.00
S2	80	15.00	5.00
S3	70	25.00	5.00
S4	60	35.00	5.00
S5	50	45.00	5.00
S6	50	43.75	6.25
S7	50	42.50	7.50
S8	50	41.25	8.75
S9	50	40.00	10.00

between two stainless steel (SS304) blocking electrodes. The measurements were performed using an IM6 frequency response analyzer over the frequency range of 10 mHz to 100 KHz at eight different temperatures viz., 0, 10, 20, 30, 40, 50, 60 and 70°C. A thermostatic bath with $\pm 0.1^\circ\text{C}$ precision was utilized to control the temperature.

2.3. Compatibility

The stability of lithium interface was investigated by monitoring the time dependence of the impedance of symmetrical Li/PVdF–HFP-based electrolyte/Li cells were measured by utilizing the same procedure for ionic conductivity measurements.

2.4. TG/DTA analysis

The thermal stability of polymer electrolyte samples was studied using TG/DTA (STA, 500 Simultaneous thermal analysis system of polymer laboratories, UK) analysis.

3. Results and discussion

3.1. Ionic conductivity

The electrochemical impedance spectroscopy is an excellent tool to characterize many of the electrical properties of materials and their interfaces with the electronically conducting electrodes. In the present study, the ionic conductivity of PVdF–HFP plasticized gels with various lithium salts has been analyzed by (a) varying the PVdF–HFP content in the gel and keeping the salt content fixed (b) varying the salt content and keeping the PVdF–HFP content constant as displayed in Table 1.

Figs. 1–3 represent the dependency of the ionic conductivity of the films containing different lithium salts, LiBF_4 , LiCF_3SO_3 and LiClO_4 , respectively for fixed salt content (5%). The complete impedance plots obtained

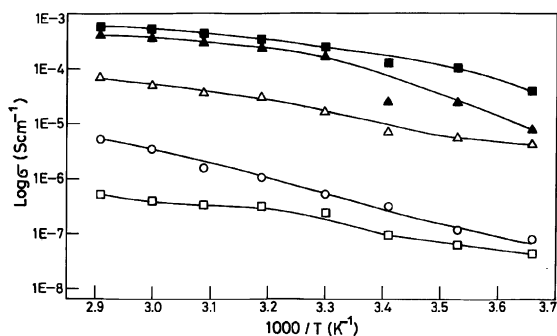


Fig. 1. Arrhenius plots of PVdF–HFP membranes for different polymer content with LiBF_4 .

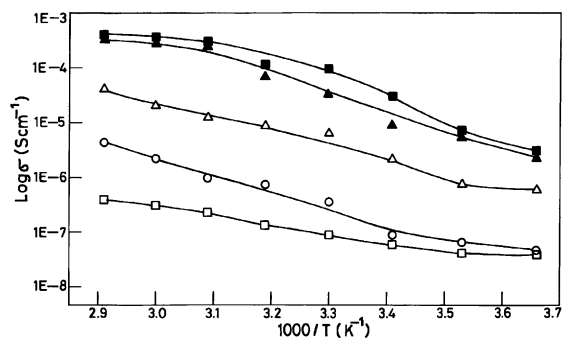


Fig. 2. Arrhenius plots of PVdF–HFP membranes for different polymer content with LiCF_3SO_3 .

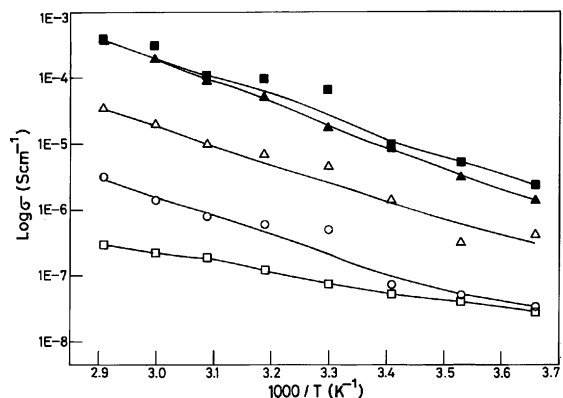


Fig. 3. Arrhenius plots of PVdF–HFP membranes for different polymer content with LiClO_4 .

for all the samples are similar in nature. It is seen from Fig. 1, for the system containing LiBF_4 as salt the ionic conductivity ranges from 10^{-7} to 10^{-4}Scm^{-1} at 0°C for different polymer PVdF–HFP content. The ionic conductivity increases monotonously (exponentially) with the decrease of PVdF–HFP content in the gel. The gel, which possesses minimum amount of polymer (50 wt.%) exhibited highest conductivity at all temperatures studied. On the other hand, the sample, which contains maximum polymer content (90%) exhibits minimum conductivity, which is 3 orders magnitude lower than that of the sample containing (50%) PVdF–HFP. This apparent increase in ionic conductivity with the decrease of polymer content is attributed to blocking effect on carrier migration of the host polymer. An increase in viscosity with polymer fraction could be realized as a microscopic interactive effect between the polymer and plasticizers, which affects the mobility [18,19]. It is also evident from the Figure that the ionic conduction obeys the VTF equation, $A = AT^{1/2}(e^{-B/k(T-T_0)})$ where the term A is proportional to the number of charge carriers and T_0 is the temperature

at which conductance tends to zero and this equation describes the transport properties in a viscous matrix [18]. It supports the idea of ionic transport taking place through the plasticizer-rich phase. The same trend has been observed for other salts studied (Figs. 2 and 3).

The variation of ionic conductivity as a function of plasticizer and salt with fixed polymer host (50%) containing different lithium salts LiBF_4 , LiCF_3SO_3 and LiClO_4 are depicted in Figs. 4–6, respectively. The ionic conductivity increases with the increase of salt content, LiBF_4 (Fig. 4) to a level i.e. up to 45% with the plasticizer content of 41.25% and then decreases even for further increase in salt content at 10%. The same trend was observed at all the temperatures studied.

Generally, contribution from plasticizer towards the enhancement of conductivity is twofold: a higher percentage of plasticizer would (i) open up the narrow rivulets of plasticizer-rich phase for greater ionic transport, and (ii) provide large free volume of relatively superior conducting phase [11]. The maximum on the conductivity–salt concentration curve may be explained as follows. Up to the concentration level, corresponding to

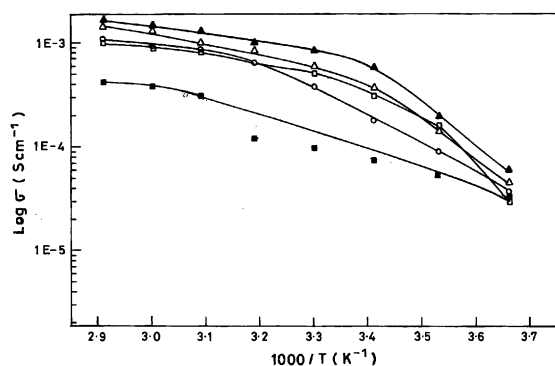


Fig. 4. Arrhenius plots of PVdF–HFP membranes for different plasticizer content with LiBF_4 .

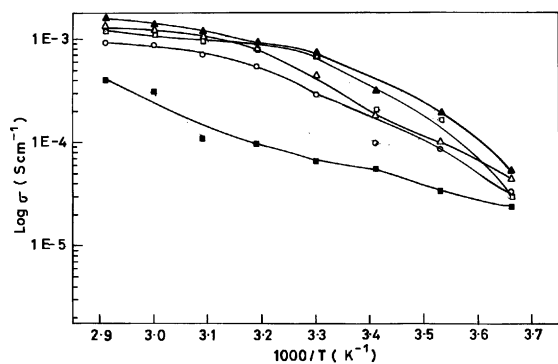


Fig. 5. Arrhenius plots of PVdF–HFP membranes for different plasticizer content with LiCF_3SO_3 .

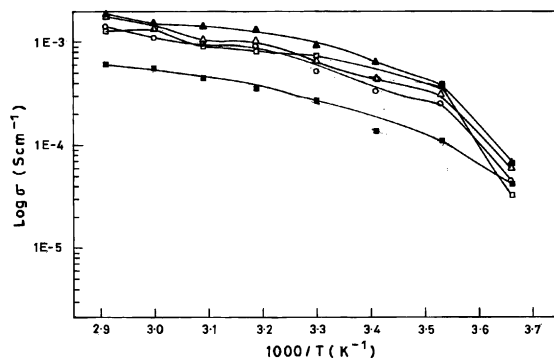
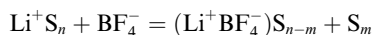
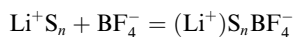


Fig. 6. Arrhenius plots of PVdF–HFP membranes for different plasticizer content with LiClO_4 .

the conductivity plateau, more and more number of ions are made available for electrolytic conduction. At higher concentration in low dielectric media, essentially two types of ion pairs are present. These may be represented by the equilibria of the membranes containing the species [20].



where S represents the solvating species. Re-dissociation of such ion pairs can occur due to long-range coulombic forces giving rise to free ions, which contribute to conductance. At higher concentrations, short-range ion–solvent interactions take over and therefore, even the number of ions dissolved in the electrolyte medium is higher, the effective number of charged species available for charge transport is get reduced.

Among the lithium salts, LiBF_4 , LiCF_3SO_3 and LiClO_4 the films containing LiBF_4 offers highest conductivity. Since all the anions are counter ions of strong acids the difference in conductivity is presumably due to the difference in lattice energies. LiBF_4 has the lowest lattice energy and therefore easier solvation of Li^+ ion by the polymer matrix, which facilitates for higher ionic conductivity. A similar observation has been reported by Immanuel et al. [21] in which MEEP was used as a host and also by us [12–14] when the ionic conductivity of PVC/PMMA blend electrolytes had been studied.

3.2. Compatibility

Lithium metal is found to be an attractive anode material for lithium secondary battery that provides a larger capacity of 3800mA h g^{-1} which is about ten times higher than that of carbon-based anode (372mA h g^{-1}) with a composition of LiC_6 . However, the cycle life of lithium metal secondary cells is very short due to the low cycling efficiency of lithium metal anode as it reacts with both aprotic and protic solvents at its surface.

Many reasons have been offered for this poor cycling, which include the electrochemical reactions between the anode and the electrolyte and loss of electronic contact between the electrode and dendritic lithium.

In the polymer electrolyte systems, on the other hand, a resistive layer covers the lithium and the resistance of this layer grows with time, which can reach values over $10\text{ K}\Omega\text{cm}^{-2}$. Although, 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. The nature of this layer depends mainly on the purity and composition of the electrolyte. This solid electrolyte interface (SEI) plays a crucial role in determining their properties, which include shelf life, safety and lithium deposition and dissolution efficiency and cycle life. Also, it has been reported [22] that the rate of SEI formation is in a time domain less than $100\mu\text{s}$ and the characteristics of the formed layer are very homogeneous.

As is well known, uncontrolled passivation phenomena affects the lithium electrode and thus of entire battery system and may lead to serious safety hazards eventually. Therefore, the criteria for the selection of proper battery electrolyte must be based not only on fast transport properties but also, and perhaps principally, on favorable interfacial properties [23,24].

In the present study, the compatibility studies have been examined with proper attention for PVdF–HFP membranes as described in the earlier section. Also the sample S8 was examined as this composition was found to be optimal in ionic conductivity points of view.

Fig. 7 displays the variation of interfacial resistance “ R_i ” as a function of time for the polymer electrolytes containing different lithium salts, namely LiBF_4 , LiCF_3SO_3

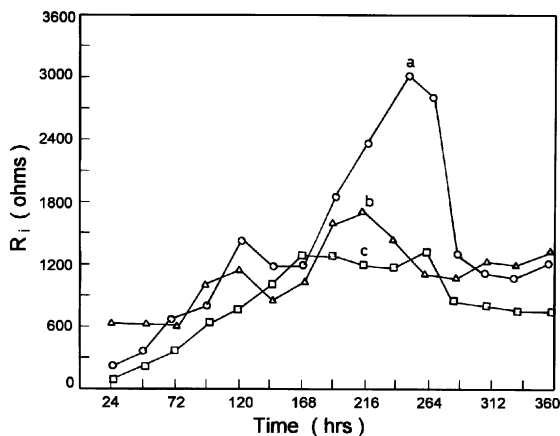


Fig. 7. Time evolution of interfacial resistance “ R_i ” of lithium electrode at 25°C Polymer electrolytes with a = LiBF_4 , b = LiCF_3SO_3 and c = LiClO_4 .

SO_3 and LiClO_4 . It is observed, from Fig. 7 that the polymer electrolyte containing LiClO_4 as salt is most suitable when lithium metal was used as anode. However, the behavior of the film with LiCF_3SO_3 is more or less similar to that of gels with LiBF_4 . The poor compatibility of polymer electrolytes containing fluorinated lithium salts with lithium metal anode may be attributed to the following reasons. As confirmed by XPS analysis the amount of the fluorine substances on the lithium surface increases accordingly to the storage time [25,26]. An important reason for the increase in “ R_i ” is supposed to be the formation of fluorine compound on lithium surface [25–27]. Also the PVdF–HFP co-polymer reacts with lithium at room temperature. The growth of interfacial resistance does not follow a regular trend for all the samples studied. After, 280h the resistance values remain unchanged. This may be attributed by assuming that the morphology of the passivation films changes with time to finally acquire a non-compact, possibly porous structure [7].

More attention should be devoted to suppress the formation of passivation films. The propylene carbonate that acts as a plasticizer may decompose in the presence of lithium and form propylene and Li_2CO_3 . Poly propylene oxide and carbon dioxide may be formed as a result of polymerization of propylene carbonate. The polymer macromolecules may be cross-linked through free radical couplings in the presence of lithium metal. Therefore, the passivated film may contain all the products of the unexpected reactions of lithium electrodes with propylene carbonate and the carbonyl groups on the polymer chains [23]. This passivation consists of Li_2CO_3 and LiHCO_3 and LiHCO_2 when carbonates are added in the electrolyte system. This passivation limits the charge transfer reaction at the electrolyte/electrode interface [24].

3.3. TG-DTA analysis

Fig. 8(a–c) show the traces of TG-DTA of polymer electrolytes containing LiBF_4 , LiCF_3SO_3 and LiClO_4 , respectively. It is observed from Fig. 8(a), for the film, which possesses LiBF_4 as salt, an endothermic peak was observed around 35°C and a corresponding weight loss about 2% at 53°C and is attributed to the presence of moisture at the time of loading the samples. The film starts decomposing at 96°C followed by an exothermic peak, which indicates the film is stable up to 96°C [12]. The DTA trace shows an endothermic peak around 130°C , which corresponds to the melting point of PVdF–HFP polymer host.

On the other hand, for the film, which contains LiCF_3SO_3 (Fig. 8b) as salt, a similar endothermic peak was observed around 40°C with a weight loss of about 2% at 50°C . After that an irreversible decomposition

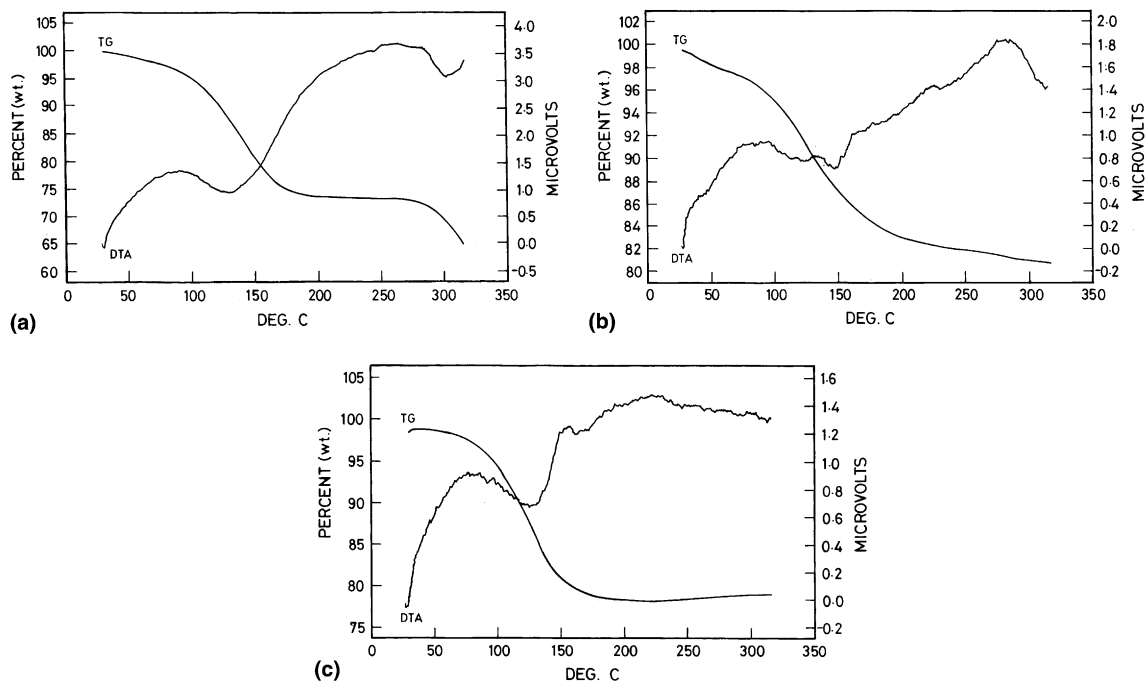


Fig. 8. TG/DTA traces of PVdF-HFP electrolytes containing (a) PVdF-HFP + EC + PC + LiBF₄; (b) PVdF-HFP + EC + PC + LiCF₃SO₃; (c) PVdF-HFP + EC + PC + LiClO₄.

occurs. On the other hand, an endothermic peak was observed around 40°C for the film containing LiCF₃SO₃ [27] and a weight loss about 3% (Fig. 8c). The decomposition of the film starts at 80°C following an endothermic peak. As mentioned earlier, a similar endothermic peak appears in both cases for the films containing LiCF₃SO₃ and LiClO₄ around 130°C that indicates the melting point of polymer host.

It is clear from these observations, that the PVdF-HFP gel electrolytes, which contain LiBF₄, LiCF₃SO₃ and LiClO₄ as salt can be operated up to 80, 75 and 80°C, respectively. These results are in accordance with our earlier results where we studied the thermal analysis of PVC/PMMA blend electrolytes with different salts [12–14].

4. Conclusions

The PVdF-HFP polymer gel electrolytes complexed with a combination of EC and PC and three different lithium salts have been prepared and their ionic conductivity studies have been made from 0 to 70°C. The ionic conductivity decreases with the increase of polymer content in the gel. Although, the PVdF-HFP gel electrolytes with LiBF₄ as salt exhibited maximum conductivity it undergoes severe passivation when lithium metal and is attributed to the poor compatibility of polymer elec-

trolytes containing fluorinated lithium salts. The TG/DTA analysis reveals that all the three electrolytes are thermally stable up to 70°C, which is fairly higher than the operating temperature of lithium polymer batteries viz., 50°C.

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