

Poly(vinylidene fluoride-hexafluoropropylene) (PVdF-HFP) based composite electrolytes for lithium batteries

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Received 6 January 2006; received in revised form 13 February 2006; accepted 15 February 2006

Available online 17 April 2006

Abstract

The composite polymer electrolyte (CPE) membranes, comprising of poly(vinylidene fluoride-hexafluoropropylene) (PVdF-HFP), aluminum oxyhydroxide, (AlO[OH]_n) of two different particle sizes 7 μm/14 nm and LiN(CF₃SO₂)₂ as lithium salt were prepared using solution casting technique. The prepared membranes were subjected to XRD, impedance spectroscopy, compatibility and transport number studies. The incorporation of nanofiller greatly enhanced the ionic conductivity and the compatibility of the composite polymer electrolyte. Also LiCr_{0.01}Mn_{1.99}O₄/CPE/Li cells were assembled and their charge–discharge profiles have been made at 70 °C. The film which possesses nanosized filler offered better electrochemical properties than those with micron sized filler. The results are discussed based on Lewis acid–base theory. © 2006 Elsevier Ltd. All rights reserved.

Keywords: Composite polymer electrolyte; Ionic conductivity; Compatibility; Lewis acid–base theory

1. Introduction

Although lithium batteries with polymer electrolytes are expected to offer safe and reliable batteries for electric vehicles and domestic applications some disadvantages like, poor interfacial properties, safety, etc., are still remaining as a problem area [1–5]. In the case of lithium ion batteries, which contain large amount of liquid electrolytes, an appreciable amount of flammable gas evolves and

subsequently leads the battery to poor safety hazards. This evolution of gas is attributed to the decomposition of a protective layer at the carbon surface [6]. However, this problem can be circumvented by replacing the liquid electrolytes by solid polymer electrolytes. Unfortunately, these electrolytes exhibit poor ionic conductivities of the order of 10⁻⁸ to 10⁻⁵ S cm⁻¹ at room temperature [2–4]. The ionic conductivity of the polymer electrolytes can be considerably enhanced by the addition of low molecular weight plasticizers, e.g., ethylene carbonate and propylene carbonate etc., Our recent studies [7–10] and other reports [11–13] clearly indicate that all plasticized polymer electrolytes loose

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their mechanical strength upon the addition of plasticizers and lead to poor interfacial properties. The mechanical properties of the polymer electrolytes can be hardened either by chemical or physical curing. This resulted in high processing cost. Tarascon et al. [14] successfully overcame these difficulties by introducing a novel membrane prepared by phase inversion method in which the mechanical property was maintained.

Recently, the preparation of polymer membranes by phase inversion technique has also drawn the attention of many researchers [14–20]. This method has several advantages. It requires the critical moisture control only at the time of assembling the cells and the mechanical property of the membrane is retained. Unfortunately, it suffers from poor rate capability [14–20]. Very recently, studies reveal, that the composite polymer electrolytes can alone offer lithium batteries with reliability and improved safety [21–24]. Many reports are available on the physical and electrochemical properties of poly(ethylene oxide) (PEO) based electrolytes [25–31]. Only a very few studies have been made on other polymer hosts like poly(acrylonitrile) (PAN) [32], poly(methyl methacrylate) (PMMA), [33] and blend polymeric systems [34,35]. However, to the best of our knowledge no attempt has been made on the development of composite polymer electrolytes based on poly(vinylidene fluoride-hexafluoropropylene) as a host. This PVdF-HFP has drawn the attention of many researchers due to its appealing properties. The high dielectric constant of $\epsilon = 8.4$ facilitates for higher concentration of charge carriers, and also comprising both amorphous and crystalline phase; the amorphous phase of the polymer helps for higher ionic conduction, whereas the crystalline phase acts as a mechanical support for the polymer electrolyte [18,19]. According to Croce et al. [21,22] and Wiczorek et al. [27] the Lewis acid–base interaction plays a vital role in the enhancement of ionic conductivity of the composite polymer electrolytes. Moreover, in the present study the filler, $\text{AlO}[\text{OH}]_n$ has a strong base and no study reports so far on this type of filler. In order to explore the possibility of employing the PVdF-HFP based composite electrolytes as a possible electrolyte for lithium batteries at elevated temperatures the cycling profiles have been done and are discussed. Also an attempt has been made to study the effect of particle size of the filler on the ionic conductivity and compatibility of the composite polymer electrolytes.

2. Experimental procedure

Poly(vinylidene fluoride-hexafluoropropylene) (PVdF-HFP) (Kynar flex 2801, Japan) and lithium bis perfluorosulfonyl imide, $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ were dried under vacuum at 90 °C for 12 h before use. The inert filler, pseudo-boehmite, $\text{AlO}[\text{OH}]_n$ (COBOT, USA) of different particle sizes 7 μm and 40 nm were also dried at 120 °C for 12 h before use. The preparation of nanocomposite electrolyte involved the dispersion of the selected inert filler and $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ salt in anhydrous tetrahydrofuran (THF), followed by the addition of PVdF-HFP of different concentrations as depicted in Table 1 and the resultant solution was cast as film in an argon atmosphere. The solvent was allowed to evaporate and the composite film was obtained and the average thickness of the film was 30–50 μm . This procedure yielded homogenous and mechanically strong membranes, which were dried under vacuum at 80 °C for 24 h.

The prepared films were sandwiched between the two stainless steel discs of diameter 1 cm and the ionic conductivity of the membranes was measured using an electrochemical impedance analyzer (IM6 – Bio Analytical Systems, USA) in the 50 mHz to 100 kHz frequency range at various temperatures viz., 0, 15, 30, 40, 50, 60,70, and 80 °C. The values of t_{Li}^+ were measured by imposing a dc polarization pulse to a cell of the lithium–composite polymer electrolyte–lithium type and by following the time evolution of the resulting current flow using the expression [11]

$$t_{\text{Li}}^+ = I_s(V - I_0R_0)/I_0(V - I_sR_s) \quad (1)$$

This method consists of measuring the ac impedance and a current loss by dc chronoamperometry, respectively. The resistance and the current across a symmetrical Li/CPE/Li cells were polarized by a

Table 1
The compositions of polymer, filler, lithium salt, and transport number of PVdF-HFP composite polymer electrolytes

S.No	Polymer (wt%)	Filler (wt%)	Salt (wt%)	t_{Li}^+ $\text{LiN}(\text{CF}_3\text{SO}_2)_2$	
				μm	nm
S1	95	0	5	4.7	4.9
S2	92.5	2.5	5	5.1	5.2
S3	90	5	5	5.3	5.4
S4	87.5	7.5	5	5.5	5.6
S5	85	10	5	6.0	6.1
S6	82.5	12.5	5	5.9	6.0
S7	80	15	5	5.9	5.9

dc voltage pulse, V. In the present study the dc voltage pulse applied to the cell was 10 mV. The measurements were taken at the initial time of the applied dc voltage pulse ($t = t_o$, $R = R_o$, $l = l_o$) and under steady conditions ($t = t_s$, $R = R_s$, $l = l_s$) at 30 °C.

The compatibility of the Li/CPE/Li symmetric cells was investigated by studying the time dependence of the impedance of the systems in an open circuit condition at 70 °C. In the present study sample, S5 was used as it exhibited maximum ionic conductivity. The $\text{LiCr}_{0.01}\text{Mn}_{1.99}\text{O}_4/\text{CPE}/\text{Li}$ cells were assembled using the procedure as reported elsewhere. The structural property of the nanocrystalline Cr^{3+} -doped LiMn_2O_4 cathode material has already been reported by one of the authors [19].

3. Results and discussion

3.1. XRD analysis

Fig. 1(a) and (b) displays the XRD patterns of PVdF-HFP polymer and PVdF-HFP + $\text{AlO}[\text{OH}]_n$ (of nanosized) + $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ composite polymer electrolyte membranes, respectively. An exactly similar peak was observed for the films with micron sized (not shown in the figure). The peaks at $2\theta = 18.2$, 20, 26.6, and 38 correspond to (100) (020), (110) and (021) crystalline peaks of PVdF. This confirms the partial crystallization of PVdF units in the copolymer and gives a semi-crystalline structure of PVdF-HFP [36]. We could not observe any discernible changes in the XRD pattern when the micron sized particle was incorporated. The

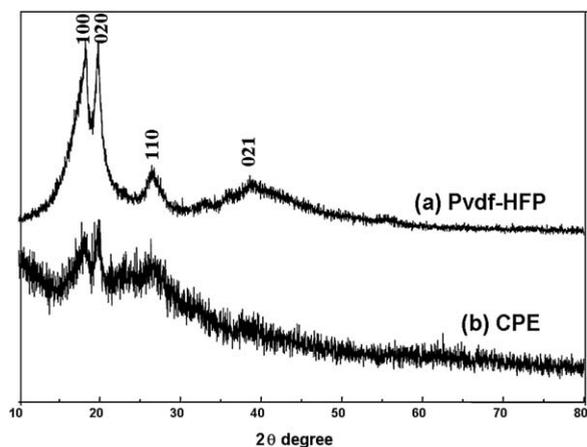


Fig. 1. XRD pattern of (a) PVdF-HFP (b) PVdF-HFP + $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ + nanosized $\text{AlO}[\text{OH}]_n$.

crystallinity of the polymer has been considerably decreased upon the addition of the inert filler and lithium salt. It is quite obvious from Fig. 1(b) that, the intensity of the crystalline peaks decreases and broadens. This reduction in crystallinity upon the addition of inert filler is attributed to small particles of inert fillers which changes the chain re-organization and facilitates for higher ionic conduction [37]. These results are also in accordance with those reported for TiO_2 incorporated PMMA/PEGDA blend composite electrolyte system [33] and $\text{PAN-LiClO}_4\text{-}\alpha\text{-Al}_2\text{O}_3$ composite system [32].

3.2. Ionic conductivity

The temperature dependence of polymer electrolyte membranes comprising PVdF-HFP- $\text{AlO}[\text{OH}]_n$ (micron sized) + $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ and PVdF-HFP- $\text{AlO}[\text{OH}]_n$ (nanosized) + $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ as a function of filler content are shown in Figs. 2 and 3,

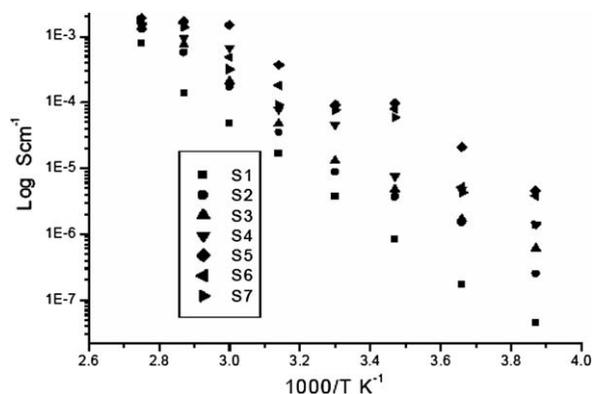


Fig. 2. Temperature dependence of PVdF-HFP membranes as a function of filler content (filler of micron sized).

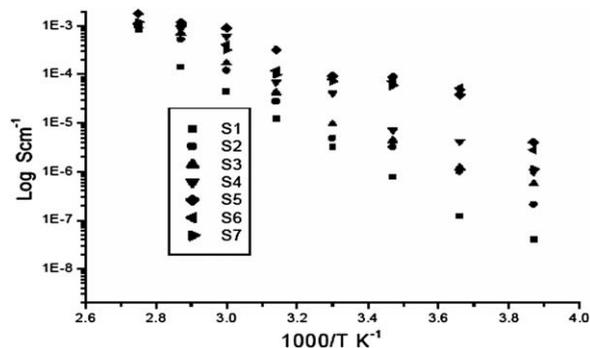


Fig. 3. Temperature dependence of PVdF-HFP membranes as a function of filler content (filler of nanosized).

respectively. The ionic conductivity of the polymer membrane has considerably been increased to one order of magnitude upon the addition of filler in the polymer host and also increases with the increase of temperature. The ionic conductivity also increases with the increase of filler content up to 10 wt% and then decreases with the increase of filler content. These results are in accordance with those reported earlier in which Al_2O_3 was used as filler in PEO-based electrolytes [38]. As commonly found in composite materials, the conductivity is not linear function of the filler concentration. At low concentration levels the diffusion effect which, tends to depress the conductivity, is effectively contrasted by the specific interactions of the ceramic surfaces, which promotes fast ion transport. Hence, an apparent enhancement in conductivity is seen in both cases (filler with micron and nanosized). On the other hand, when the concentration of the filler was increased the dilution effect predominates and the conductivity decreases [21]. Thus, maximum conductivity is achieved only in the concentration region of 8–10 wt%. According to Appetecchi and co-workers [22] their NMR studies reveal that the local dynamics of the lithium ions, in particular lithium mobility, is not changed by filler which supports the idea that the enhancement of conductivity by adding a filler is caused by stabilizing and increasing the fraction of amorphous phase. Our XRD result also substantiates this point. However, indeed, this point does not hold good solely for the enhancement of conductivity where the polymer has amorphous phase by its own nature. According to Croce et al. [21], the Lewis acid groups of the added inert filler may compete with the Lewis acid–lithium cations for the formation of complexes with the PEO chains as well as the anions of the added lithium salt. Subsequently, this results a structural modifications on the filler surfaces, due to the specific actions of the polar surface groups of the inorganic filler. The Lewis acid–base interaction centers reacts with the electrolytic species, thus lowering the ionic coupling and promotes the salt dissociation via a sort of “ion–filler complex” formation. In the present study, the filler, $\text{AlO}[\text{OH}]_n$, which has a basic center can react with the Lewis acid centers of the polymer chain and these interactions lead to the reduction in the crystallinity of the polymer host and indeed, this effect could be the reason for the observed enhancement in the ionic conductivity for both systems studied [27].

3.3. Transference number

In order to support the ionic conductivity data, the transference number measurements have been made as a complimentary test for all CPE samples. Table 1 shows the lithium transference number for the different contents of filler. Indeed, the results are consistent with conductivity data by showing an increase in t_{Li}^+ when passing from the ceramic-free to the filler added composite electrolytes. The transference number values may equally be affected by the interfacial properties with lithium metal anode also [39]. More interestingly, the transference number of the nanofiller incorporated composite polymer electrolytes exhibit higher values than the electrolytes with micron sized which, further supports the ionic conductivity results.

3.4. Compatibility

It is generally known, that the reactivity of lithium electrode affects lithium metal anode/electrolyte interface due to uncontrolled passivation phenomena which in turn leads the formation of a thick and non-uniform surface layers [40]. These layers cause an uneven lithium deposition during the charging process which in turn leading to dendritic growth and cell short-circuiting eventually. Aurbach et al. [41] have made a systematic study on the electrochemical processes of lithium electrodes and their surface chemistry, morphology and performance of lithium metal anodes using EDAX, FTIR spectra analysis. The authors also concluded that the life cycle of lithium batteries with lithium metal anode can be improved by operating at high charging or low discharging rates. Therefore, the interfacial properties of lithium metal anode with composite polymer electrolytes also play a vital role in lithium polymer batteries for the practical applications. As described by Abraham and co-workers [42], the interfacial resistance can be measured from the Cole–Cole impedance plots (not shown in the figure) in which the large semi-circles represent a parallel combination of resistance (R_{film}) and capacitance associated with the passivation film on the Li electrode. A small semicircle is due to the charge transfer resistance in parallel with the double layer capacitance. The intercept of the large semicircle at high frequency on the Z -axis is mostly associated with the interfacial resistance “ R_i ” of the system. In the present study the influence of the particle size of the inert filler on the Li/CPE/Li cells

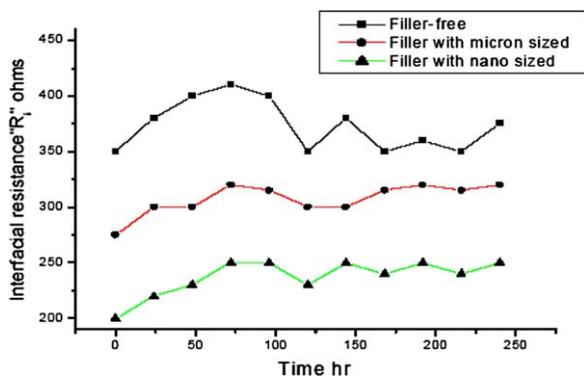


Fig. 4. The variation of interfacial resistance as a function of time for the Li/CPE/Li symmetric cells at 70 °C.

have been analyzed at 70 °C. The sample S5 was taken into account for this study as it exhibited highest ionic conductivity among the samples studied. The variation of the interfacial resistance, “ R_i ” as a function of time for the Li/CPE/Li symmetric cells is displayed in Fig. 4. It is quite obvious from Fig. 4 that the interfacial resistance values have considerably been reduced upon the addition of inert filler (i.e., the interfacial values are lower than the filler-free electrolytes). The addition of the fillers traps any remaining traces of organic solvent impurities and this may account for the enhanced interfacial stability of the composite polymer electrolytes and it can also be believed that the passivation process may basically involve a reaction between the lithium metal and the anions of the lithium salt with the formation of a thin, compact inorganic-layer and favors for a good lithium cyclability [22]. Also of importance that the composite polymer electrolyte with nanosized fillers exhibits better compatibility than the filler of micron sized. According to Kumar et al. [24] that nanosized inert fillers are more compatible than the fillers with micron sized. As depicted in Fig. 5, the inert particles depending upon the volume fraction would tend to minimize the area of lithium electrode exposed to polymers containing O, OH-species and thus reduce the passivation process. It is also foreseeable that smaller size particles for a similar volume fraction of the ceramic phase would impart an improved performance as compared to larger size particles because they will cover more surface area [24]. The formation of an insulated layer of ceramic particles at the electrode surface is probable at higher volume fraction of a passive ceramic phase. This insulating layer will impede electrode reactions. This may very well have happened when excessive amount of the

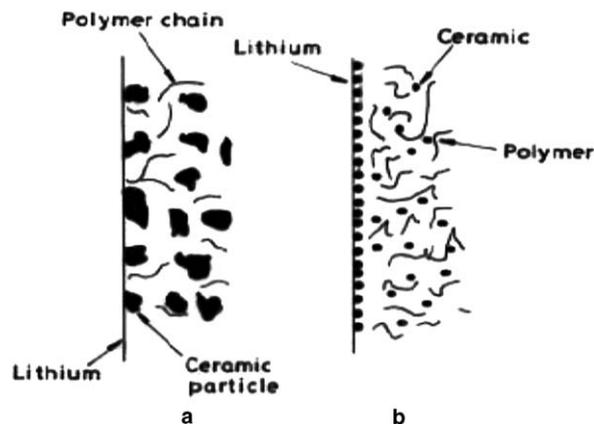


Fig. 5. Schematic representation of polymer chain and inert filler of (a) nanosize (b) micron size in composite polymer electrolytes (adapted from Ref. [23]).

passive ceramic phase were introduced into the polymer matrix. Also the PVdF-HFP co-polymer reacts with lithium at ambient and elevated temperatures. The growth of interfacial resistance does not follow a regular trend for all the samples studied. After, 120 h 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 [13].

3.5. Charge–discharge studies

Fig. 6 demonstrates the charge–discharge behavior of $\text{LiCr}_{0.01}\text{Mn}_{1.99}\text{O}_4/\text{PVdF-HFP-AIO}[\text{OH}]_n/\text{Li}$ cells at 70 °C. In the present study, the sample S5 has been employed as a separator as it was found to be optimal in ionic conductivity and compatibility points of view. The lower and upper cut-off

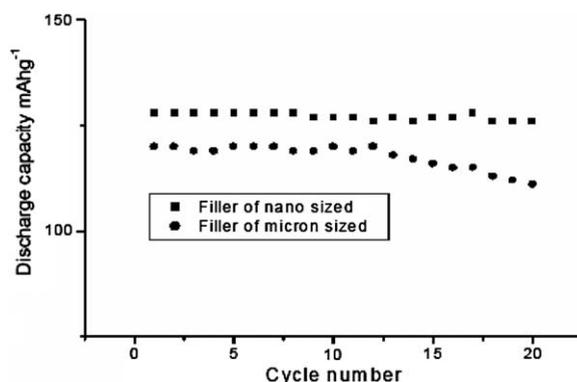


Fig. 6. The discharge capacity versus cycle number of $\text{LiCr}_{0.01}\text{Mn}_{1.99}\text{O}_4/\text{CPE/Li}$ cells at 70 °C.

voltage of the cell was fixed as 2.8 V and 4.2 V, respectively for the fear of decomposition of the electrolyte. The cells were cycled at 0.1 C rate. The polymer cell composed of $\text{LiCr}_{0.01}\text{Mn}_{1.99}\text{O}_4/\text{PVdF-HFP-AIO}[\text{OH}]_n$ 10% (micron sized)- $\text{LiN}(\text{CF}_3\text{SO}_2)_2/\text{Li}$ and $\text{LiCr}_{0.01}\text{Mn}_{1.99}\text{O}_4/\text{PVdF-HFP-AIO}[\text{OH}]_n$ 10% (nm sized)- $\text{LiN}(\text{CF}_3\text{SO}_2)_2/\text{Li}$ delivered an initial discharge capacity of 123 mA h g^{-1} and 127 mA h g^{-1} and final discharge capacity of 119 mA h g^{-1} and 125 mA h g^{-1} after 20 cycles and their fade in capacity per cycle of the cells is 0.20 and 0.25 mA h g^{-1} , respectively. The cell exhibited higher discharge capacity when nanosized filler was incorporated. The cells which possess the membrane of micron sized filler undergo slightly higher fade in capacity after 15 cycles and is attributed to higher interfacial resistance of the system, $\text{Li}/\text{PVdF-HFP-AIO}[\text{OH}]_n$ 10%- $\text{LiN}(\text{CF}_3\text{SO}_2)_2/\text{Li}$ as depicted in Fig. 4. A similar observation has been reported by Yamamoto et al. [29] where they observed for $\text{PEO-LiBF}_4\text{-BaTiO}_3$ systems. In addition to that, the structural characteristics and composition of the cathode materials also play a vital role on that. The fade in capacity of the systems may also be attributed to the Jahn–Teller distortion of the cathode material, $\text{LiCr}_{0.01}\text{Mn}_{1.99}\text{O}_4$ when operated below 3.5 V and also at higher temperature especially above 50°C [43–45].

4. Conclusions

In the present study, the PVdF-HFP composite polymer electrolytes incorporated with $\text{AIO}[\text{OH}]_n$ as an inert filler of two different particle sizes and $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ as lithium salt were prepared and their electrochemical studies have been made. The incorporation of the inert filler not only reduces the crystallinity of the polymer host and acts as ‘solid plasticizer’ capable of enhancing the transport properties and also provides better interfacial property towards lithium metal anode. The nanofillers added composite electrolytes are more compatible than the fillers of micron sized. The cycling behavior of the $\text{LiCr}_{0.01}\text{Mn}_{1.99}\text{O}_4/\text{CPE}/\text{Li}$ cells shows convincing results and may be a potential candidate for lithium polymer batteries for hybrid electric vehicle applications at elevated temperatures.

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