Review Article

Review on composite polymer electrolytes for lithium batteries

A. Manuel Stephan[1], K.S. Nahm*

School of Chemical Engineering and Technology, Chonbuk National University, Chonju, Jeounju 561-756, South Korea

Abstract

This paper reviews the state of the art of composite polymer electrolytes (CPE) in view of their electrochemical and physical properties for the applications in lithium batteries. This review mainly encompasses on composite polymer electrolyte hosts namely poly(ethylene oxide) (PEO), poly(acrylonitrile) (PAN), poly(methyl methacrylate) (PMMA) and poly(vinylidene fluoride) (PVdF) studied so far. Also the ionic conductivity, transference number, compatibility and the cycling behavior of poly(vinylidene fluoride-hexafluoro propylene) (PVdF-HFP)–[AlO(OH)]$_n$–LiPF$_6$/LiClO$_4$ composite electrolytes have been studied and the results are discussed.
© 2006 Elsevier Ltd. All rights reserved.

Keywords: Composite electrolytes; Inorganic filler; Lewis acid–base theory

1. Introduction

The development of lithium batteries has gained an unprecedented significance in the last two decades as the demand for portable telecommunication devices, computers and eventually hybrid electric vehicles has been an ever-increasing one [1,2]. The advantages such as no-leakage of electrolyte, higher energy density, flexible geometry and improved safety hazards have drawn the attention of many researchers on the development of lithium polymer batteries [3,4].

The development of polymer electrolytes has gone through three stages namely: (i) dry solid polymer electrolyte, (ii) gel polymer electrolytes, and (iii) composite polymer electrolytes. In dry solid polymer electrolytes the polymer host itself is used as a solid solvent along with lithium salt and does not contain any organic liquids. However, these dry polymer electrolyte systems (PEO–LiX) offer very low ionic conductivity of the order of 10^{-6} S cm^{-1} at ambient temperature that

excludes this type of membranes from practical applications [5,6]. Hence, large research efforts have been devoted to lower the ambient-temperature region of operations of the (PEO–LiX) matrix. The most common approach is addition of low-molecular weight liquid plasticizers of both cyclic carbonic acid esters and chain-like esters (e.g. propylene carbonate, dimethyl carbonate, diethyl carbonate, etc.). Poly(ethylene oxide) (PEO) was the earliest and extensively studied system. Although, the ionic conduction of PEO was discovered by Fenton et al. [7] in 1973, its technological importance was recognized only in the early of 1980s [8–11]. However, these electrolytes offered very low ionic conductivity. The poly(acrylonitrile) (PAN) based electrolytes on the other hand, exhibit exceptional ionic conductivity of the order of 10^{-3} S cm^{-1} at ambient temperature, appreciable transference number (0.6) and wide electrochemical stability window (<4.5 V). Unfortunately, these electrolytes undergo severe passivation upon contact with lithium metal anode [12–14]. Iijima et al. [15], Appetecchi et al. [16], Feuillede et al. [17] and Zhou et al. [18] have explored the possibility of using poly(methyl methacrylate) (PMMA) host as possible electrolytes for lithium batteries. But the poor mechanical strength of plasticized PMMA offset these electrolytes from practical applications. Studies have also been made on poly(vinyl chloride) (PVC)

* Corresponding author. Tel.: +82 63 270 2311; fax: +82 63 270 2306.
  E-mail addresses: amanstephan@yahoo.com (A. Manuel Stephan), nahmks@moak.chonbuk.ac.kr (K.S. Nahm).
[1] On leave from Central Electrochemical Research Institute, Karaikudi 630 006, India.

based electrolytes. However, these electrolytes offer poor ionic conductivity and compatibility towards lithium metal anode [19,20]. The possibility of enhancing the poor mechanical strength of PMMA electrolytes by blending with PVC has also been explored by one of the authors [21–23]. Though the mechanical property of the PMMA electrolyte had been increased by blending with PVC, because of the poor ionic conductivity, it could not be employed for practical lithium batteries at ambient temperature. Reports are also available on other blend polymeric systems [24,25].

By virtue of the appealing properties, recently, the poly-(vinylidene fluoride) (PVdF) has been identified as a potential host for lithium polymer batteries. This PVdF itself has a dielectric constant, 'ε', of 8.4, which assists for greater ionization of salt and thus provides higher charge carriers. This polymer host is expected to be more anodically stable because of the strong electron-withdrawing functional group. Moreover, the fluorinated polymers are not stable chemically leading to poor interfacial properties with lithium metal anode and the reaction between lithium and fluorine results in the formation of LiF owing to poor safety hazards eventually [26].

Very recently, the poly(vinylidene fluoride-hexa fluoropropylene) (PVdF-HFP) (88:12) has drawn the attention of many researchers. This copolymer comprising an amorphous phase of HFP which helps to entrap large amount of liquid electrolytes and the PVdF crystalline phase acts as a mechanical support for the polymer matrix. Further, studies on PVdF-HFP gel electrolytes are progressing [27–30].

However, all gel polymer hosts lose their mechanical strength when they are plasticized. Also, the gain in ionic conductivity is accompanied by a loss of mechanical strength adversely and also leads to poor compatibility with the lithium electrodes and this high reactivity of lithium metal results in serious problems in terms of battery cyclability and eventually safety. In order to retain the mechanical properties of polymer gel electrolytes, the gel films have to be hardened either by chemical or by physical curing (high energy radiation) and this results in high processing costs.

The Bellcore's group introduced a novel method for the preparation of porous polymer membrane for plastic–lithium ion battery using phase inversion technique [31]. This method requires the critical moisture control only at the time of assembling the cells and the mechanical strength of the membrane is maintained. One of the authors has made an extensive study on this process with PVdF-HFP membranes [32–36]. Unfortunately, the polymer membranes prepared by this technique undergo poor rate-capability [37].

Recent studies reveal, the composite polymer electrolytes (CPE) alone can offer lithium polymer batteries with improved electrolyte/electrode compatibilities and safety hazards [38–40]. One of the most promising ways to improve the morphological and electrochemical properties of polymer electrolytes is addition of ceramic fillers [38–41]. The highly conducting ceramic fillers, zeolites [42], ionites [43] as well as electrically neutral ceramic fillers [44] have been investigated. It has been well established that the addition of ceramic fillers improves the conductivity of polymer hosts and their interfacial properties in contact with the lithium electrode. This increase in ionic conductivity is explained by enhanced degree of amorphocity of the polymer chain or hindered recrystallization [45] Fig. 1 shows the impedance response of Li/CPE/Li symmetric cells as a function of time stored at 90 °C. The composite electrolytes as protonic conductors also find applications in fuel cell applications [46–49]. But in all the cases the particle size and the characteristics of the ceramic fillers play a vital role on the electrochemical properties of the electrolytes.

In general, the ceramic fillers for the polymer matrix are broadly classified into two categories: active and passive. The active component materials are participated in conduction process e.g. Li_3N, $LiAl_2O_3$ while in inactive, the materials such as Al_2O_3, SiO_2, MgO do not involve in the lithium transport process. The selection of fillers between active and passive components is quite arbitrary.

In a pioneering research work, Weston and Steele [50] first demonstrated the effect of incorporating inert filler (α-alumina) in the PEO system. The mechanical strength and the ionic conductivity were significantly enhanced upon the addition of inert particles in the polymer composite systems. Also the change in entropy of alumina added fillers on ionic conductivity studies were reported for PEO [51] and for PEO blend based systems [52]. The crystalline structure that plays a crucial role on the ionic conductivity of PEO was modified by adding
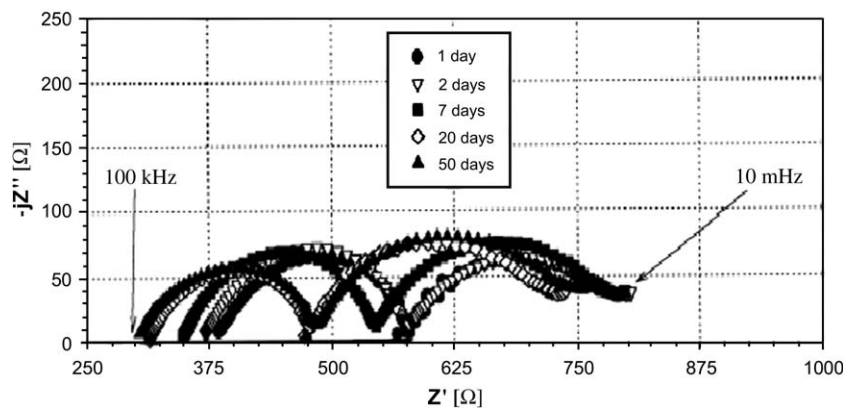

Fig. 1. Impedance response of Li/LiCF$_3$SO$_3$ + 20w/o/Li cell at progressive storage times and at 90 °C. Frequency range: 10 mHz–100 kHz. Electrode surface: 0.5 cm^2 [45].

ceramic additives was reported by Wieczorek et al. [53]. The molecular structure and dynamics of $LiClO_4$ in the poly(ethylene oxide) with dimethyl ether and diglycol system was analyzed using infrared spectroscopy [54]. Reports are also available on similar studies for other systems like $NaClO_4$ [55], miscibility of lithium [56], $PEO-NaH_4I-Al_2O_3$ [57], $LiClO_4$ in pyridene matrix [58], and NH_4SCN [59].

The ionic conductivity and ultra structure were discussed based on Lewis acid–base interactions of $AlBr_3$, $AlCl_3$ and α-Al_2O_3 inert fillers added $PEO-LiClO_4$ electrolytes by Wieczorek et al. [60]. The results inferred the Lewis base interactions occurring between various chemical moieties of the composite electrolyte systems. Aluminum halides interact with polyethers and form aluminum halide complexes and thus stiffen the polymer electrolytes, also the ClO_4^- ion complexes with aluminum halides act as a plasticizing agent. The addition of Lewis acid results in a decrease in the degree of crystallinity of PEO-based electrolytes and followed by an increase in ionic conductivity. These results were also confirmed by DSC data.

While studying the DSC, Li NMR and complex impedance measurements of low-molecular weight PEG with lithium salt, Panero et al. [61] observed that the addition of up to 30 wt.% inert filler, γ-$LiAlO_2$, improved the mechanical properties and is found to have negligible effect on ionic conductivity. Kumar and Scanlon [62] reviewed the state of the art of CPE based on ionic conductivity, transport number and electrode–electrolyte interfacial reactions. They also substantiated that the ceramic fillers such as nitrides (AIN, BN) will have better interfacial properties than SiO_2 or Al_2O_3 because the passivation of lithium metal will result in the formation of Li_3N that facilitates for high ionic conductivity. They also proved that nanosized ceramic fillers are found to have better compatibility with lithium metal than micron sized fillers [62]. The cation transport number was increased from 0.1 to 0.2 upon the addition of SiO_2 (10 wt.%) in the $PEO-LiN(CF_3SO_2)_2$ system [63]. However, Liu et al. [64] were able to increase the transport number up to 0.56 for SiO_2 incorporated $PEO-LiBF_4$ system. In a similar study, Kim et al. [65] have enhanced the ionic conductivity of PEO-based electrolyte by incorporating the SiO_2 coated with trimethylsilyl in which, lithium bis(perfluoro ethyl sulfonyl)imide (LIBETI) was used as salt. The CPE exhibited ionic conductivity of the order of 1.5×10^{-5} S cm^{-1} at 25 °C and the electrochemical stability more than 4.8 V. The enhancement of ionic conductivity was attributed to increased dispersibility as well as non-impeding role of coated SiO_2. The incorporation of SiO_2 as an inert filler in PEO was made by Krawiec et al. [66] and found that the layered nanocomposite polymer electrolytes based on PEO offered better electrochemical characteristics because of the apparent synergism between the silicate host and the polymer. Table 1 shows the differential calorimetry data for the nanocomposite polymer electrolytes (NCEs) containing Al_2O_3 grains of 13 nm. The addition of γ-$LiAlO_2$ in the PEO-based electrolytes considerably reduces not only the crystallinity of the electrolytes but also improves its interfacial stability towards lithium [67]. In a pioneering research, Golodnitsky et al. [68] found in

Table 1
Differential scanning calorimetry data for nanocomposite polymer electrolytes (NCEs) containing Al_2O_3 grains of 13 nm [66]

Al_2O_3 (wt.%)	T_g (°C)[b]	T_m (°C)[c]	PEO crystallinity (%)
Pristine	64	97	
0	−38	58	
1	−37	55	53
3	−38	53	51
5	−37	54	51
5[a]	−37	53	51
10	−37	48	28
10[a]	−33	44	21
20	38	52	30
20[a]	−35	56	41
30	−38	52	30
50	57	59	

[a] Systems containing conventional microsize Al_2O_3.
[b] T_g = Glass transition temperature.
[c] T_m = Crystalline melting point.

$PEO-LiI$ system that the addition of ethylene carbonate, PMMA and PAN is beneficial while the addition of PMA, polybutyl acrylate and PVdF though made polymer electrolyte stiffer but reduced the ionic conductivity. The effect of salt concentration on the molal ionic conductivity of various systems was reported [69]. The enhancement of conductivity was achieved for the $PEO-LiClO_4$ system. The results were discussed based on DSC and FTIR studies. The authors concluded that the changes in conductivity result from acid–base type interactions involving polyether oxygen, filler acid or base centers and alkali metal cations. The effect of the filler is to change the formation of ion aggregates. The region in which the enhancement of ionic conductivity is observed corresponds to a decrease in the fraction of contact-ion pairs and high aggregates: this is due to the location of filler molecules in the vicinity of the co-ordination sphere of Li$^+$ cation. The mechanism was adopted by the same authors for the low-molecular weight poly(ethylene glycol) systems also [70].

A review also documents on polyether composite electrolytes and studies on PVDF-gel electrolytes are also presented [71]. Kim et al. [72] attempted to correlate the glass transition temperature, T_g, and melting point, T_m, of poly(ethylene oxide)-based electrolytes with 29 different inert fillers. Factors generally affect the T_g, also influence T_m and in the present study the authors found these parameters were not varied independently.

The electrochemical properties of mixed phase composite polymer electrolytes based on PEO, $LiClO_4$, $LiBF_4$, $LiPF_6$, $LiCF_3SO_3$, $LiN(CF_3SO_3)_2$ with ferroelectric materials ($BaTiO_3$, $PbTiO_3$, $LiNbO_3$) have been reported [73]. The conductivity was enhanced considerably upon the incorporation of the ceramic filler. This phenomenon was expressed in terms of association tendency of anions with lithium-cation and the spontaneous polarization of ferroelectric ceramic particles due to their particular crystal structure [73].

Impedance analysis of $PEO/LiClO_4/Al_2O_3$ composite solid polymer electrolytes was made with platinum and stainless steel blocking electrodes by Qian et al. [74]. The room temperature conductivity was enhanced upon the addition of Al_2O_3

particles. An increase in the diameter of high frequency and a decrease in the slope of low frequency have been attributed to the applied d.c. potential in the experimental procedures.

Kumar et al. [75] explored the possibility of using MgO as filler in PEO–LiBF$_4$ system. They have also proposed a structure–conductivity correlation using DSC and conductivity data. They also found that the incorporation of MgO in PEO host suppresses the PEO melting temperature and retards its crystallization kinetics. Also a content of 30 wt.% of ceramic filler affects the ionic conductivity of the composite electrolyte adversely.

The addition of inorganic filler, LiN$_2$O$_3$ in the polymer hosts comprising PEO-grafted (polymethacrylate) not only increases the ionic conductivity of the systems but also enhances the ionic mobility [76]. The addition of LiAl$_2$O$_3$ in the polymer host increases the ionic conductivity when LiClO$_4$ was used as salt. While on the other hand, little influence was observed when LiCF$_3$SO$_3$ was added. Bloise and co-workers [77,78] probed the NMR properties of both nuclei ^{1}H and ^{7}Li and studied the effects of ceramics and carbon black filler particles on the mobility of PEO chains. Results suggested that the Li–F interaction was found to be weaker in the composite electrolyte prepared with α-Al$_2$O$_3$ when compared to other electrolytes prepared with γ-Al$_2$O$_3$. A similar study was demonstrated by Chung et al. [79] for PEO-based electrolyte incorporated with TiO$_2$/Al$_2$O$_3$ and LiClO$_4$. The NMR studies revealed that the increase in ionic conductivity is not attributable to a corresponding increase in the segmental motion of polymer but are due to the weakening of polyether-cation association induced by the nanoparticles.

The effect of size of inorganic particles on the crystalline–amorphous transition of PEO–LiBF$_4$ systems was analyzed using DSC analysis [80]. These specimens were thermally cycled (cooling–heating) between ambient temperature and 100 °C. DSC studies revealed that the nanosized inorganic filler was found to be the most effective material for reducing the crystallinity of PEO-based polymeric hosts. The same group [81] reported the DSC analysis for PEO/LiBF$_4$/TiO$_2$ and ZrO$_2$ also. Scanlon et al. [82] have identified that the interaction between polymer chain and inorganic fillers facilitates for better ionic conductivity enhancements. This interaction is influenced by the particle size and mass of the particles. The nature of the interaction is believed to be dipole–dipole interaction and driven by a dielectric constant gradient. Also of importance, the interaction is also temperature dependent. The polymer phase was identified as a medium of transport and reservoir for conducting ions. The ceramic filler also improves the transport of charge carriers through the localized influence on the polymer chain conformation. The importance of using nanosized inorganic filler in the polymer hosts to enhance ionic conductivity and the effect of dielectric constant on the ionic conductivity of MgO and BaTiO$_3$ added PEO–LiBF$_4$ system have been discussed. The authors concluded that the ceramic not only facilitates for better ionic conductivity but also interacts with the polymer phase and the nature of interaction depends upon the size of the particles. An amorphous structure was achieved for the PEO/LiBF$_4$/LiPF$_6$–Al$_2$O$_3$

polymer electrolyte system by optimizing particle size of Al$_2$O$_3$. Nanosized Al$_2$O$_3$ filler was found to be more effective in reducing the crystallinity of PEO than micron sized particles. It has also been proven that a mixture of two salts rather than a single salt stabilizes the amorphous phase of polymer [82]. The influence of zeolite on the physical and electrochemical properties, like impedance spectroscopy, cyclic voltammetry, DSC and SEM of the PEO–LiBF$_4$ systems have been reported [83].

A majority of the studies have been made on polyether at moderate temperatures where such electrolytes exhibit macroscopic uniformity. Relatively a very few attention was paid to sub-ambient temperature conductivity [84]. Furthermore, their studies revealed that the temperature dependence of ionic conductivity of the composite electrolytes follow Arrhenius empirical relation at sub-ambient temperature down to glass transition temperature, T_g, and VTF equation at high temperature.

On contrary to all studies, Kasemagi and co-workers [85] reported that the incorporation of quasi-spherical nanoparticles of α-Al$_2$O$_3$ to LiCl, LiBr and LiI salts in amorphous PEO adversely reduces the ionic conductivity of the polymer electrolytes. This reduction in ionic conductivity was attributed to the ion-pairing and ion-clustering effects in that particular system.

Croce et al. [86] proposed a model to account for the role of ceramic fillers on the transport properties of PEO-based composite electrolytes. This model was substantiated by electrochemical studies such as ionic conductivity, lithium transference number, etc. They also concluded that the role of incorporated filler in the polymer matrix is not only preventing crystallization of the polymer chain but also promotes specific interaction between the surface groups and both PEO segments and the electrolyte ionic species which subsequently, increases the fraction of free Li$^+$ motions. Dissnayake et al. [87] proposed a new model based on the interaction of Lewis acid–base theory in which they found filler particles are not involved in the enhancement of ionic conductivity. Rather they observed that the conductivity enhancement is due to an interaction between the ionic species and the surface groups of the fillers. Furthermore, it is attributed that the ionic conductivity is increased due to the creation of additional sites and a qualitative model has also been proposed for the system composed of (PEO)$_9$–LiTFSI–Al$_2$O$_3$. The CPE with acidic surface group system exhibited highest conductivity among the fillers studied with basic, neutral and weak acidic. The same group [88] found a similar kind of interaction between the ionic species and the O/OH groups on the inert filler surface of the (PEO)$_9$–LiCF$_3$SO$_3$–Al$_2$O$_3$ system. Choi and co-worker [89] observed two antagonistic effects on the ionic conductivity of SiC incorporated PEO–LiClO$_4$ system. The incorporation of SiC considerably decreases the glass transition temperature, T_g, which enhances the polymer chain motion and increases volume fraction of the amorphous phase, which obviously increases the ionic transport process.

Using high resolution NMR, Dai et al. [90] found that Li has at least two environments in the PEO–LiI systems: one solvated by PEO and one in ionic clusters. The confluence of the conductivity jump and the charge in Li environment

suggest that the conduction mechanism in concentrated electrolyte system is quite different than that of more diluted polymer electrolytes. Wieczorek et al. [91,92] applied the Lewis acid–base theory to analyze the ultra structure and the ionic conductivity of several composite ether alkali metal solid electrolytes. The authors incorporated three different fillers namely Lewis acid centers (AlCl$_3$), Lewis base centers (poly(*N,N* dimethylacrylamide) as well as amphoteric Lewis acid–base character (α-Al$_2$O$_3$) in the PEO–LiClO$_4$ system. Since PEO is known as a Lewis base and Li$^+$ cation as a Lewis acid the phenomena occurring in composite electrolyte were explained in terms of equilibria between various Lewis acid–base reactions occurring in the composite electrolyte systems. The same group [93] also substantiated that the ionic conductivity occurs only in the amorphous phase of the polymer–salt electrolyte system. The authors found in a system composed of both organic (polyacrylamide) and inorganic (Al$_2$O$_3$) fillers that the inorganic filler increases the glass transition temperature and on contrary, organic filler reduces the glass transition temperature.

A few researchers have intensively made the interfacial properties of composite polymer electrolytes with lithium metal anode [94–96]. Appetecchi et al. [94] prepared several composite electrolyte samples composed of PEO– with two different lithium salts, LiBF$_4$ and LiCF$_3$SO$_3$ and γ-LiAlO$_2$ as filler by a new solvent-free method. This synthesis procedure with the dispersed particles concurs to provide these composite electrolytes with an exceptionally high stability with the lithium metal electrode. Furthermore, these dry polymer electrolytes offered very high efficiency (99%). This in turn suggests the suitability of the electrolytes for the fabrication of improved rechargeable lithium polymer batteries. In a similar study, Li et al. [95] studied the interfacial properties of PEO-based electrolytes with two different salts namely LiClO$_4$ and Li(CF$_3$SO$_2$)$_2$. The interfacial resistance of the CPE-containing LiClO$_4$ was found to be higher than that of with Li(CF$_3$SO$_2$)$_2$ even after annealing at 80 °C. According to Kumar et al. [96] the nanosized fillers are more compatible to reduce the interfacial resistance than fillers with micron sized.

At least one order of ionic conductivity has been increased upon the incorporation of BaTiO$_3$ filler in the PEO-based electrolytes [97]. The increase in transport number and ionic conductivity of the polymer host after the incorporation of the filler has been explained on the basis of the spontaneous polarization of the ferroelectric material due to its particular crystal structure. The addition of BaTiO$_3$ filler had greatly enhanced the lithium/electrolyte interface stability. Golodnitsky et al. [98] addressed the conduction mechanism that takes place on the grain boundaries which was ignored so far. The effect of doping CaI$_2$ and changing the Li/EO ratio and the concentration of the filler has also been discussed with SEM and ECS data. In a system composed of PEO–LiClO$_4$–SiO$_2$/TiO$_2$, Scrosati et al. [99] and Croce et al. [100] found that the incorporation of inert filler not only enhances the mechanical strength but also performs both as a sort of ''solid plasticizer'' for the polymeric chain by kinetically inhibiting their crystallization and their re-organization at ambient temperature and

as a sort of ''solid solvent'' by interacting with ionic species of the salt.

On contrary to the above results, Shin and Passerini [101] could not find any remarkable change in the ionic conductivity and transference number of PEO-based electrolytes. In fact, 7 nm SiO$_2$ lowered the diffusion co-efficient significantly. The lithium transport number of SiO$_2$ incorporated electrolytes exhibited lower values than those with γ-LiAlO$_2$ incorporated and pristine one. Very recently, Wang et al. [102] achieved a novel composite electrolyte of highest transference number of 0.7 with maximum ionic conductivity. More interestingly, the conducting ceramic filler/mat, La$_{0.055}$Li$_{0.35}$TiO$_3$, was introduced in the polymer matrix by Ji et al. [103] and thus this ceramic filler is believed to penetrate the cross section of the electrolyte. The role of functional nanofillers on the ionic conductivity of the PEO-based electrolytes has been reported.

Most of the literatures are available only on the studies made on poly(ethylene oxide)-based matrices. A very few studies have been made on other polymeric materials as possible composite electrolyte hosts such as poly(acrylonitrile), poly(methyl methacrylate) and poly(ethylene glycol). A series of α-Al$_2$O$_3$ containing poly(acrylonitrile)-based composite electrolytes were prepared by Chen-Yang et al. [104] with high ionic conductivity and mechanical property at ambient temperature. The CPE with highest ionic conductivity was achieved for the composition with 7.5% of α-Al$_2$O$_3$ and 0.6 LiClO$_4$ per PAN repeat unit. The prepared PAN-based electrolytes were found to be optimal in stress and strain points of view to form good interface with electrodes. Nanocomposite electrolytes PAN/LiClO$_4$/Al$_2$O$_3$ have been prepared and their infrared spectra were also reported [105]. The addition of nanoceramics can help the dissolution of the lithium salt and the dissociation of the Li$^+$-nitrile. Based on the Lewis acid–base type of interactions, it is proposed that the competitions between the Li$^+$ ion and the hydrogen on the surface of acidic nano-oxides and between ClO$_4^-$ anions and the oxygen on the surface of basic nano-oxides help to separate the Li$^+$ClO$_4^-$ ion pairs. Meanwhile, such competition also dissociates the LiI-nitrile interactions. These interactions increase the contents of free charge carriers in the electrolytes and enhance the ionic conductivity of the nanocomposite polymer electrolytes. The Raman and a.c. impedance analysis of CPE with PAN as a host is also reported [106]. Chen and Chang [107] demonstrated that the addition of cetyl pyridium chloride (CPC)-modified montmorillinite increases the ionic conductivity of PAN-based electrolytes of two orders magnitude over that of PAN–LiCF$_3$SO$_3$ system. The interactions between silicate layer, the nitrile group and lithium-cation were investigated by FTIR, solid-state NMR and DEA studies. A strong interaction that occurs between silicate layer and LiCF$_3$SO$_3$ salt system was also identified. The dependence of ionic conductivity on the free volume of PAN–LiCF$_3$SO$_3$ system using positron annihilation life-time spectroscopy has also been reported [108].

The microscopic interactions of fully amorphous trifunctional polyether (3PEG) and poly(ethylene methylene oxide) (PMEG) complexed with two different lithium salts and

nanoparticulates of 20 nm TiO_2 and Al_2O_3 have been reported [109]. The addition of TiO_2 provides an increase of ionic conductivity of half-order, and on contrary, Al_2O_3 reduces the ionic conductivity. The results were discussed based on electrostatic interactions involving dielectric properties of the fillers, interaction between polymer-filler and ionic species and fillers when the effect of crystallization was ignored.

A novel hyperbranched polymer, poly[bis(diethylene glycol)benzoate] capped with a 3,5-bis[(3′,6′,9′-trioxodecyl)-oxy] benzoyl group (poly-Bz1a), was prepared, and the composite electrolyte comprising $LiN(CF_3SO_2)_2$ and poly-Bz1a/$LiN(CF_3SO_2)_2$ was reported by Itoh et al. [110]. The poly-Bz1a/$LiN(CF_3SO_2)_2$ electrolyte exhibited higher ionic conductivity compared with a polymer electrolyte based on poly[bis(diethylene glycol)benzoate] capped with an acetyl group (poly-Acla), and the ionic conductivity of poly-Bz1a/$LiN(CF_3SO_2)_2$ electrolyte was found to be 7×10^{-4} S cm^{-1} at 80 °C and 1×10^{-6} S cm^{-1} at 30 °C, respectively. The existence of a 3,5-bis[(3′,6′,9′-trioxodecyl)oxy]benzoyl group as a branching unit present at ends in the base polymer improved significantly ionic conductivity of the hyperbranched polymer electrolytes. An electrochemical stability window of 4.2 V at 70 °C was achieved and the film was found to be stable until 300 °C.

The cycling behavior of poly(methyl methacrylate)/poly-(ethylene glycol diacrylate) blend with $LiCoO_2$/carbon couple has been reported [111]. The cells are found to deliver higher capacity even at high rate (C/2). The DSC, NMR, XRD and ionic conductivity properties of PEG-based electrolytes have been analyzed [112]. The variation of crystallinity of the polymeric electrolyte systems is correlated with the DSC data. Very recently, a complete study like ionic conductivity, morphology, electrochemical and spectroscopic measurements on PEG-based electrolytes incorporated with both organic and inorganic fillers [113,114] and hectorite based on PEG [115] have been reported. Chiang et al. [116] observed one order enhancement of ionic conduction on PVdF host upon the addition of nano-tube TiO_2 with $LiPF_6$. Using photo-electron spectroscopy (XPS) the change in $C1_S$ and $F1_S$ and $F1_S$ spin-orbital splitting of PVdF upon the addition of nano-tube TiO_2 was observed. The results revealed that the fluorine atom of PVdF and the oxygen atom of TiO_2 are coordinating with the dissociated Li$^+$ ions through Lewis acid–base interactions.

The formation of different ionic aggregates of Al_2O_3 added PEG methyl ether (PEGME)–$LiClO_4$ and PEG dimethyl ether (PEGDME)–$LiClO_4$ electrolytes have been identified using three different methods [117]. The first two methods were based on deconvolution of FTIR 624 cm^{-1} and Raman 930 cm^{-1} perchlorate anion modes whereas the third mode involved in the salt concentration depended on ionic conductivity. From the results, the authors concluded that PEODME-based electrolytes are superior to PEGME-based electrolytes as the strong interaction of polar –OH terminal group on the PEGME with ions and filler surfaces is a detriment.

In view of the development of long-life, high efficiency, rechargeable polymer electrolyte lithium batteries, properties of cathode materials [118] and the importance of using

Table 2
Properties of composite polymer electrolytes [120]

LiX	Ceramic filler	Conductivity (S cm^{-1}) 90 °C	Lithium transference 30 °C	Lithium interface resistance (Ohm cm^{-2})	
$LiCF_3SO_3$	γ-$LiAlO_2$	9.0×10^{-4}	2.9×10^{-6}	0.29	40 (after 70 days)
$LiBF_4$	γ-$LiAlO_2$	6.0×10^{-4}	2.9×10^{-7}	0.26	200 (after 70 days)
$LiClO_4$	TiO_2	1.8×10^{-3}	2.3×10^{-5}	0.5–0.6	55 (initial)
$LiClO_4$	Al_2O_3	1.1×10^{-3}	2.9×10^{-5}	0.31–0.33	80 (after 55 days)

nanocomposite polymer electrolytes for lithium batteries [119–122] have also been reported. Table 2 shows the properties of some of the composite polymer electrolytes [120].

1.1. Lithium-composite polymer electrolyte batteries

A very few articles document the cycling behavior of lithium polymer batteries with composite polymer electrolytes. A liquid-free ceramic incorporated composite electrolyte, PEO–$LiCF_3SO_3$–$LiAlO_2$ was prepared and was employed as a separator in Li/$LiMn_2O_4$ cells [123]. The authors estimated the ratio of number of cycles that any battery can sustain for different values of lithium excess (Q_E) to lithium stoichiometric amount (Q_S) to be more than 95% and this promising value could be improved by dry composite polymer electrolytes for long cycle life batteries. The same group [124] reported the cycling behavior of PEO–$LiCF_3SO_3$–γ-$LiAlO_2$ in the 3 V region of $LiMn_2O_4$ cells.

Li et al. [125] studied the cycling performance of PEO-based composite electrolytes with three different inert fillers namely $BaTiO_3$, TiO_2 and $Al_2O_3SiO_2$ and $Li(CF_3SO_2)_2N$ as lithium salt. The lithium cell comprising $LiNi_{0.8}Co_{0.2}O_2$/CPE/Li with $BaTiO_3$ as filler exhibited good cycling performance and was attributed to improved interfacial stability between the electrolyte and electrode. In an independent study [126], in addition to the lithium salt, $Li(CF_3SO_2)_2N$, they incorporated $LiPF_6$ in the same electrolyte. Their studies revealed that the incorporation of $LiPF_6$ reduces the capacity fading of the cell drastically up to 0.28% per cycle. The same authors [127] reported the cycling behavior of $LiNi_{0.8}Co_{0.2}O_2$/CPE/Li cells at 70 °C. The CPE based on PEO with a hyperbranched poly[bis(triethylene glycol)benzoate] capped with an acetyl group (HBP), a ceramic filler, $BaTiO_3$ and $LiPF_6$ as lithium salt. The conductivity of the polymer electrolyte was found to be of the order of 10^{-4} S cm^{-1} at room temperature. The time dependence of the bulk resistance, R_b, the interfacial resistance R_i and charge-transfer resistance R_{ct} have been measured at 60 °C. The cycling behavior of $LiNi_{0.8}Co_{0.2}O_2$/CPE/Li cells for different cut-off voltages has also been studied (Fig. 2). The cell delivered a capacity of 150 mA h g^{-1}, which is comparable to that of liquid electrolyte. The capacity fade per cycle 0.12% was attributed to the upper cut-off voltage of the cell. Table 3 displays the tensile strength of the composite polymer electrolytes at various temperatures.
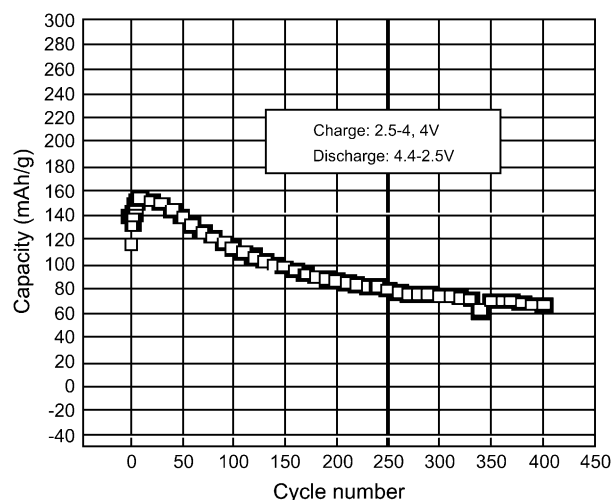
Fig. 2. Cycling performance of the cell Li/[PEO−10 wt.% HBP]$_{10}$ (Li-imide-10 wt.%)]−10 wt.%.BaTiO$_3$/LiNi$_{0.8}$Co$_{0.2}$/Al at 60 °C. Current density: 0.2 mA/cm^2. Cut-off voltage: 2.5–4.4 V [127].

Fig. 3. Discharge cycling behavior of a Li/P(EO)$_{35}$ LiCF$_3$SO$_3$:5%SiO$_2$/LiFePO$_4$ polymer battery at different temperatures and current densities [128].

Appetecchi et al. [128] exploited the ionic conductivity of PEO-based electrolytes at high temperature for electric vehicle applications. They assembled a cell by the direct lamination of the components, namely the lithium foil anode, PEO-based electrolyte and LiFePO$_4$ composite cathode. The results confirmed the good performance of this Li/LiFePO$_4$ cell in terms of capacity, charge−discharge efficiency and cycle life. A fade in capacity was observed at moderate temperatures and at high rates and are attributed to a decrease in the ionic conductivity of polymer electrolyte. However, Li/LiFePO$_4$ system has been found to be optimal in terms of specific energy and power density for temperatures above 90 °C. The discharge cycling behavior of Li/CPE/LiFePO$_4$ polymer battery at different temperatures is shown in Fig. 3. Very recently, Jiang and co-workers [129] introduced a novel composite electrolyte

Table 3
Tensile strength of the composite polymer electrolyte films at various temperatures [127]

Samples broken point (MPa)	Temperature 100% (°C)	Elongation	(MPa)
[(PEO−10 wt.% HBP)$_{10}$	30	2.7	3.6
(Li-imide−10 wt.%	40	1.7	
LiPF$_6$)]−10 wt.% BaTiO$_3$	50	1.4	
	60	0.56	1.3
	70	0.33	
[(PEO−10 wt.% HBP)$_{25}$	30	3.4	
(Li-imide−10 wt.%	60	0.6	
LiPF6)]−10 wt.% BaTiO$_3$			
[(PEO−20 wt.% HBP)$_{12}$	40	0.33[a]	
(Li-imide)]−10 wt.% BaTiO$_3$	60	0.26[a]	
[PEO$_{10}$(Li-imide)]−10 wt.% BaTiO$_3$	30	0.67	
PEO−10 wt.% BaTiO$_3$	60	17	
		10	
PEO	30	14	

[a] Maximum strength yield point.

composed of polyurethane acrylate (PUA) with nanosized SiO$_2$ as ceramic filler and LiN(CF$_3$SO$_2$)$_2$ as salt. The cell, Li/PUA−SiO$_2$/Li$_{0.33}$MnO$_2$, exhibited a high initial capacity of about 192 mA h g^{-1} at 60 °C and a faster capacity fading when hydrophilic SiO$_2$ was added. However, the fade in capacity could be considerably reduced upon the addition of hydrophilic nanosize SiO$_2$ powders. Also the cycling behavior of Li/LiMn$_3$O$_6$ cells with low particle size filler dispersed composite polymer electrolyte has been reported recently [130].

Panero et al. [131] have analyzed the charge−discharge profile of LiNi$_{0.5}$Mn$_{1.5}$O$_4$/Li and LiNi$_{0.8}$Co$_{0.16}$Al$_{0.04}$O$_2$/Li cells with PAN-based electrolytes. The PAN-based electrolyte, which exhibited an ionic conductivity of the order of 0.8 × 10^{-2} S cm^{-1}, comprised propylene carbonate, Al$_2$O$_3$ as an inert filler and LiPF$_6$ as lithium salt. The electrochemical stability of the electrolyte was found to be above 5.5 V vs Li which makes it suitable for high voltage lithium battery applications. The cells were able to cycle even at C/3 rates and some decay in capacity could be noticed which is attributed to the poor cell structure and electrode formulation. A unique performance of a novel rechargeable battery with a cathode of phospho-olivine structure has been demonstrated by Croce and co-workers [132]. This battery has some promising features in terms of cycle life and rate-capability. Under the present circumstances the battery appears to be quite suitable for electric vehicle applications, which is so urgently required for the control of air in large urban areas.

Based on the literature available, so far to the best of our knowledge no attempt has been made on the AlO[OH]$_n$ incorporated PVdF-HFP composite as possible electrolyte for lithium polymer batteries for elevated temperature applications. Taking into account the appealing properties of PVDF-HFP as mentioned earlier, the present study has been made on the electrochemical properties of these electrolytes complexed with two different lithium salts namely LiClO$_4$ and LiPF$_6$. The interaction of Lewis acid groups of the added ceramics (e.g. −OH groups of the AlO[OH]$_n$) with polymer chain is discussed and also cycling behavior with nanocrystalline LiCr$_{0.01}$Mn$_{1.99}$O$_4$/CPE/Li cells has been studied and is presented.

2. Experimental procedure

2.1. Sample preparation

The composite polymer electrolyte samples were prepared by solution casting technique as reported elsewhere [19–23]. The PVdF-HFP (Kynar flex 2751, Elf Atochem, Japan), lithium hexafluoro phosphate (LiPF$_6$), lithium perchlorate (LiClO$_4$), and aluminum oxyhydroxide (AlO[OH]$_n$) (pseudo-boehmite) were dried by annealing them under vacuum at 100, 80, 90 and 250 °C, respectively, for 24 h. All components, namely the selected lithium salt, polymer and the inert filler, pseudo-boehmite, of particle size 40 nm (Cobot, USA) were dissolved in an anhydrous tetrahydrofuran (THF). We set the total weight of polymer, inert filler and lithium salt to be identical (100%) when preparing the films of various filler 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 (50–80 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 4. 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 samples was measured by sandwiching the samples between two stainless steel blocking electrodes. The measurements were performed using an electrochemical impedance analyzer (Princeton EG & G, USA) between 100 kHz and 10 mHz at various temperatures ranging from −15 to 90 °C. A thermostatic bath with 0.1 °C precision was utilized to control the temperature.

2.3. Compatibility studies

The stability of lithium interface was investigated by monitoring the time dependence of the impedance of symmetrical Li/PVdF-HFP-composite electrolyte/Li cells by utilizing the same procedure for ionic conductivity measurements. The symmetric cells were stored at 60 °C.

2.4. Transference number

The lithium ion transference number, t_{Li^+} of the samples was measured by utilizing the method reported in Ref. [16]. The measurements are taken at the initial time of the applied d.c. voltage pulse ($t = t_o, R = R_o, I = I_o$) and under steady conditions ($t = t_s, R = R_s, I = I_s$). By using the values, the t_{Li^+} is given by the equation:

$$t_{Li^+} = I_s(V - I_oR_o)/I_o(V - I_sR_s) \tag{1}$$

where V is the value of the d.c. voltage pulse applied to the cell for the chrono amperometric analysis. (In the present study $V = 5$ mV.)

2.5. Charge–discharge studies

The lithium cells composed of nanocrystalline LiCr$_{0.01}$Mn$_{1.99}$O$_4$/CPE/Li was assembled by stacking the lithium metal anode, CPE and composite cathode in a coin type cell. The preparation and characterization of composite LiCr$_{0.01}$Mn$_{1.99}$O$_4$ have already been reported by one of the authors [34].

3. Results and discussions

3.1. XRD analysis

Fig. 4a and b displays the XRD pattern of PVdF-HFP polymer and PVdF-HFP−AlO[OH]$_n$−LiPF$_6$ sample. The peaks at $2\theta = 18.2, 20, 26.6$ and 38 corresponds 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 [29]. A similar pattern was observed when LiClO$_4$ was incorporated in the polymer host. The crystallinity of the polymer has considerably been decreased upon the addition of the inert filler and lithium salt. It is quite obvious from Fig. 4b that the intensity of the crystalline peaks decreases and broadens. This reduction in crystallinity upon the addition of inert filler is attributed

Table 4
Composition of polymer, inert filler and lithium salt with corresponding transference number

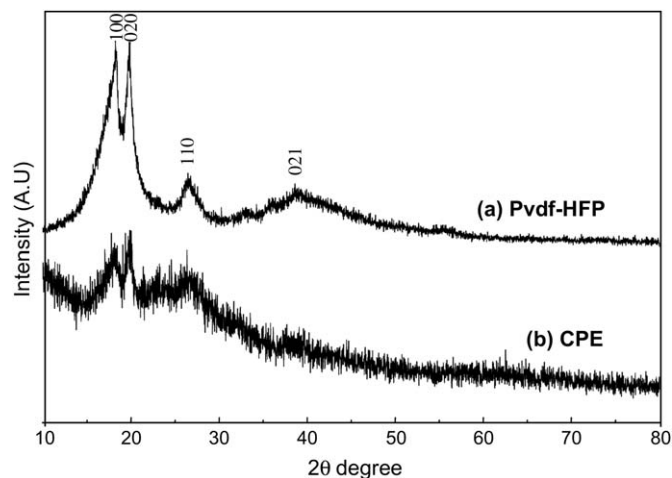| S. no	Polymer (wt.%)	AlO[OH]$_n$	Salt: LiClO$_4$/LiPF$_6$	Transference number	
				LiPF$_6$	LiClO$_4$
S1	95	0	5	0.30	0.34
S2	90	5	5	0.40	0.40
S3	87.5	7.5	5	0.45	0.43
S4	85	10	5	0.50	0.48
S5	82.5	12.5	5	0.56	0.50
S6	80	15	5	0.52	0.50
S7	75	20	5	0.52	0.49

Fig. 4. XRD patterns of: (a) PVdF-HFP polymer and (b) composite polymer electrolyte (CPE).

to small particles of inert filler which changes the chain re-organization and facilitates for higher ionic conduction [64,133] These results are also in accordance with those reported for TiO$_2$ incorporated PMMA/PEGDA blend composite electrolyte system [111] and PAN−LiClO$_4$−α-Al$_2$O$_3$ composite system [104].

3.2. Ionic conductivity

Figs. 5 and 6 depict the ionic conductivity as a function of filler concentration, [AlO(OH)]$_n$, in the polymer host for fixed lithium salt content (5%), LiPF$_6$ and LiClO$_4$, respectively. It is clear from the figure that the ionic conductivity has considerably been increased (up to one order) in both cases upon the addition of inert filler. The ionic conductivity of the inert filler system is higher than the undoped system for all the temperatures studied. The ionic conductivity increases with the increase of filler content up to 12.5% and decreases further even when the concentration of the filler was increased. These results are in accordance with those reported earlier in which Al$_2$O$_3$ was used as filler in PEO-based electrolytes [74]. As commonly found in composite materials, the conductivity is not a linear function of the filler concentration. At low concentration levels the dilution 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. At higher filler content, the dilution effect predominates and the conductivity is lowered. On the other hand, when the concentration of the filler was increased the dilution effect predominates and the conductivity decreases [86]. Thus the maximum conductivity is achieved only in the concentration region of 8−10 wt.%. According to the NMR studies of Scrosati and co-workers [44] 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
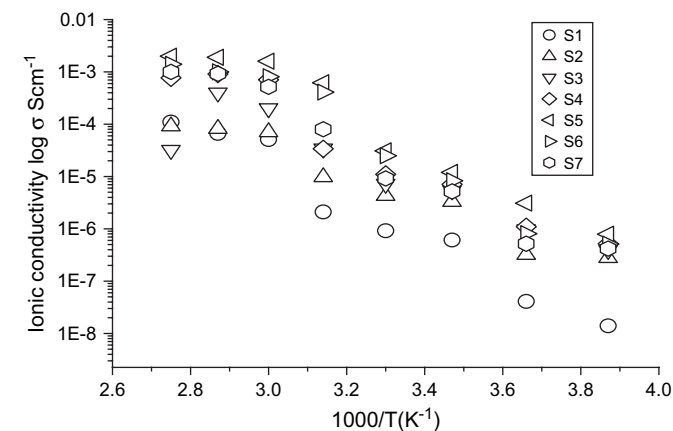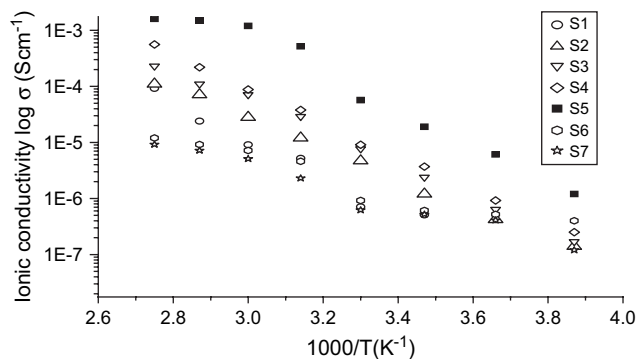

Fig. 6. Temperature dependence of PVdF-HFP−AlO[OH]$_n$−LiClO$_4$ composite polymer electrolyte as a function of ionic conductivity (samples S1− S7).

polymer has amorphous phase by its own nature. According to Scrosati et al. [86], 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 in 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 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, AlO[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 [92].

It is also clear from both figures (Figs. 5 and 6) that the films with LiPF$_6$ as salt exhibited higher ionic conductivity than those with LiClO$_4$. Since both anions are counter ions of strong acids the difference in conductivity is presumably due to the difference in lattice energies. LiPF$_6$ has the lower lattice energy and bulky fluorinated anion and therefore leads to an easier solvation of Li$^+$ ion by the polymer matrix, which facilitates for higher ionic conductivity. Similar observation has been reported by Immanuel et al. [134] in which MEEP was used as a host and also by us [21−23] when the ionic conductivity of PVC/PMMA blend electrolytes had been studied.

3.3. Compatibility

Lithium metal is found to be an attractive anode material for lithium secondary battery that provides a larger capacity of 3800 mA h g^{-1}, which is about 10 times higher than that of carbon-based anode (372 mA 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

Fig. 5. Temperature dependence of PVdF-HFP−AlO[OH]$_n$−LiPF$_6$ composite polymer electrolyte as a function of ionic conductivity (samples S1−S7).

the lithium and the resistance of this layer grows with time, which can reach values over 10 kOhm 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 [135] that the rate of SEI formation is in a time domain less than 100 μs and the characteristics of the formed layer are very inhomogeneous. As is well known, uncontrolled passivation phenomena affects the lithium electrode and thus the 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 [132,136]. 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 S5 was examined as this composition was found to be optimal in ionic conductivity point of view.

Fig. 7 displays the variation of interfacial resistance "R_i" as a function of time for the composite polymer electrolytes containing two different lithium salts, namely LiClO$_4$ and LiPF$_6$. It is observed from the figure that the polymer electrolyte containing LiClO$_4$ as salt is more suitable when lithium metal was used as anode. On the other hand, the film with LiPF$_6$ as salt exhibits a little higher interfacial resistance values. 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 according to the storage time [137,138]. An important reason for the increase in "R_i" is supposed to be the formation of fluorine compound on lithium surface [135–138]. Also the PVdF-HFP copolymer reacts with lithium at ambient and elevated temperatures. The growth of interfacial resistance does
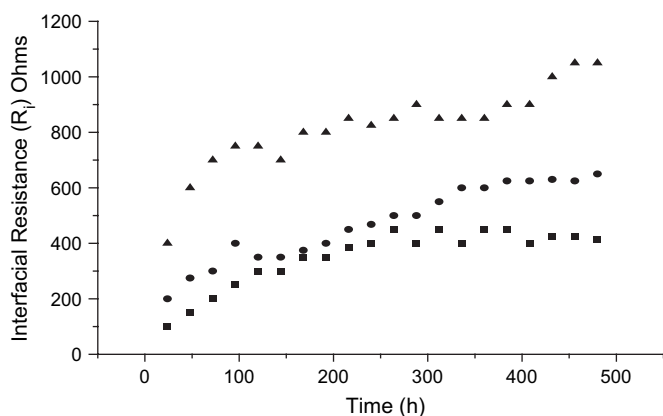
not follow a regular trend for all the samples studied. After 200 h the resistance values remain unchanged. This may be attributed by assuming that the morphology of the passivation films changes with time to finally acquire a non-compact, possibly porous structure [16]. Furthermore it is quite obvious from the figure that the interfacial resistance of the polymer host has considerably been reduced upon the incorporation of the inert filler (lower than filler-free membrane). According to Kumar et al. [62] nanosize inert fillers are more compatible than the fillers with micron size. As depicted in Fig. 8, 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 [62]. 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 passive ceramic phase was introduced into the polymer matrix.

3.4. Transference number

In order to substantiate the conductivity results further, we have measured the Li$^+$ transference number, t_{Li^+}, for all the samples and are displayed in Table 4. This table reports the results in terms of numerical values of t_{Li^+}. The transference number values may equally be affected by the interfacial properties with lithium metal anode also [139]. An apparent increase in the transference number, t_{Li^+} (Table 1), is observed when passing from the filler-free to the filler incorporated composite electrolytes. This further supports the ionic conductivity results.

Fig. 7. Variation of interfacial resistance 'R_i' as a function of time for the symmetric cells stored at 60 °C. (▲) PVdF-HFP–LiPF$_6$; (●) PVdF-HFP–AlO[OH]$_n$–LiPF$_6$; (■) PVdF-HFP–AlO[OH]$_n$–LiClO$_4$.
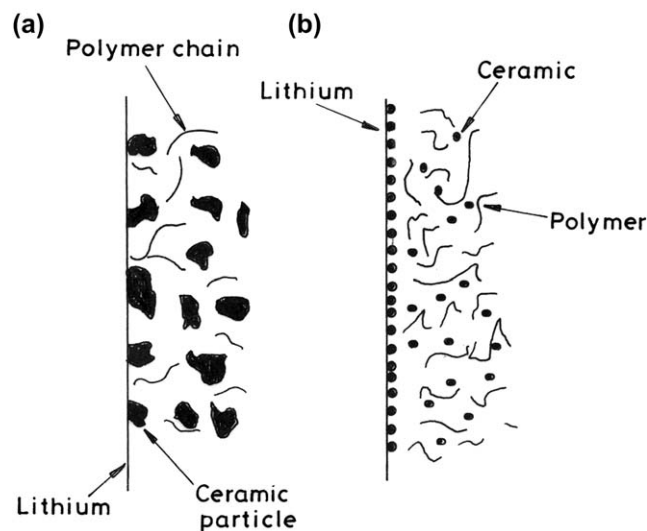

Fig. 8. Schematic representation of polymer host, nano and micron sized inorganic filler in the polymer host. Particles of (a) micron sized (b) nanosized [62].
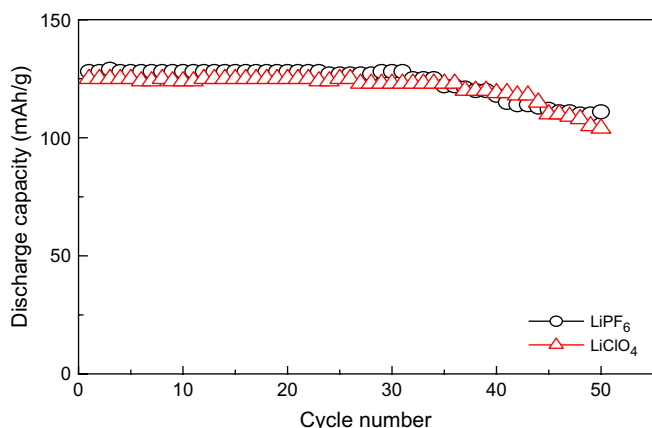
Fig. 9. Cycling behavior of $LiCr_{0.01}Mn_{1.99}O_4$/CPE/Li cells at 60 °C. ■ $LiCr_{0.01}Mn_{1.99}O_4$/PVdF-HFP + AlO[OH]$_n$ 10% + LiPF$_6$/Li.; ● $LiCr_{0.01}Mn_{1.99}O_4$/PVdF-HFP + AlO[OH]$_n$ 10% + LiClO$_4$/Li.

3.5. Charge–discharge studies

Fig. 9 demonstrates the charge–discharge behavior of $LiCr_{0.01}Mn_{1.99}O_4$/PVdF-HFP + AlO[OH]$_n$ 10% + LiPF$_6$/Li and $LiMn_2O_4$/PVdF-HFP + AlO[OH]$_n$ 10% + LiPF$_6$/Li cells at 60 °C. In the present study, the sample S5 has been employed as it was found to be optimal in ionic conductivity and from compatibility point of view. The lower and upper cut-off voltage of the cell was fixed as 2.8 and 4.2 V, respectively, for the fear of decomposition of the electrolyte. The cells were cycled at 0.1C rate. The polymer cell composed of $LiCr_{0.01}Mn_{1.99}O_4$/PVdF-HFP + AlO[OH]$_n$ 10% + LiPF$_6$/Li and $LiCr_{0.01}Mn_{1.99}O_4$/PVdF-HFP + AlO[OH]$_n$ 10% + LiPF$_6$/Li delivered an initial capacity of 128 and 125 mA h g^{-1} and their fade in capacity of the cells is 0.32 and 0.36 mA h g^{-1}, respectively. The cell which possess LiPF$_6$ salt undergoes fade in capacity even after 25 cycles and is attributed to high interfacial resistance of the system, Li/PVdF-HFP + AlO[OH]$_n$ 10% + LiPF$_6$/Li as depicted in Fig. 4. A similar observation has been reported for PEO–LiBF$_4$–BaTiO$_3$ systems by Yamamoto et al. [125]. In addition to that, the 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, $LiMn_2O_4$, when operated at higher temperature especially above 50 °C [140–143].

4. Conclusions

Based on the literature available, so far, much studies have been devoted on the development of poly(ethylene oxide)-based composite electrolytes. Only a very few literatures are available on other composite polymer electrolytes. In the present study, the PVdF-HFP composite polymer electrolytes incorporated with AlO[OH]$_n$ as an inert filler with two different lithium salts namely, LiPF$_6$ and LiClO$_4$ have been 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 but also provides

better interfacial property towards lithium metal anode. The cycling behavior of the $LiCr_{0.01}Mn_{1.99}O_4$/CPE/Li cells shows convincing results at elevated temperature and may be employed as a separator for lithium polymer batteries for hybrid electric vehicle applications.

Acknowledgements

References

[1] Scrosati B. Applications of electroactive polymers. London: Chapman and Hall; 1993.
[2] MacCallum JR, Vincent CA, editors. Polymer electrolyte reviews 1 & 2. London: Elsevier; 1987 & 1989.
[3] Gray FM. Solid polymer electrolytes – fundamental and technological applications. London, New York: VCH; 1991.
[4] Armand MB, Chabagno JM, Duclot M. Extended. Abstracts, second international meeting on solid electrolytes, St. Andrews, Scotland; 20–22 Sep., 1978.
[5] Gray FM. Polymer electrolytes, RSC materials monographs. Cambridge: The Royal Society of Chemistry; 1997.
[6] Armand MB, Chabagno JM, Duclot M. In: Vashista P, Mundy JN, Shenoy GK, editors. Fast ion transport in solids. Amsterdam: Elsevier; 1979. p. 131.
[7] Fenton DE, Parker JM, Wright PV. Polymer 1973;14:589.
[8] Gray FM, MacCallum JR, Vincent CA. Solid State Ionics 1986;18 & 19: 282–6.
[9] Gorecki W, Andreani R, Bertheir C, Armand M, Malli M, Roose J, et al. Solid State Ionics 1986;18 & 19:295–9.
[10] Kelly IE, Owen JR, Steele BCH. J Power Sources 1985;14:13–21.
[11] Moulin JF, Damman P, Dosiere M. Polymer 1999;40:171–81.
[12] Wang ZX, Huang BY, Huang H, Chen LQ, Xue RJ, Wang FS. Electrochim Acta 1996;41:1443–6.
[13] Abraham KM, Alamgir M. J Electrochem Soc 1990;137:1657.
[14] Hong H, Liquan C, Xuejie H, Rongjian X. Electrochim Acta 1992;37: 1671–3.
[15] Iijima T, Toyoguchi Y, Eda N. (Japanese) Denki Kagaku 1985;53:619.
[16] Appetecchi GB, Croce F, Scrosati B. Electrochim Acta 1995;40:991–7.
[17] Feuillade G, Perche Ph. J Appl Electrochem 1975;5:63.
[18] Zhou YF, Xie S, Ge XW, Chen CH, Amine K. J Appl Electrochem 2004;34:1119.
[19] Mary Sukeshini A, Nishimoto A, Watanabe M. Solid State Ionics 1996;86–88:385–93.
[20] Alamgir M, Abraham KM. J Electrochem Soc 1993;140:L96.
[21] Manuel Stephan A, Karan RT, Renganathan NG, Pitchumani S, Muniyandi N, Ramamoorthy P. J Power Sources 1999;81–82:752–9.
[22] Manuel Stephan A, Kumar TP, Karan RT, Renganathan NG, Pitchumani S, Shrisudersan J, et al. Solid State Ionics 2000;130:123–32.
[23] Manuel Stephan A, Kumar TP, Karan RT, Renganathan NG, Pitchumani S, Muniyandi N. J Power Sources 2000;89:80–7.
[24] Misra R, Rao KJ. Solid State Ionics 1998;106:113–27.
[25] Li X, Hsu SL. J Polym Sci Polym Phys 1984;22:1331.
[26] Choe HS, Giaccai J, Alamgir M, Abraham KM. Electrochim Acta 1995;40:2289–93.
[27] Capiglia C, Saito Y, Kataoka H, Kodama T, Quartarone E, Mustarelli P. Solid State Ionics 2000;131:291–9.
[28] Manuel Stephan A, Gopukumar S, Renganathan NG, Anbu Kulandainathan M. Eur Polym J 2005;41:15–21.
[29] Saikia D, Kumar A. Electrochim Acta 2004;49:2581–9.

[30] Quartarone E, Brusa M, Mustarelli P, Tomasi C, Magistris A. Electro-chim Acta 1998;44:677–81.
[31] Tarascon JM, Gozdz AZ, Schmutz C, Shokoohi F, Warren PC. Solid State Ionics 1996;86–88:49–54.
[32] Saito Y, Kataoka H, Manuel Stephan A. Macromolecules 2001;34:6955–7.
[33] Manuel Stephan A, Renganathan NG, Gopukumar S, Dale-Teeter. Mater Chem Phys 2004;85:6–11.
[34] Manuel Stephan A, Dale-Teeters. Electrochim Acta 2003;48:2143–8.
[35] Saito Y, Manuel Stephan A, Kataoka H. Solid State Ionics 2003;160:149–53.
[36] Manuel Stephan A, Saito Y. Solid State Ionics 2002;148:475–81.
[37] Song JY, Wang YY, Wan CC. J Electrochem Soc 2000;147:3219.
[38] Croce F, Appetecchi GB, Perci L, Scrosati B. Nature 1998;394:456–8.
[39] Appetecchi GB, Croce F, Persi L, Ronci F, Scrosati B. J Electrochem Soc 2000;147:4448.
[40] Bronstein LM, Karlinsey RL, Ritter K, Joo CG, Stein B, Zw JW. J Mater Chem 2004;14:1812.
[41] Itoh T, Miyamura Y, Iohikawa Y, Uno T, Kubo M, Yamamoto O. J Power Sources 2003;119–121:403–8.
[42] Kaarup SS, West K, Christiansen Zachau B. Solid State Ionics 1980;28–30:375–80.
[43] Wieczorek W. Mater Sci Eng B 1992;15:108.
[44] Capuoano F, Croce F, Scrosati B. J Electrochem Soc 1991;138:1918.
[45] Appetecchi GB, Croce F, Persi L, Ronci F, Scrosati B. Electrochim Acta 2000;45:1481–90.
[46] Kumar B, Fellner JP. J Power Sources 2003;123:132–8.
[47] Miyake N, Wainright JS, Savinell RF. J Electrochem Soc 2001;148:A898.
[48] Adjemian KT, Lee SJ, Srinivasan S, Benziger J, Bocarsly AB. J Electrochem Soc 2002;149:A256.
[49] Watanabe M, Uchida H, Seki Y, Emori M, Stonehart P. J Electrochem Soc 1996;143:3847.
[50] Weston JE, Steele BCH. Solid State Ionics 1982;7:75–9.
[51] Almond DP, West AR. Solid State Ionics 1986;18 & 19:1105–9.
[52] Wieczorek W. Solid State Ionics 1992;53–56:1064–70.
[53] Wieczorek W, Such K, Wycislik H, Plocharski J. Solid State Ionics 1989;36:255–7.
[54] Salomon M, Xu M, Eyring EM, Petrucci S. J Phys Chem 1994;98:8234.
[55] Wieczorek W, Such K, Chung SH, Stevens JR. J Phys Chem 1994;98:9047.
[56] Molnar A, Eisenberg A. Macromolecules 1992;25:5774.
[57] Chandra A, Srivastava PC, Chandra S. J Mater Sci 1995;30:3633.
[58] Li J, Khan MI. Macromolecules 1993;26:4544.
[59] Zalewska A, Wieczorek W, Steven JR. J Phys Chem 1996;100:11382.
[60] Wieczorek W, Zalewska A, Raducha D, Florjanczyk Z, Stevens JR. J Phys Chem 1998;102:352.
[61] Panero S, Scrosati B, Greenbaum SG. Electrochim Acta 1992;37:1533–9.
[62] Kumar B, Scanlon LG. J Power Sources 1994;52:261.
[63] Capiglia C, Mustarelli P, Quartarone E, Tomasi C, Magistris A. Solid State Ionics 1999;118:73–9.
[64] Liu Y, Lee JY, Hong L. J Power Sources 2004;129:303–13.
[65] Kim JW, Ji KS, Lee JP, Park JW. J Power Sources 2003;119–121:415–21.
[66] Krawiec W, Scanlon Jr LG, Fellner JP, Vaia RA, Vasudevan S, Giannelis EP. J Power Sources 1995;54:310–5.
[67] Borghini MC, Mastragonstino M, Passerini S, Scrosati B. J Electrochem Soc 1995;142:2118.
[68] Golodnitsky D, Ardel G, Strauss E, Peled E, Lareach Y, Rosenberg Y. J Electrochem Soc 1997;144:3484.
[69] Wieczorek W, Rachuda D, Zalewska A, Stevens JR. J Phys Chem B 1998;102:8725.
[70] Wieczorek W, Lipka P, Zukowska G, Wycislik H. J Phys Chem B 1998;102:6968.
[71] Mustarelli P, Quartarone E, Tomasi C, Magistris A. Solid State Ionics 2000;135:81–6.
[72] Kim YW, Lee W, Choi BK. Electrochim Acta 2000;45:1473–7.
[73] Sun HY, Takeda Y, Imanishi N, Yamamoto O, Sohn HS. J Electrochem Soc 2000;147:2462.
[74] Qian X, Gu N, Cheng Z, Yang X, Wang E, Dong S. Electrochim Acta 2001;46:1829–36.
[75] Kumar B, Scanlon L, Marsh R, Mason R, Higgins R, Baldwin R. Electrochim Acta 2001;46:1515–21.
[76] Morita M, Fujisaki T, Yoshimoto N, Ishikawa M. Electrochim Acta 2001;46:1565–9.
[77] Bloise AC, Tambelli CC, Franco RWA, Donoso JP, Magon CJ, Souza MF, et al. Electrochim Acta 2001;46:1571–9.
[78] Tambelli CC, Bloise AC, Rosario AV, Pereira EC, Magon CJ, Donoso JP. Electrochim Acta 2002;47:1677–82.
[79] Chung SH, Wang Y, Persi L, Croce F, Greenbaum SG, Scrosati B, et al. J Power Sources 2001;97–98:644–8.
[80] Kumar B, Rodrigues SJ. J Electrochem Soc 2001;148:A1336.
[81] Kumar B, Scanlon LG. Solid State Ionics 1999;124:239–54.
[82] Kumar B, Rodrigues SJ, Scanlon LG. J Electrochem Soc 2001;148:A1191.
[83] Munichandraiah N, Scanlon LG, Marsh RA, Kumar B, Sircar AK. J Appl Electrochem 1995;25:857.
[84] Wieczorek W, Chung SH, Stevens JR. J Polym Sci Polym Phys 1996;34:2911.
[85] Kasemagi H, Klinterberg M, Aabloo A, Thomas JO. J Mater Chem 2001;11:3191.
[86] Croce F, Persi L, Scrosati B, Serraino-Fiory F, Plichta E, Hendrikson MA. Electrochim Acta 2001;46:2457–61.
[87] Jayathilaka PARD, Dissnayake MAKL, Abinsson I, Mellander BE. Electrochim Acta 2002;47:3257–68.
[88] Dissanayake MAKL, Jayathilaka PARD, Bokalawala RSP, Albinsson I, Mellander BE. J Power Sources 2003;119–121:409–14.
[89] Choi BK, Shin KH. Solid State Ionics 1996;86–88:303–6.
[90] Dai Y, Wang Y, Greenbaum SG, Bajue SA, Golodnitsky D, Ardel G, et al. Electrochim Acta 1998;43:1557–66.
[91] Wieczorek K, Zalewska A, Raducha D, Florjanczyk Z, Stevens JR, Ferry A, et al. Macromolecules 1996;29:143–55.
[92] Wieczorek K, Steven JR, Florjanczyk Z. Solid State Ionics 1996;85:67–72.
[93] Stevens JR, Wieczorek W. Ionically. Can J Chem 1994;74:2106.
[94] Appetecchi GB, Croce F, Doutzenberg G, Mastragostino M, Ronci F, Scrosati B, et al. J Electrochem Soc 1998;145:4126.
[95] Li Q, Sun HY, Takeda Y, Imanishi N, Yang J, Yamamoto O. J Power Sources 2001;94:201–5.
[96] Kumar B, Scanlon LG, Spry RJ. J Power Sources 2001;96:337–45.
[97] Sun HY, Sohn HJ, Yamamoto O, Takeda Y, Imanishi N. J Electrochem Soc 1999;148:1672.
[98] Golodnitsky D, Ardel G, Peled E. Solid State Ionics 2002;147:141–55.
[99] Scrosati B, Croce F, Persi L. J Electrochem Soc 2000;147:1718.
[100] Croce F, Curini R, Martinelli A, Persi L, Ronci F, Scrosati B. J Phys Chem B 1999;103:10632.
[101] Shin JH, Passerini S. J Electrochem Soc 2004;151:A238.
[102] Wang C, Zhang XW, Appleby AJ. J Electrochem Soc 2005;152:A205.
[103] Ji KS, Moon HS, Kim JW, Park JW. J Power Sources 2003;117:124–30.
[104] Chen-Yang YW, Chen HC, Lin FC, Chen CC. Solid State Ionics 2002;150:327–35.
[105] Wang Z, Huang H, Chen L. Electrochem Solid State Lett 2003;6:E40.
[106] Wang ZX, Gao WD, Chen LQ, Mo YJ, Huang XJ. J Electrochem Soc 2002;149:E148.
[107] Chen HW, Chang FC. J Polym Sci Part B Polym Phys 2001;39:2407.
[108] Forsyth M, Sun JZ, MacFarlane DR, Hill AJ. J Polym Sci Part B Polym Phys 2000;38:341.
[109] Best AS, Adebahr J, Jacobsson P, MacFarlane DR, Forsyth M. Macromolecules 2001;34:4569.
[110] Itoh I, Ichikawa Y, Miyamura Y, Uno T, Kubo M, Yamamoto O. Solid State Ionics 2002;150:337–45.
[111] Kim HS, Kum KS, Cho II W, Woncho B, Rhee WH. J Power Sources 2003;124:221–4.
[112] Joykumar Singh Th, Bhat SV. J Power Sources 2004;129:280–7.
[113] Di Noto V, Zago V. J Electrochem Soc 2004;151:A216.

[114] Di Noto V, Zago V, Pace G, Fauri M. J Electrochem Soc 2004; 151:A224.

[115] Singhal RS, Michel DC, Martin JD, Khan SA, Fedkiw PS. J Power Sources 2004;128:247–55.

[116] Chiang CY, Jaipal Reddy M, Peter P, Chu. Solid State Ionics 2005; 175:631–5.

[117] Marcinek M, Ciosek M, Ukowska GZ, Wieczorek W, Jeffrey KR, Stevens JR. Solid State Ionics 2005;176:367–76.

[118] Selvaggi A, Croce F, Scrosati B. J Power Sources 1990;32:389–96.

[119] Wieczorek W. Electrochim Acta 1995;40:2251–8.

[120] Croce F, Persi L, Ronci F, Scrosati B. Solid State Ionics 2000;135: 47–52.

[121] Quartarone E, Mustarelli P, Magistris A. Solid State Ionics 1998;110: 1–14.

[122] Croce F, Epifanio AD, Hassoun J, Reale P, Scrosati B. J Power Sources 2003;119–121:399–402.

[123] Appetecchi GB, Croce F, Mastragastino M, Scrosati B, Soavi F, Zanelli A. J Electrochem Soc 1998;145:4133.

[124] Mastragostino M, Soavi F, Zanelli A. J Power Sources 1999;81–82: 729–33.

[125] Li Q, Takeda Y, Imanish N, Yang J, Sun JY, Yamamoto O. J Power Sources 2001;97–98:795–7.

[126] Li Q, Imanishi N, Hirano A, Takeda Y, Yamamoto O. J Power Sources 2002;110:38–45.

[127] Li Q, Itoh T, Imanishi N, Hirano A, Takeda Y, Yamamoto O. Solid State Ionics 2003;159:97–109.

[128] Appetecchi GB, Hassoun J, Scrosati B, Croce F, Cassel F, Salomon M. J Power Sources 2003;124:246–53.

[129] Jiang G, Maeda S, Yang H, Saito Y, Tanase S, Sakai T. J Power Sources 2005;141:143–8.

[130] Persi L, Croce F, Scrosati B, Plichta E, Hendrickson MA. J Electrochem Soc 2002;149:A212.

[131] Panero S, Satothi D, Epifano AD, Scrosati B. J Electrochem Soc 2002; 149:A414.

[132] Croce F, Flory FS, Persi L, Scrosati B. Electrochem Solid State Lett 2001;4:A121.

[133] Scrosati B, Croce F, Panero S. J Power Sources 2001;100:93–100.

[134] Immanuel Selvaraj I, Chaklanobis S, Chandrasekhar V. J Electrochem Soc 1995;142:366.

[135] Fauteax D. J Electrochem Soc Proc 1994;94–28:379–84.

[136] Kuratomi J, Iguchi T, Bando T, Aihara Y, Ono T, Kuwana K. J Power Sources 2001;97–98:801–3.

[137] Kanamura K, Tamura H, Shiraishi S, Takehara Z. J Electrochem Soc 1995;142:340–7.

[138] Ismail I, Noda A, Nishimoto A, Watanabe M. Electrochim Acta 2001; 46:1595–603.

[139] Evans J, Vincent CA, Bruce PG. Polymer 1987;28:2325–8.

[140] Fey GTK, Lu CZ, Prem Kumar T. J Power Sources 2003;115:332–45.

[141] Jiang DH, Shin JY, Oh SM. J Electrochem Soc 1996;143:2204–11.

[142] Xia Y, Zhou Y, Yoshio M. J Electrochem Soc 1997;144:2593–600.

[143] Gummow RJ, de Kock A, Thackeray MM. Solid State Ionics 1994;69: 59–64.