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## TOPICAL REVIEW

# Solid polymer electrolytes: materials designing and all-solid-state battery applications: an overview

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## Abstract

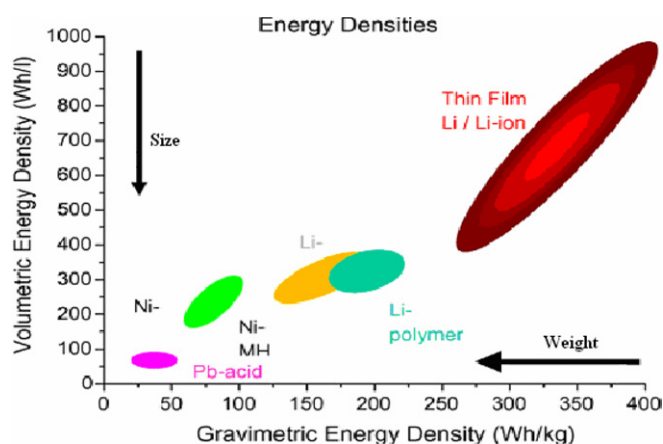
Polymer electrolytes are promising materials for electrochemical device applications, namely, high energy density rechargeable batteries, fuel cells, supercapacitors, electrochromic displays, etc. The area of polymer electrolytes has gone through various developmental stages, i.e. from dry solid polymer electrolyte (SPE) systems to plasticized, gels, rubbery to micro/nano-composite polymer electrolytes. The polymer gel electrolytes, incorporating organic solvents, exhibit room temperature conductivity as high as  $\sim 10^{-3} \text{ S cm}^{-1}$ , while dry SPEs still suffer from poor ionic conductivity lower than  $10^{-5} \text{ S cm}^{-1}$ . Several approaches have been adopted to enhance the room temperature conductivity in the vicinity of  $10^{-4} \text{ S cm}^{-1}$  as well as to improve the mechanical stability and interfacial activity of SPEs. In this review, the criteria of an ideal polymer electrolyte for electrochemical device applications have been discussed in brief along with presenting an overall glimpse of the progress made in polymer electrolyte materials designing, their broad classification and the recent advancements made in this branch of materials science. The characteristic advantages of employing polymer electrolyte membranes in all-solid-state battery applications have also been discussed.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

Looking at the variety of energy requirements, major research efforts have presently been focused on developing materials for rechargeable batteries. In the recent past,  $\text{Li}^+$ -ion based batteries have outperformed the other battery systems, namely, Pb-acid, Ni-Cd, Ni-MH, etc and accounted for  $\sim 70\%$  of the worldwide sales [1]. This can be clearly visualized in figure 1 illustrating different battery systems in terms of their volumetric energy density ( $\text{Wh l}^{-1}$ ) and gravimetric energy density ( $\text{Wh kg}^{-1}$ ) as well as the relative weights and sizes [2]. Lithium battery systems look very promising as far as their possibilities of performance enhancements and scaling up to larger sizes are concerned [3]. During the late 1990s, the

majority of commercial lithium batteries were fabricated with  $\text{Li}^+$ -salt solution as electrolytes immobilized in a variety of polymer matrices. This has ultimately led to the development of plastic Li-ion (PLiON) batteries in which hybrid polymer electrolytes (HPEs), consisting of a polymer matrix swollen with  $\text{Li}^+$ -salt solution, were used [4, 5]. The motivation behind using lithium salt as the electrolyte is based on the fact that lithium, being the lightest of all metals, when used as an anode in contact with  $\text{Li}^+$ -salt electrolytes, provides a wider electropositive potential window. Hence, the batteries based on  $\text{Li/Li}^+$ -salt can facilitate a very high energy density. In fact, these batteries are being manufactured presently on a large scale and used as rechargeable power packs in a wide variety of digital appliances, namely, phones, PCs.



**Figure 1.** Comparison of energy densities of different battery systems.

However, lithium metal and most of the lithium salts are highly reactive, especially in open humid ambience; hence, handling of these materials needs special care. Furthermore, it has usually been observed that at the lithium metal anode/electrolyte interface, an insulating passivation layer is formed. This, in turn, results in an increase in the internal resistance of the batteries [6]. Other common drawbacks, usually associated with the batteries based on liquid/aqueous electrolytes, namely, limited temperature range of operation, corrosion of the electrodes, problem of hermetic sealing, growth of metal dendrites from anode to cathode through the electrolyte medium during multiple charge–discharge cyclings leading eventually to internal short circuiting of the batteries, etc, may also be encountered which may lead to an early failure of the battery system. If these problems could be tackled appropriately, lithium-salt solution batteries may achieve complete commercial success. Anyway, to eliminate and/or minimize the shortcomings of liquid/aqueous electrolytes, the way out suggested is to replace them by some suitable solid electrolytes. Solid electrolytes are a new class of solid state ionic materials, also termed as ‘superionic solids’ or ‘fast ion conductors’, which exhibit an exceptionally high ionic conduction at room temperature close to that in the range of liquid/aqueous electrolytes. In fact, these solid state ionic materials attracted tremendous technological attention worldwide after the discovery of two groups of solid electrolyte systems:  $M\text{Ag}_4\text{I}_5$  ( $M = \text{Rb}, \text{K}, \text{NH}_4$ ) and  $\text{Na-}\beta$ -alumina in 1967 exhibiting exceptionally high  $\text{Ag}^+$ - and  $\text{Na}^+$ -ion conduction ( $\sim 10^{-1} \text{ S cm}^{-1}$ ) at room/moderate-high temperature, respectively [7, 8]. A large number of such materials, involving a variety of ions, namely,  $\text{H}^+$ ,  $\text{Ag}^+$ ,  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{F}^-$ ,  $\text{O}^{2-}$ , etc as mobile species and broadly grouped into different phases such as polycrystalline/crystalline, glassy/amorphous, composite, ceramic and polymeric, have been reported since then in the last four decades [9–16]. It needs a special mention that in the last 25 years, remarkable achievements have been recorded specially in the area of polymeric electrolyte materials. Polymer electrolytes show tremendous technological potentials to develop a wide variety of thin/flexible all-solid-state electrochemical

devices. This paper is devoted to mainly reviewing the progress made in the field of polymer electrolytes, namely, their materials designing. However, a brief discussion on the various techniques commonly employed to characterize the materials/ion transport behaviour is given along with the applicability of these materials in a wide variety of solid state electrochemical devices.

A polymer electrolyte is an ion conducting membrane with moderate-high ionic conductivity ( $\leq 10^{-4} \text{ S cm}^{-1}$ ) at room temperature. The first ion conducting polymer: poly(ethylene oxide) (PEO) complexed/dissolved with alkali metal salt, was discovered in 1973 [17]. This was followed by the practical demonstration of a first all-solid-state film battery, based on poly(ethylene oxide) (PEO)–Li-salt complexed solid polymer electrolyte (SPE) membrane in 1979 [18]. These novel discoveries inspired scientists/researchers both from academic institutions and industrial sectors to intensively pursue research in this area of materials science. Consequently, a large number of polymer electrolyte materials involving different kinds of transporting ions, namely,  $\text{H}^+$ ,  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ag}^+$ ,  $\text{Mg}^{2+}$  etc, have been reported since then. As already mentioned, the polymer electrolytes show great technological promise of fabricating a variety of all-solid-state electrochemical power sources, namely, mini/macro primary/secondary batteries, fuel cells, supercapacitors, etc; hence, the applications of these materials in electrochemical devices are being explored extensively at different R&D laboratories as well as at commercial scales. Various theoretical approaches have been adopted to understand the mechanism of ion transport in the polymer electrolyte materials as well as the physical/ chemical processes occurring at the polymer electrolyte/electrode interfaces [13–16, 19, 20]. A number of books/monographs/research papers have been published which deal with materials designing aspects as well as a variety of techniques usually employed during material/structure/thermal/ion transport characterization studies in the polymer electrolyte systems [13–16].

It is worth pointing out that there existed a preconceived notion that fast ion transport in SPEs was predominantly due to the existence of amorphous phase in the polymeric host. Accordingly, it was thought that the larger the degree of amorphosity, the higher would be the ionic conduction in SPEs [21]. Consequently, major research investigations in the past were directed towards creating large and stable amorphous phase in the polymeric hosts of low glass transition temperatures ( $T_g$ ), in order to have a good flexibility of the polymer chains supporting faster ion transport. Nevertheless, this old concept has recently been overturned by Gadjourava and co-workers [22] who have experimentally demonstrated that the static and ordered crystalline environments in the polymer host could also support high ion conduction in SPEs, as discussed below in section 4.

For the purpose of reliable all-solid-state electrochemical device applications, the polymer electrolyte materials should inherently possess the following properties [13, 19, 23].

- Ionic conductivity  $\sigma \geq 10^{-4} \text{ S cm}^{-1}$  at room temperature. This enables us to achieve a performance level close to that of the liquid electrolyte-based devices.

- *Ionic transference number*  $t_{\text{ion}} \sim 1$ . This is not only absolutely desirable but the polymer electrolyte should preferably be a single-ion (namely, cation) conducting system. For battery applications, the polymer electrolyte should perfectly act as an ion conducting medium and as an electronic separator. However, the majority of the polymer electrolytes reported so far, although exhibiting negligible electronic conduction, show the cationic transference number  $\leq 0.5$ . This is indicative of the fact that at the maximum only half of the potential transporting ions move in the polymer electrolytes [24–26]. Obviously, the larger the cationic transference number (close to unity), the smaller would be the concentration polarization effect in the electrolytes during charge–discharge steps, and hence, the higher would be the power density achievable in the battery [23].
- *High chemical, thermal and electrochemical stabilities.* The solid state electrochemical devices are fabricated by sandwiching the polymer electrolyte membranes between appropriate cathode and anode materials. In order to avoid undesired chemical reactions proceeding at the electrode/electrolyte interfaces, the polymer electrolytes should possess a high chemical stability. Furthermore, to have a wider temperature range during battery operations, polymer electrolytes should be thermally stable. They should also have a good electrochemical stability domain extending from 0 V to as high as 4–5 V.
- *High mechanical strength.* The polymer electrolytes should be mechanically stable, so that the scaling up and large-scale manufacturing of the devices could be realized.
- *Compatibility with the electrode materials.* Finally, the polymer electrolytes should be compatible with the variety of electrode materials. Hence, adequate and possibly non-toxic anode/cathode materials should be identified. Presently, major effort has been diverted to exploring such active electrode materials which would improve the performance level of the electrochemical devices.

Presently, large numbers of rechargeable batteries based on  $\text{Li}^+$  ion conducting polymer electrolytes membranes are being manufactured on a commercial scale. It has also been projected that Li-batteries would not only provide very high specific energy/specific power but would be safe in operation with flexible packaging in a variety of shapes/sizes and would be available at a relatively lower cost. Hence,  $\text{Li}^+$ -ion polymer electrolyte show great promise as future energy materials in the development of power sources for a variety of small/large scale requirements including electric vehicle (EV) operations. Some key features for  $\text{Li}^+$ -ion conducting polymer electrolyte batteries projected for EVs ( $\sim 2010$ ) are listed in table 1 [27].

In the following sections, the progress made in designing polymer electrolyte materials for the purpose of battery applications has been reviewed. In view of recent advancements in synthesizing a wide variety of new solid state ionic polymeric electrolyte materials, remarkable achievements are expected especially in the area of rechargeable battery technology. As already mentioned, SPEs offer great promise of fabricating flexible, light-weighted high/low energy density all-solid-state primary/secondary

**Table 1.** Criteria projected by the United States Advanced Battery Consortium (USABC) for the batteries to be used in EVs (year  $\sim 2010$ ).

Power density ( $\text{W l}^{-1}$ )	600
Specific power ( $\text{W kg}^{-1}$ )	400
Energy density <sup>a</sup> ( $\text{Wh l}^{-1}$ )	300
Specific density <sup>a</sup> ( $\text{Wh kg}^{-1}$ )	200
Life: shelf (yr):	10
cycles	1000
Price ( $\$/\text{kWh}$ )	<100
Normal recharge time (h)	<3–6
Operating environment ( $^{\circ}\text{C}$ )	–40 to 85

<sup>a</sup>C/3 discharge rate.

batteries with reasonable long shelf-life and wider operational temperatures. This paper gives an overall glimpse of the developments recorded during the last 2–3 decades in this exciting area of polymeric electrolytes especially in materials synthesis and in their broad classifications. The techniques widely employed to cast polymer electrolyte membranes, to characterize the material/ion-transport properties and to fabricate all-solid-batteries are also discussed briefly along with some recent results on a few newly synthesized polymer electrolyte membranes investigated at the present laboratory. Finally, this paper concludes with a brief mention of the recent developments made in designing some novel SPE materials.

## 2. Polymer electrolyte materials designing and broad classification

After the discovery of the first ion conducting polymeric material in 1973 [17], the prime objective has been to synthesize polymer electrolytes with room temperature ionic conductivity close to that of liquid/aqueous electrolytes. The materials designing in the development of polymer electrolytes has passed through several stages since then. As mentioned, a large number of polymer electrolyte systems, involving a variety of transporting ions, namely,  $\text{H}^+$ ,  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ag}^+$ , etc, are now known today. However, in order that polymer electrolyte materials exhibit reasonably good electrolytic properties essential for electrochemical device applications, the polymer hosts should possess some basic characteristic features. Table 2 lists a few selected polymers, their chemical formulae and thermal characteristics, namely, glass transition ( $T_g$ )/melting point ( $T_m$ ) temperatures, which are commonly employed as hosts for the complex variety of ionic salts and/or synthesis of ion conducting polymers. On the basis of various preparation routes adopted during the film casting as well as on their physical conditions, the polymer electrolyte materials have been divided into following broad categories [28, 29].

- Conventional polymer–salt complex or dry SPE.* Dry SPEs are prepared by complexing/dissolving ionic salts into coordinating polar polymer hosts, namely, poly(ethylene oxide) (PEO), poly(propylene oxide) (PPO), etc [14, 30]. The casting of the film/membrane is done either by the usual solution cast method or by a recently adopted novel hot-press technique. The film casting techniques are discussed briefly in section 3.

**Table 2.** Some selected polymer hosts, their corresponding chemical formulae and  $T_g/T_m$  values.

Polymer host point	Repeat unit	Glass transition temperature $T_g$ ( $^{\circ}\text{C}$ )	Melting $T_m$ ( $^{\circ}\text{C}$ )
Poly(ethylene oxide)	$-(\text{CH}_2\text{CH}_2\text{O})_n-$	-64	65
Poly(propylene oxide)	$-(\text{CH}(\text{-CH}_3)\text{CH}_2\text{O})_n-$	-60	— <sup>a</sup>
Poly(dimethylsiloxane)	$-\text{[SiO}(\text{-CH}_3)_2\text{]}_n-$	-127	-40
Poly(acrylonitrile)	$-(\text{CH}_2\text{CH}(\text{-CN}))_n-$	125	317
Poly(methyl methacrylate)	$-(\text{CH}_2\text{C}(\text{-CH}_3)(\text{-COOCH}_3))_n-$	105	— <sup>a</sup>
Poly(vinyl chloride)	$-(\text{CH}_2\text{CHCl})_n-$	82	— <sup>a</sup>
Poly(vinylidene fluoride)	$-(\text{CH}_2\text{CF}_2)_n-$	-40	171
Poly(vinylidene fluoride-hexafluoropropylene)	$-(\text{CH}_2\text{CF}_2)_n-\text{[CF}_2\text{CF}(\text{CF}_3)]_m-$	-65	135

<sup>a</sup> Amorphous polymer.

- (ii) *Plasticized polymer–salt complex.* They are prepared by adding liquid plasticizers into dry SPEs in such a way that a compromise between solid polymer and liquid electrolyte exists. The magnitude of ambient conductivity gets substantially enhanced by this, but at the cost of deterioration in the mechanical integrity of the film as well as increased corrosive reactivity of polymer electrolyte towards the metal electrode.
- (iii) *Polymer gel electrolyte.* Gel electrolytes are usually obtained by incorporating large amount of organic liquid solvent(s)/liquid plasticizer into the polymer matrix capable of forming stable gel with a polymer host structure [5, 19]. Polymer gel electrolytes also offer high ambient conductivities but suffer from similar disadvantages as mentioned for the plasticized polymer electrolytes.
- (iv) *Rubbery electrolyte.* They are actually ‘polymer-in-salt’ systems, in contrast to ‘salt-in-polymer,’ i.e. the three categories (i)–(iii) mentioned. In rubbery electrolyte, a large amount of salt is mixed with a small amount of polymer, namely, poly(ethylene oxide) (PEO), poly(propylene oxide) (PPO), etc [31, 32]. The glass transition temperature of these materials is usually low to maintain the rubbery state at room temperature which in turn provides high conductivity. However, the complexed/dissolved salts have the tendency to crystallize, hence, hampering their uses in practical electrochemical devices.
- (v) *Composite polymer electrolyte (CPEs).* CPEs are basically analogous to the usual two-phase composite solid electrolyte systems. They are also prepared simply by dispersing a small fraction of micro/nano-size inorganic (ceramic)/organic filler particles into the conventional SPE host [33, 34]. SPEs act as phase I, while filler materials as phase II dispersoid. As a consequence of dispersal, the ionic conductivity, the mechanical stability and the interfacial activity of SPEs usually get enhanced substantially. The size of the filler particles and, hence, their surface area play a significant role in improving these physical properties [35–38].

The phenomenon of ion transport in the above five categories of polymer electrolyte materials could not be understood clearly as yet due to the lack of knowledge of the exact structural property correlations. However, the macroscopic studies on the basic ionic parameters and their temperature variations

provide a wealth of information regarding ion dynamics. On the basis of temperature dependent conductivity studies, it has been observed that these systems usually exhibit two dominant conduction mechanisms [39] which divide these materials further into two separate groups. One group of polymer electrolytes obeys the Vogel–Tamman–Fulcher (VTF) type relationship, expressed by the following equation:

$$\sigma = AT^{-1/2}\exp[-E_a/(T - T_0)],$$

where  $A$  is the pre-exponential factor,  $E_a$  is the activation energy and  $T_0$  is the equilibrium glass transition temperature close to  $T_g$  of the polymer electrolyte material.  $E_a$  can be computed from the non-linear-least-square fit of the data from  $\log \sigma$  versus  $1/T$  plots. The other group follows the usual Arrhenius type equation:

$$\sigma = \sigma_0\exp(-E_a/kT),$$

where the activation energy  $E_a$  can be computed from the linear-least-square fit of the data from  $\log \sigma$  versus  $1/T$  plots. The VTF conductivity versus reciprocal temperature plot is typically non-linear which is indicative of a conductivity mechanism involving ionic hopping motion coupled with the relaxation/breathing and/or segmental motion of polymeric chains. The materials exhibiting linear Arrhenius variations indicate ion transport via a simple hopping mechanism decoupled from the polymer-chain breathing.

A detailed discussion on the above five categories of polymer electrolytes and their materials designing is given below.

### 2.1. Conventional polymer–salt complex or dry SPE

As already pointed out, after the discovery of the first SPE material: a poly(ethylene oxide) (PEO):alkali metal salt complex, in 1973, followed by an experimental demonstration of the first all-solid-state battery based on the PEO:Li<sup>+</sup>-ion polymer electrolyte in 1979, the activity in this area was enhanced tremendously. As a consequence, a wide variety of SPEs have been synthesized in the last nearly three decades. The majority of good dry solid polymeric electrolytes reported so far are based on high molecular weight polymers, namely, poly(ethylene oxide) (PEO) and/or poly(propylene oxide) (PPO) complexed/dissolved with different Li<sup>+</sup>-ion salts [13].



The reason for the preference of PEO/PPO as the polymer host has been mainly due to the fact that they usually form stable dry complexes exhibiting a relatively higher ionic conductivity than other solvating polymers. The sequential oxyethylene group:  $-\text{CH}_2-\text{CH}_2-\text{O}-$  (see table 2), and the polar groups:  $-\text{O}-$ ,  $-\text{H}-$ ,  $-\text{C}-\text{H}-$ , in the polymer chains have the ability to dissolve/complex the ionic salts [13, 14]. The formation of the polymer–salt complex:  $\text{PEO}_n\text{-salt}$  (where  $n$  = number of ether oxygen per mole of salt), is governed by competition between solvation and lattice energies of the polymer and inorganic salt [40]. Low lattice energy of both the polymer and inorganic salt favours an increased stability in the resultant SPE. Higher ionic conductivity is obtained at a lower salt/EO ratio. However, as a general trend, both the conductivity and  $\text{Li}^+$ -ion transference number have been found to decrease as the  $\text{Li}^+$ -salt concentration is increased [41]. The reasons assigned for this decrease have been the hindrance to the motion of polymer chains inhibiting ion transport as well as the formation of ion pairs which in turn results in the reduction in the number of free lithium ions available for conduction [42]. The formation of positively and/or negatively charged ion triplets has also been observed at higher concentrations and temperatures [13]. The ion-pair formation at a high salt concentration could be experimentally verified by NMR studies [43]. In PEO–salt complexes, the ion pairing has been found to set in when the cation:ether-oxygen ratio exceeds 1:8, while the ratio 1:4 leads to the formation of ion aggregates [13]. Consequently, the maximum ionic conductivity obtainable in PEO–salt complexes gets restricted due to an upper permissible limit of the salt concentration in the host polymer. A wide variety of lithium salts:  $\text{LiX}$  (where  $X = \text{I}, \text{Cl}, \text{Br}, \text{ClO}_4, \text{CF}_3\text{SO}_3, \text{BF}_4, \text{AsF}_6$ , etc), can be complexed with PEO to form SPE membranes. The basic structure of SPE membranes involves PEO chains coiled around  $\text{Li}^+$ -ions, separating them from  $X =$  counteranions [44]. This favours the dissolution of  $\text{LiX}$ -salt in the PEO matrix following a solvating mechanism which is approximately akin to that in liquid electrolytes. However, the ion ( $\text{Li}^+$ ) transport in the polymer electrolytes, a consequence of local relaxation as well as segmental motion of the polymer chains, is more favourable in the presence of high degree of amorphosity in the host polymer. PEO generally crystallizes below  $70^\circ\text{C}$  which also approximately corresponds to the melting point of the polymer. Above this temperature, PEO predominantly exists in the amorphous state. Hence, a practically useful conductivity value ( $\geq 10^{-4} \text{ S cm}^{-1}$ ) in the polymer–salt complex:  $\text{PEO}:\text{LiX}$ , is easily achievable in the temperature range  $70\text{--}90^\circ\text{C}$  [13]. Intensive efforts have been made such that a higher degree of amorphous phase of the polymer hosts exists at room temperature. Moreover, there exist possibilities that the anions may also migrate within the polymer electrolyte. This is not desirable, as it would deteriorate the device performance by way of self-discharge as well as possible degradation of the electrode surface. In order to minimize the anion migration, salts containing large organic anions such as lithium bis(trifluoromethylsulfonyl)-imide (LiTFSI) and lithium bis(trifluoromethyl sulfonyl)-methide (LiTFSM) were complexed with PEO [40]. Since

**Table 3.** Some important polymer–salt complexes SPEs and their conductivity values.

Polymer electrolytes	Conductivity ( $\text{S cm}^{-1}$ )	Temperature ( $^\circ\text{C}$ )	Reference
$(\text{PEO})_x\text{-LiClO}_4$	$1 \times 10^{-7}$	27	[51]
$\text{PEO-LiN}(\text{CF}_3\text{SO}_2)_2$	$1 \times 10^{-4}$	Room temperature	[40]
$\text{PEO-LiCF}_3\text{SO}_3$	$1 \times 10^{-9}$	40	[52]
$\text{PEO-LiBF}_4$	$1 \times 10^{-6}$	25	[53]
$\text{MEEP-NaCF}_3\text{SO}_3$	$1 \times 10^{-5}$	25	[54]
$\text{PEO-NH}_4\text{I}$	$1 \times 10^{-5}$	23	[55]
$\text{PEO-NH}_4\text{ClO}_4$	$1 \times 10^{-5}$	30	[56]
$(\text{PEO})_8\text{-Cu}(\text{ClO}_4)_2$	$2 \times 10^{-5}$	25	[57]
$(\text{PPO})_{12}\text{-NaCF}_3\text{SO}_3$	$1 \times 10^{-5}$	45	[58]
$(\text{PVAc})\text{-LiCF}_3\text{SO}_3$	$1 \times 10^{-9}$	40	[59]

the electrons in these anions are highly delocalized, the salts act as plasticizer, hence, resulting in more flexible polymer chains in the polymer electrolytes. The polymer electrolytes, complexed with such salts, contain a high degree of amorphosity supporting high cation transport, hence, giving a higher conductivity value with minimum anion migration [45]. New polymer electrolyte structures, based on the modified PEO main polymer chain with grafted polymers, block copolymers, cross-linked polymer networks, etc have also been attempted [13, 19, 46–49]. This also resulted in polymer electrolytes with a lower degree of crystallinity and a low glass transition temperature  $T_g$ . A detailed discussion of such structural modifications can be found in the literature [13, 48–50]. Table 3 lists some important SPEs along with their conductivity values.

## 2.2. Plasticized polymer–salt complexes

As mentioned, the practically useful conductivity value ( $\geq 10^{-4} \text{ S cm}^{-1}$ ) in PEO-based dry SPEs could be achievable only beyond  $T_m \sim 70^\circ\text{C}$  which also corresponds to semicrystalline–amorphous phase transition temperature of the PEO host polymer. Extensive efforts have been made to bring down this conductivity value around room temperature so that practical devices operating at ambient condition can be realized. One of the most common approaches adopted has been the mixing of a substantial amount of liquid plasticizers, namely, low molecular weight poly(ethylene glycol) (PEG) and/or aprotic organic solvents such as dimethylsulfoxide (DMSO) with the dry SPE matrix. Such an addition not only decreases the degree of crystallinity but also increases the segmental motion of the polymer chain. The mixing of the plasticizers may also support ion dissociation; as a result, a greater number of migrating ions becomes available for charge transport. It has been observed that the room temperature conductivity of the polymer–salt complex:  $\text{PEO-LiCF}_3\text{SO}_3$ , plasticized with poly(ethylene glycol) (PEG), increased many fold with increasing PEG content [60]. This has been attributed to the reduced crystallinity as well as increased free volume. However, since the hydroxyl end group of PEG reacts with lithium metal, the use of such a plasticized polymer–salt complex as electrolyte hampers the

**Table 4.** Some important plasticized polymer–salt complexes and their conductivity values.

Polymer electrolytes	Conductivity (S cm <sup>-1</sup> )	Temperature (°C)	Reference
(PEO) <sub>8</sub> –LiClO <sub>4</sub> (EC:PC, 20 mol%)	1 × 10 <sup>-3</sup>	20	[14]
(PEO) <sub>8</sub> –LiClO <sub>4</sub> (PC, 50 wt%)	8 × 10 <sup>-4</sup>	20	[14]
PEO–LiCF <sub>3</sub> SO <sub>3</sub> plasticized with PEG	~10 <sup>-3</sup>	25	[60]
PEO–LiBF <sub>4</sub> with 12-crown-4	7 × 10 <sup>-4</sup>	Room temperature	[62]

battery operation. To avoid this, attempts have been made to replace the hydroxyl end groups of PEG by methoxy end groups [61]. The crown ethers have also been used as plasticizers to enhance the ionic conductivity of polymer electrolytes. Nagasubramanian and Stefano [62] studied the effect of addition of 12-crown-4 ethers on the conductivity and interfacial kinetics of PEO–LiX ( $X = \text{CF}_3\text{SO}_3, \text{BF}_4, \text{ClO}_4$ ) complexes. The maximum conductivity ( $\sim 7 \times 10^{-4} \text{ S cm}^{-1}$ ) was obtained for the polymer–salt complex: PEO–LiBF<sub>4</sub>, when the 12-crown-4-to-Li ratio was kept as low as 0.003. They also discussed that 12-crown-4-incorporated polymer electrolyte samples yielded a lower charge-transfer resistance when used in an electrochemical cell. Benedict *et al* [63] explored the possibility of using dibutyl phthalate (DBP) as plasticizer in PEO–LiAsF<sub>6</sub> complexes. Some important plasticized polymer–salt electrolytes and their conductivity values are listed in table 4. It has been observed that adding plasticizers results, in general, in conductivity enhancements in SPEs. Nevertheless, this simultaneously leads to some adverse effects. The mechanical integrity of the polymer electrolyte membranes gets seriously deteriorated as well as the reactivity of the electrolytes towards the metal anode increases [64, 65]. Hence, the gain in conductivity is simultaneously accompanied by the loss of solid state configuration as well as lack of compatibility with the electrode. In other words, many of the important intrinsic features of the polymer electrolytes are lost when the liquid plasticizers are added to the polymer–salt complexes; hence, they do not remain much use during their applications in the all-solid-state electrochemical devices. The plasticized SPEs also suffer from problems of low cation transport number which ultimately leads to the usual polarization effect in the battery.

### 2.3. Polymer gel electrolytes

Polymer gel electrolytes are characterized by relatively higher ambient ionic conductivity values as compared with SPEs. They are usually prepared by incorporating a large amount of liquid plasticizer and/or solvent(s) to a SPE matrix. They consist of a polymer network swollen with solvent(s) and, hence, possess both the cohesive properties of solids and the diffusive transport properties of liquids. Due to this dual characteristic, the gel electrolytes have their own importance in a variety of electrochemical device applications. However, the mechanical strength of gel

electrolytes is also poor. By adding components which can be cross-linked and/or thermoset with the gel electrolytes, the mechanical stability can be substantially improved [66]. In 1975, Fenullade and Perche [67] demonstrated the idea of plasticizing polymers with an aprotic solution containing an alkali metal salt. The organic solution of the alkali metal salt remained trapped within the matrix of the polymer and resulted in the formation of gels with a very high ionic conduction close to that of the liquid electrolytes. Since then, polymer gel electrolytes with a number of polymer hosts, namely, poly(ethylene oxide) (PEO) [68], poly(vinylidene fluoride) (PVdF) [69, 70], poly(acrylonitrile) (PAN) [71–73], poly(methyl methacrylate) (PMMA) [74, 75], poly(vinylidene fluoride-hexafluoropropylene) (PVdF-co-HFP) [76, 77], etc have been synthesized which exhibited conductivity values in the range  $\sim 10^{-4}$ – $10^{-3} \text{ S cm}^{-1}$  at ambient temperature. Table 5 lists some important polymer gel electrolytes with their conductivity values. ‘Polymer gel electrolytes’ are alternatively called ‘polymer hybrids’ and ‘gelionics’. Usually, low-evaporation solvents, namely, ethylene carbonate (EC), propylene carbonate (PC), dimethyl formamide (DMF), diethyl carbonate (DEC), dimethyl carbonate (DMC), etc are used as ‘plasticizers’ [19]. In order to form gel electrolytes, the plasticizers should possess some specific properties, listed in table 6. It has been observed that plasticization increases the degree of amorphosity in the polymer host with a single glass transition temperature which may be as low as  $-40^\circ\text{C}$ . This, in turn, increases the ionic mobility within the gel electrolytes and, hence, the overall increase in the ionic conductivity, on account of diffusive transport property in the liquidus phase. However, the presence of liquid plasticizers in excessive amount in gel electrolytes leads to a number of drawbacks commonly faced in liquid/aqueous electrolytes, as pointed out earlier. The other problem encountered, especially when Li<sup>+</sup>-ion conducting gel electrolytes are used in the lithium battery, has been the reactivity of the electrolyte with the lithium metal surface. This, in turn, affects the stability window of the electrolytes [78]. To avoid this problem, especially in lithium ion batteries, intercalation electrodes are used in place of pure lithium metal.

PEO-based gel electrolytes, consisting of EC and/or PC as plasticizers and lithium salts, namely, LiClO<sub>4</sub>, LiCF<sub>3</sub>SO<sub>3</sub>, LiN(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>, etc, formed soft solids with very high room temperature conductivity of  $\sim 10^{-3} \text{ S cm}^{-1}$  [68, 85]. However, the mechanical strength of the gels was found to be poor mainly due to the problem of solubility of PEO in the solvents [68]. Nevertheless, cross-linking of PEO could minimize this problem and, hence, the mechanical stability of the gel electrolyte could be enhanced. Cross-linking of the polymer host can be done by exposing it to a variety of radiation, namely, UV [86], thermal [87], photo [88], electron beam [89], etc which also helps to trap the liquid electrolyte within the polymer host matrix. PAN and PVdF-based polymer gels are the most widely studied polymer gel electrolyte systems. PAN polymer with dispersed salts and plasticizers in molar wt(%) forms homogeneous hybrid electrolyte films. Due to the absence of oxygen atoms in the PAN polymer matrix, a greater dissociation of lithium salts could be expected.

**Table 5.** Some important polymer gel electrolytes and their conductivity values.

Polymer gel electrolytes	Conductivity (S cm <sup>-1</sup> )	Temperature (°C)	Reference
PAN-EC/PC/DMF-LiClO <sub>4</sub>	~4 × 10 <sup>-4</sup>	22	[71]
PMMA-EC/PC-LiClO <sub>4</sub>	~1 × 10 <sup>-3</sup>	25	[74]
PAN-EC/PC-LiClO <sub>4</sub>	~4 × 10 <sup>-3</sup>	25	[79]
PVC-EC/PC-LiClO <sub>4</sub>	~1 × 10 <sup>-3</sup>	25	[79]
PAN-EC/PC-LiCF <sub>3</sub> SO <sub>3</sub>	~1 × 10 <sup>-3</sup>	20	[80]
PAN-EC/DEC-LiClO <sub>4</sub>	~4 × 10 <sup>-3</sup>	Room temperature	[81]
PVdF-EC/PC-LiBF <sub>4</sub>	~6 × 10 <sup>-3</sup>	Room temperature	[81]
PVdF-HFP-EC/DEC-LiN(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub>	~1 × 10 <sup>-3</sup>	Room temperature	[82]
PMMA-EC/PC/γBL-LiCF <sub>3</sub> SO <sub>3</sub>	~1 × 10 <sup>-3</sup>	Room temperature	[83]
PMMA-EC/DMC-LiN(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub>	~1 × 10 <sup>-3</sup>	Room temperature	[84]

**Table 6.** Physical properties of some organic solvents commonly used as plasticizers.

Parameter	Melting point MP (°C)	Boiling point BP (°C)	Density g (cm <sup>-3</sup> )	Dielectric constant, ε	Molecular weight	Solubility (J cm <sup>-3</sup> ) <sup>1/2</sup>
Dimethyl carbonate (DMC)	2.4	90	1.06	3.12	90.08	20.3
Diethyl carbonate (DEC)	-43.0	126	0.9752	2.82	118.13	18.0
γ-butyrolactone (BL)	-43.3	204	1.1284	39.0	86.09	25.8
Propylene carbonate (PC)	-48.8	242	1.2047	66.14	102.09	27.2
Ethylene carbonate (EC)	36.4	248	1.3214	89.78	88.06	30.1

Hence, in PAN-based gel electrolytes complexed with lithium salts, the Li<sup>+</sup>-ion transference number has been observed to be much higher than 0.5 [90]. With lithium salts, namely, LiTFSI and LiTFSM, a transference number as high as 0.7 was achieved. Croce *et al* [91] examined the electrochemical properties of PAN-based gel electrolytes containing different lithium salts such as LiClO<sub>4</sub>, LiAsF<sub>6</sub> and Li(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>. They also observed that the ionic conductivity and the lithium ion transference number were very high in these systems. However, the application of these electrolytes in rechargeable lithium polymer batteries was restricted, which they attributed to the instability of the lithium electrode surface. PVdF was chosen as another polymer host for the formation of Li<sup>+</sup>-ion conducting gel electrolytes due to the fact that it possesses a strong electron-withdrawing functional group (-C-F) as well as a high dielectric constant (ε = 8.4), which helps in greater dissociation of lithium salts. PVdF-based gel electrolyte films containing EC/PC as plasticizers and lithium salts such as LiCF<sub>3</sub>SO<sub>3</sub>, LiPF<sub>6</sub> or LiN(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub> were cast by a novel thermal extrusion/hot-press method [92]. The mechanical strength of the as-cast polymer gel electrolyte films varied with the PVdF content, while the viscosity of the medium and the concentration of the lithium salt controlled the magnitude of the conductivity. Although the PVdF-based gel electrolytes offer excellent electrochemical properties, they are not very stable towards lithium and lithium salts due to a fluorinated polymer host leading to poor interfacial properties between lithium and fluorine. It has also been observed that the electrolyte properties could be improved substantially when PVdF was co-polymerized with hexafluoropropylene (HFP). PVdF-HFP co-polymer exhibited greater solubility towards organic solvents as well as having lower crystallinity with a reduced glass transition temperature than pure PVdF polymer in the gel [5, 93].

#### 2.4. Rubbery electrolytes

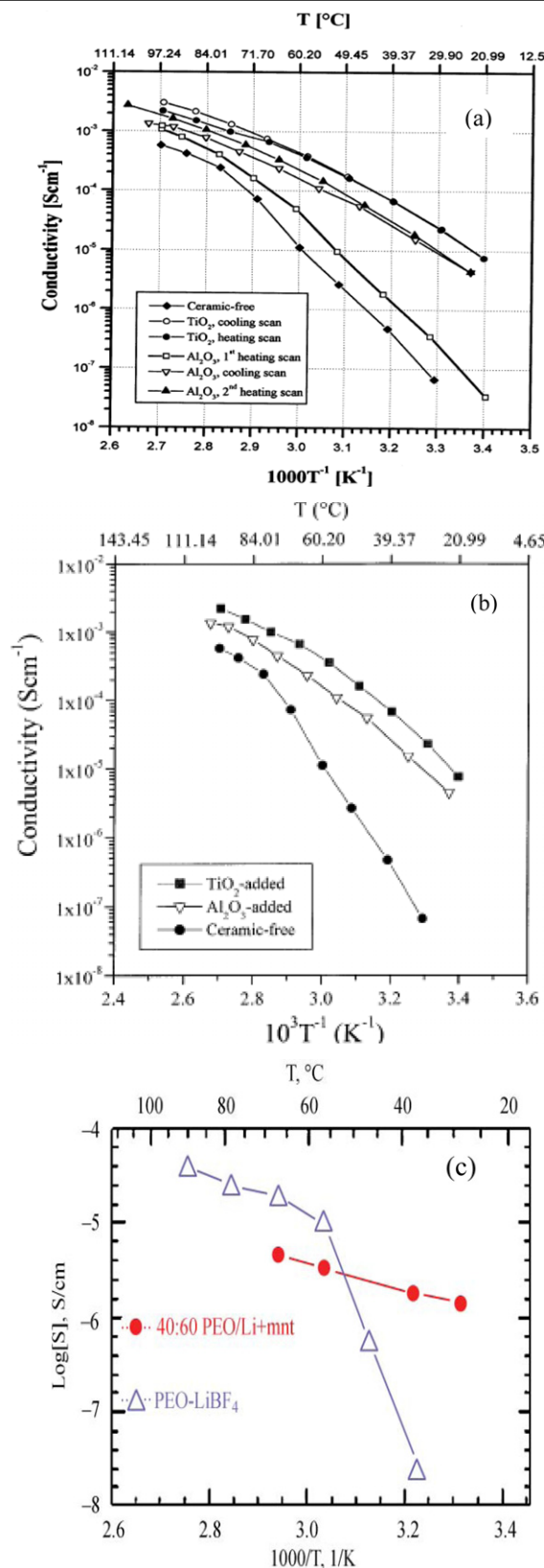
'Rubbery electrolyte', a novel polymer electrolyte system, was introduced for the first time by Angell and co-workers [31]. They synthesized rubbery electrolyte by dissolving/complexing a mixture of different lithium salts into polymer hosts such as PEO and PPO. They also referred to this polymer electrolyte as the 'polymer-in-salt' system, as it contains a very high salt content and a low amount of polymer host. This is in contrast to SPEs, usually referred to as salt-in-polymer systems, in which the salt concentration is considerably low in the polymer host. According to Angell *et al* [31], a small amount of high molecular weight polymer soluble in the melt of salt mixture exhibits a rubbery character by means of the entanglement mechanism and facilitates high ion conduction due to decoupled cation motion. They reported room temperature conductivity as high as 2 × 10<sup>-2</sup> S cm<sup>-1</sup> for the polymer-in-salt mixture: AlCl<sub>3</sub>-LiBr-LiClO<sub>4</sub>-PPO [32]. In the case of salt-in-polymer SPEs, maximum conductivity was normally achieved around the metal-ether-oxygen (M:EO) mole ratio ~1:16. This corresponds to one Li<sup>+</sup> ion per about 16 repeat units of ether oxygens. However, in polymer-in-salt rubbery electrolytes, M:EO ~3:1 [94] provides high ionic conduction. Typically, when a small amount of polymer is added to the salts mixture, it leads to the formation of rubbery materials having low glass transition temperature. Although a very high ambient conductivity could be realized in the rubbery electrolytes, the salt tends to crystallize at lower temperatures. This, in turn, affects the electrochemical stability of the electrolytes, and hence, their uses in practical electrochemical devices are restricted. Very few rubbery electrolyte systems with high ion conduction are known. Attempts have been made to explain the mechanism of ion transport in these systems. It has been widely accepted that the high degree of ion aggregates/clusters and their transport through the bulk lead to the



high ionic transport in these polymer-in-salt systems [95–97]. Ferry *et al* [95] studied the role of the PAN polymer matrix on the transport of the ionic species in the polymer-in-salt electrolyte in terms of salt stabilization and, hence, suppression of crystallization. It was also suggested that a dramatic enhancement in the ionic conductivity of polymer-in-salt reflects a ‘dynamic connectivity effect’ in a phase-separated electrolyte passing through a ‘smeared’ percolation threshold. At a critical cluster concentration, all the separated single clusters get connected to form an infinite cluster and, thus, promote the process of fast cationic transport through the entire electrolyte. Recently, Forsyth *et al* [98] reported a PAN-based  $\text{Li}^+$  ion conducting rubbery electrolyte and explained the fast ion transport on the basis of connectivity percolation of the ionic clusters decoupled from the polymer segmental motion.

### 2.5. Composite polymer electrolytes

As pointed out earlier, one of the major problems preventing the successful operation of lithium polymer batteries has been the reactivity at the  $\text{Li}/\text{Li}^+$  interface and growth of a passivation layer at the  $\text{Li}$ -metal surface causing an increase in the internal resistance. The other serious concern is the safety associated with lithium batteries. Some recent investigations revealed that these shortcomings of the lithium battery can be eliminated/minimized by using composite solid polymer electrolytes (CSPEs) instead of conventional/gel/plasticized polymer electrolytes. CSPEs are SPEs dispersed with nano/micro-sized filler particles of inert ceramic materials. CSPEs, especially in the lithium polymer batteries, offer enhanced electrode/electrolyte compatibility as well as safety. Dispersal of nano/micro-ceramic fillers particles in SPE hosts also improves the morphological, electrochemical and mechanical properties of the SPE membranes [35, 99–101]. The effects of dispersing filler particles of high conducting zeolites, ionites, solid superacid sulfated-zirconia as well as insulating ceramic materials such as  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$  and  $\text{TiO}_2$  on various physical/electrolytic properties of CSPEs have been investigated by various workers [102–109]. It has been observed, in general, that the particle size and the physical nature of the dispersoid particles play a significant role. Hence, dispersal of nano-sized filler particles has been found to be more effective in the composite SPE systems, especially in terms of improvements in the physical, mechanical and electrochemical properties. This new class of materials has been referred to as ‘nano-composite polymer electrolytes (NCPEs)’ [110–115]. As a result of dispersal of nano-dimension ceramic filler particles in the conventional SPEs host, an enhancement of 1–2 orders of magnitude in room temperature conductivity from that of the undispersed system could be achieved along with a substantial improvement in the mechanical integrity of the electrolyte membrane as well as electrode/electrolyte interfacial activity. Figures 2 and 3 show  $\log \sigma$  versus  $1/T$  plots for a few representative NCPE systems which clearly indicate the enhancement in the room temperature conductivity values after dispersal of filler particles.  $\log \sigma - 1/T$  plots of figure 3 are for the systems recently synthesized at the present laboratory



**Figure 2.**  $\log \sigma$  versus  $1/T$  plots for some important NCPE systems: (a)  $\text{PEO}_8\text{LiClO}_4 + \text{TiO}_2$ ,  $\text{PEO}_8\text{LiClO}_4 + \text{SiO}_2$  and  $\text{PEO}_8\text{LiClO}_4 + \text{Al}_2\text{O}_3$  (reprinted from [104] by permission of ECS—The Electrochemical Society); (b)  $\text{P}(\text{EO})_8\text{LiClO}_4$  dispersed with  $\text{TiO}_2$  and  $\text{Al}_2\text{O}_3$  (reprinted with permission from [36] copyright 2000 Elsevier); (c)  $\text{PEO-Li}^+$  montmorillonite (mnt) nano-composite (reprinted from [29] by permission of the Royal Society of Chemistry).

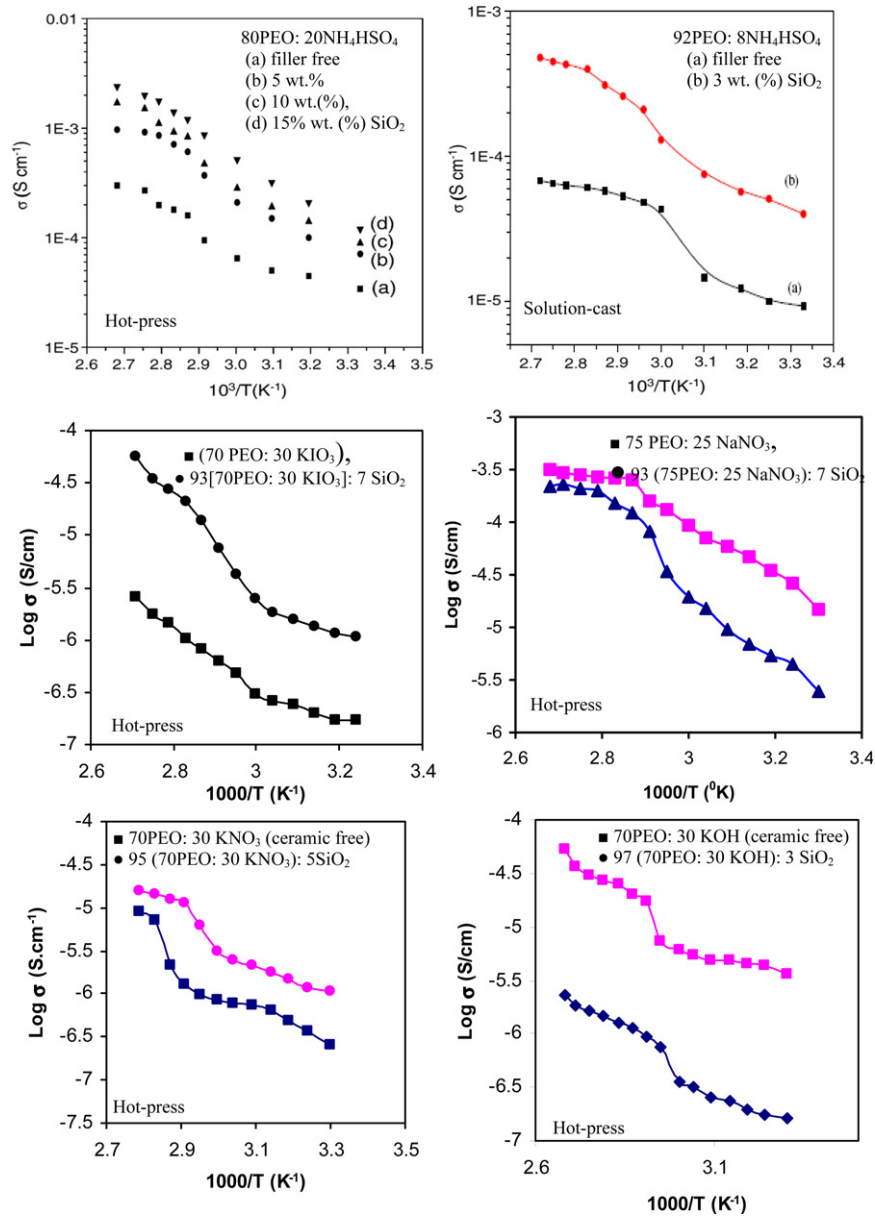
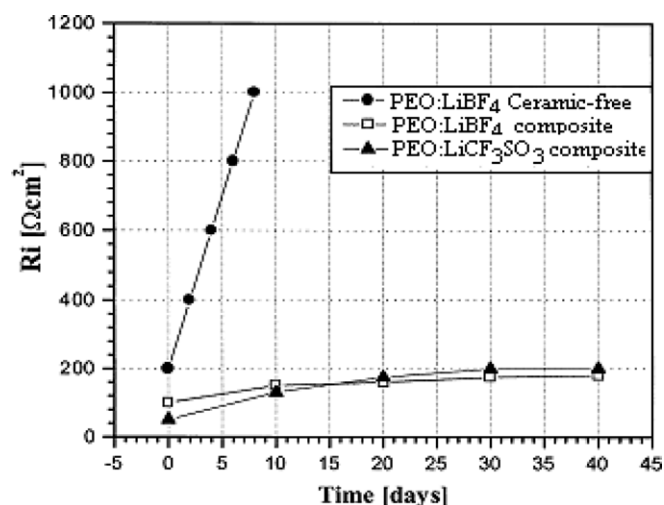


Figure 3. Log  $\sigma$  versus  $1/T$  plots for some polymer electrolytes synthesized at the present laboratory (reprinted from [115]).

using hot-press as well as solution cast methods [115]. As also mentioned, dispersal of nanoparticles also brings about substantial improvements in the mechanical stability of the films as well as interfacial activity at the electrode/electrolyte interface by curbing the formation of the passivation layer which causes an increase in the internal resistance of the battery. The improvement in the interfacial activity can be evidently seen in figure 4 which illustrates the time evolution of internal resistance at the Li/electrolyte interfacial contact for ceramic-free and NCPE films. Table 7 lists some important CPEs and their conductivity values. Weston and Steele [34], in their pioneering research, for the first time demonstrated the idea of incorporating electrochemically inert ceramic filler particles of  $\alpha$ -alumina in the poly(ethylene oxide) (PEO) system and reported significant enhancement in the mechanical strength of the polymer. The enhancements in the room temperature conductivity of conventional solid polymeric

electrolytes (SPEs) as a result of dispersal of ceramic filler particles have been reported in the past by several research groups. However, it still remains to be addressed clearly as to what effective role the filler particles play in promoting the ion transport. Pedel and co-workers [116] for the first time identified through  $^7\text{Li}$  NMR studies that the addition of nano-sized  $\text{Al}_2\text{O}_3$  in PEO-Li polymer electrolyte suppresses the formation of crystalline phase which, in turn, resulted in the increase in the conductivity. Weiczorek *et al* [117, 118] observed that the size of the filler particles plays a crucial role and demonstrated a significant increase in the conductivity of the PEO-NaI :  $\text{Al}_2\text{O}_3$  CPE when the size of the  $\text{Al}_2\text{O}_3$  particles is smaller than  $4\ \mu\text{m}$ . They also suggested that the surface groups of the ceramic particles play an active role in promoting local structural modifications. Wiczorek *et al* [110, 119] applied the Lewis acid-base theory to analyse the structure and the ionic conductivity of a number of CPEs complexed

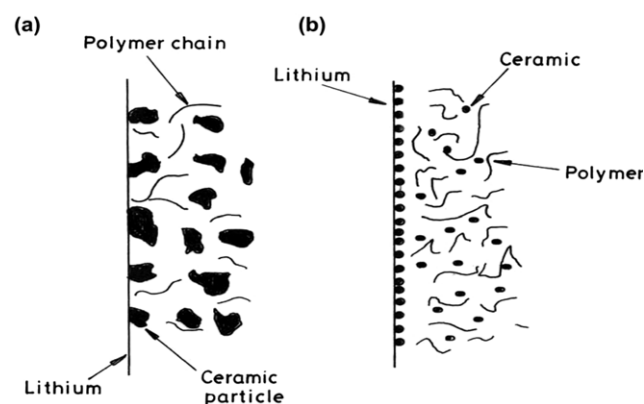


**Figure 4.** Evolution of interfacial resistance ( $R_i$ ) with time at the lithium metal electrode/electrolyte contact (reprinted with permission from [36] copyright 2000 Elsevier).

with alkali metal salts. They incorporated filler particles of three different characters, namely, Lewis acid centres ( $\text{AlCl}_3$ ), Lewis base centres poly(*N,N* dimethylacrylamide) and amphoteric Lewis acid–base ( $\alpha\text{-Al}_2\text{O}_3$ ) in the PEO– $\text{LiClO}_4$  system. Since PEO has a Lewis base and  $\text{Li}^+$  cation has a Lewis acid character, the phenomena occurring in the composite electrolyte could be explained in terms of equilibrium between various Lewis acid–base reactions. Scrosati *et al* [120] and Croce *et al* [121] reported substantial enhancements in the room temperature conductivity and mechanical integrity of polymer electrolytes: PEO– $\text{LiClO}_4$ , by incorporating inert submicrometre particles of  $\text{SiO}_2$  and  $\text{TiO}_2$ . According to them the filler particles behave like solid plasticizers which kinetically inhibit the crystallization of PEO chains and, hence, supplement the increase in amorphosity in PEO when annealed at  $\sim 70^\circ\text{C}$ . This, in turn, lowers the temperature of stabilization of the amorphous phase in the CPEs and, hence, increases the practical applicable range of conductivity of the electrolytes. Due to Lewis acid–base interactions occurring at the ceramic surface states and (PEO :  $\text{LiClO}_4$ ) interfaces, the ceramic filler particles may also have preferential pathways for  $\text{Li}^+$ -migration [37, 122, 123]. Croce *et al* [107] recently confirmed this hypothesis by dispersing a functionalized ceramic filler superacid sulfated-zirconia ( $\text{SO}_4^{2-}\text{-ZrO}_2$ ) into the PEO– $\text{LiBF}_4$  matrix. As a result of dispersal of this unique ceramic filler, due to its specific surface state conditions, an exceptional increase in the lithium transference number could be achieved [107]. Xi *et al* [109] also observed enhancement in the ionic conductivity and other electrochemical properties of the polymer electrolyte host: PEO– $\text{LiClO}_4$ , when dispersed with solid superacid sulfated-zirconia ( $\text{SO}_4^{2-}\text{-ZrO}_2$ ). Enhancement in the room temperature conductivity and electrochemical properties have also been reported for the other polymer electrolyte systems based on PEO : lithium salts ( $\text{LiClO}_4$ ,  $\text{LiBF}_4$ ,  $\text{LiPF}_6$ ,  $\text{LiCF}_3\text{SO}_3$ ) dispersed with submicrometre size particles of ferroelectric materials, namely,  $\text{BaTiO}_3$ ,  $\text{PbTiO}_3$ ,  $\text{LiNbO}_3$  [124, 125].

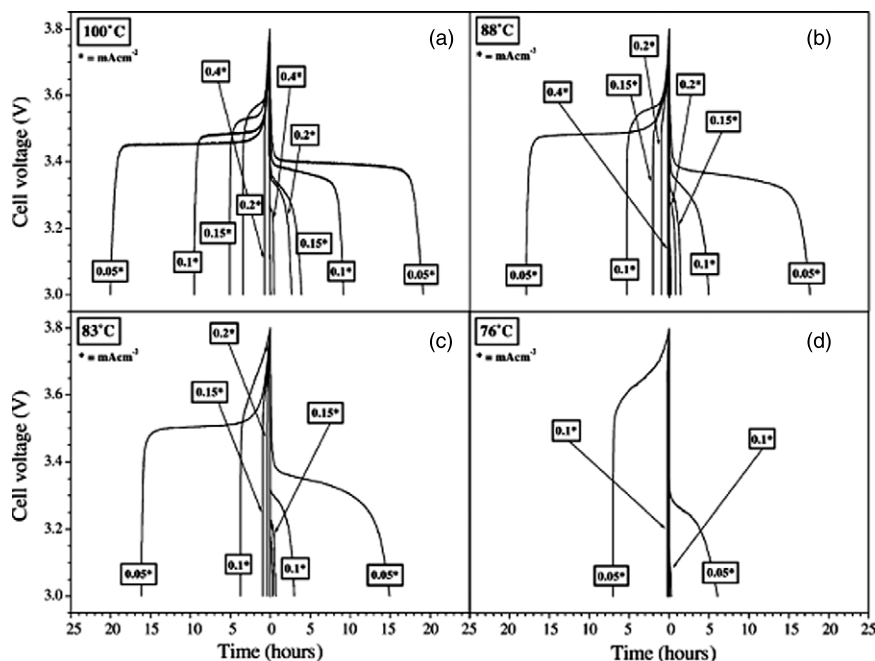
**Table 7.** Some important CPE and their conductivity values.

Composite polymer electrolytes	Conductivity ( $\text{S cm}^{-1}$ )	Temperature ( $^\circ\text{C}$ )	Reference
PEO– $\text{LiI-Al}_2\text{O}_3$	$\sim 1 \times 10^{-4}$	Room temperature	[38]
PEO– $\text{LiBF}_4$ –superacid– $\text{ZrO}_2$	$\sim 1 \times 10^{-6}$	Room temperature	[107]
PEO– $\text{LiClO}_4$ – $\alpha\text{-Al}_2\text{O}_3$	$\sim 1 \times 10^{-5}$	25	[110]
PEO– $\text{NaI-SiO}_2$	$\sim 5 \times 10^{-6}$	25	[111]
PEO– $\text{LiClO}_4$ – $\text{SiC}$	$\sim 1 \times 10^{-7}$	30	[112]
PEO– $\text{NH}_4\text{I-Al}_2\text{O}_3$	$\sim 8 \times 10^{-4}$	70	[113]
PEO– $\text{LiClO}_4$ – $\text{SiO}_2$	$\sim 1 \times 10^{-5}$	Room temperature	[114]
PEO– $\text{NH}_4\text{HSO}_4$ – $\text{SiO}_2$	$\sim 6 \times 10^{-5}$	Room temperature	[115]
PEO– $\text{LiCF}_3\text{SO}_3$ – $\gamma\text{-LiAlO}_4$	$\sim 3 \times 10^{-6}$	30	[119]
PEO– $\text{LiClO}_4$ – $\text{BaTiO}_3$	$\sim 1 \times 10^{-3}$	70	[125]
PEO– $\text{LiClO}_4$ – $\text{TiO}_2$	$\sim 2 \times 10^{-5}$	30	[121]
PEO– $\text{LiClO}_4$ – $\text{Al}_2\text{O}_3$	$\sim 1 \times 10^{-5}$	30	[121]
PEO– $\text{LiBF}_4$ – $\text{TiO}_2$	$\sim 1 \times 10^{-5}$	Room temperature	[128]
PEO– $\text{LiBF}_4$ – $\text{ZrO}_2$	$\sim 1 \times 10^{-5}$	Room temperature	[128]



**Figure 5.** Schematic representation of polymer host, nano- and micrometre sized inorganic filler in the polymer host. Particle size: (a) micrometre, (b) nanometre (reprinted with permission [126] copyright 1994 Elsevier).

A comprehensive review on the state-of-the-art modifications in ionic conductivity, transference number and electrode–electrolyte interfacial activity of the composite SPE systems has been presented by Kumar and Scanlon [126]. According to them dispersal of nano-sized filler particles leads to better electrode/electrolyte compatibility as compared with micrometre sized particles, as shown in figure 5. On the basis of DSC analysis, they explained the effect of size of particles on the crystalline–amorphous transition of polymer electrolyte: PEO :  $\text{LiBF}_4$ , dispersed with inorganic filler, namely,  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ , etc [127]. The nano-sized inorganic filler was found to be very effective in reducing the crystallinity in PEO-based polymeric host. Kumar and Coworker [128, 129] also carried out similar DSC studies on the PEO :  $\text{LiBF}_4$  dispersed with nano-sized ceramic filler particles of materials with a high dielectric constant, namely,  $\text{TiO}_2$ ,  $\text{ZrO}_2$ , and identified that interactions between polymer chain and high dielectric constant



**Figure 6.** The discharge characteristics of lithium polymer battery Li/CPE/LiFePO<sub>4</sub> at different temperatures (reprinted with permission from [137] copyright 2003 Elsevier).

inorganic fillers are influenced by the size and mass of the particles which lead to a better enhancement in the ionic conductivity. The nature of the interaction has been believed to be dipole–dipole type driven by a dielectric constant gradient. Morita *et al* [130] observed enhancement in the conductivity as well as ionic mobility when inorganic filler LiN<sub>2</sub>O<sub>3</sub> was added to the polymeric electrolyte hosts comprising PEO-grafted-(polymethacrylate) complexed with lithium salt. Bloise and co-workers [131, 132] using the NMR technique probed both <sup>1</sup>H and <sup>7</sup>Li-ion and studied the effects of adding filler particles of ceramics and carbon black on the segmental motion of PEO chains. They also suggested that Li–F interaction depends on the chemical nature of the filler materials and reported a relatively weaker interaction in the polymer electrolyte dispersed with  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> than that with  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. Chung *et al* [133] also drew an identical conclusion for the PEO:LiClO<sub>4</sub> polymer system dispersed with TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> filler particles. The NMR studies further revealed that the enhancement in the ionic conductivity cannot be regarded as belonging to the corresponding increase in the segmental motion of polymer chains but it is mainly due to the weakening of polymer–cation association induced by the nanoparticles.

The phenomenon occurring at the electrode/electrolyte interface plays a most significant role with regard to electrochemical device performances of the solid electrolytes. Hence, studies on interfacial properties, which strongly depend on the nature and particle size of the dispersed material, have been carried out very intensively by a number of research groups especially on Li<sup>+</sup>-ion conducting CPEs with lithium metal anode [134–136]. Appetecchi *et al* [134] synthesized CPE membranes: (PEO:LiBF<sub>4</sub>) and (PEO:LiCF<sub>3</sub>SO<sub>3</sub>), dispersed with  $\gamma$ -LiAlO<sub>4</sub> particles using a novel solvent-free/dry hot-press (extrusion) casting technique.

The CPEs were found exceptionally stable with the Li-metal anode. Furthermore, the dry CPEs exhibit a relatively high electrolytic efficiency and, hence, are more suitable for the fabrication of improved rechargeable lithium polymer batteries. In a similar study, Li *et al* [135] studied the interfacial properties of PEO-based CPEs complexed with two different salts, namely LiClO<sub>4</sub> and Li(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>. The interfacial resistance of the CPE containing LiClO<sub>4</sub> was found to be higher than that containing Li(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub> even after annealing at 80 °C. According to Kumar *et al* [136] the dispersal of nano-sized fillers makes the CPE more compatible with the Li anode resulting in a reduced interfacial resistance as compared with micrometre sized particles.

Appetecchi *et al* [137] asserted that as the ionic conductivity of PEO-based NCPEs is very high at higher temperatures, they can be suitably exploited in the EV applications. They fabricated a cell by direct lamination of the components, namely, lithium foil as anode, hot-pressed synthesized PEO-based NCPE and LiFePO<sub>4</sub> composite as cathode. The discharge characteristics of their lithium polymer battery: Li/CPE/LiFePO<sub>4</sub>, at different temperatures is shown in figure 6. The batteries exhibited very good cell performance at high temperature (>90 °C) especially during low current drains in terms of capacity, charge–discharge efficiency and cycle life. However, the capacity of the battery faded at moderate temperatures and at high discharge rates which they attributed to the decrease in the ionic conductivity of polymer electrolyte. Croce *et al* [138] reported charge–discharge cyclic behaviour of cells using CPEs dispersed with filler particles of low dimension and a Li/LiMnO<sub>6</sub> electrode couple. The same research group demonstrated the performance of several rechargeable batteries based on Li<sup>+</sup>-ion conductive CPEs and a number of appropriate electrode couples [139]. These batteries showed promising features in terms of cycle life as



well as rate capacity and appear suitable for EV applications. Very recently, Jiang and co-workers [140] introduced a novel CPE composed of polyurethane acrylate (PUA) dispersed with nano-sized  $\text{SiO}_2$  as a ceramic filler and  $\text{LiN}(\text{CF}_3\text{SO}_3)_2$  as a complexing salt. The cell  $\text{Li}/\text{CPE}/\text{Li}_{0.33}\text{MnO}_2$  exhibited a high initial capacity of about  $192 \text{ mAh g}^{-1}$  at  $60^\circ\text{C}$  but a faster capacity fading, which could be considerably reduced using hydrophilic nano-sized  $\text{SiO}_2$  powders.

### 3. Polymer electrolytes: film casting, characterization techniques, battery fabrication

#### 3.1. Film casting techniques

Polymer electrolyte films are generally cast by the following two routes:

- *Solution cast method.* This is a traditional procedure for casting polymer electrolyte films as well as gels. In this technique, appropriate amounts of polymer and complexing salt are dissolved separately in a common solvent, then mixed together and stirred magnetically for sufficient time ensuring salt complexation in the polymer host. For casting CPE films, filler particles of micro/nano-dimensions are added during stirring. The obtained viscous mother liquor is then poured into a Petri dish for the film formation through slow evaporation of the solvent followed by vacuum drying.
- *Hot-press (extrusion) technique.* This is a novel technique, originally proposed by Gray *et al* [49] and adopted recently by many groups with slight modifications [115, 134, 141, 142]. Hot-press casting has several advantages over the traditional solution cast method and has been recognized as the most rapid, least expensive, completely dry/solution free procedure for casting polymer electrolyte films. In this technique, dry powders of polymer and complexing salt (for casting conventional SPE films) and/or polymer, complexing salt and filler particles of micro/nano-dimension (for casting CPE films) in appropriate ratio are physically mixed, then the homogeneously mixed powder is heated around the melting point temperature of the host polymer for sufficient time with mixing continued to ensure complete salt complexation. As a result, a soft lump/slurry is obtained which is then pressed between two cold metal blocks/twin-roller, giving rise to a uniform, stable polymer electrolyte film of  $\sim\mu\text{m}$  thickness.

#### 3.2. Characterization techniques

The characterization of polymer electrolyte film material is done using a variety of analytical techniques. The confirmation of salt complexation as well as dispersal of filler particles in the host polymer electrolyte can be made by spectroscopic methods, namely, FTIR/IR, Raman, etc and/or XRD analysis. The ion-polymer association in both crystalline and amorphous phases can be known by monitoring the changes in the vibrational modes. X-ray and neutron diffraction studies give detailed information on the

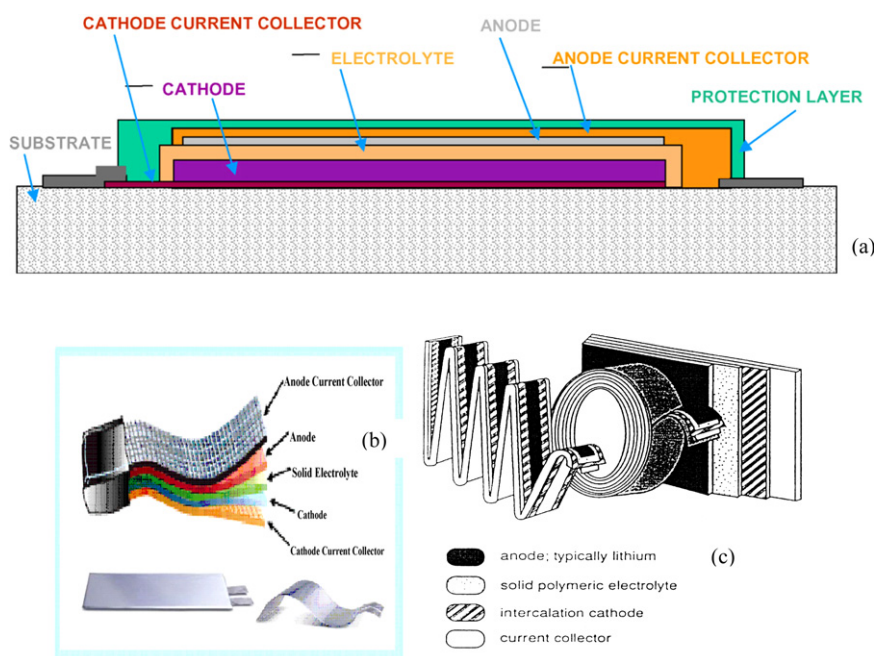
structural aspect, namely, crystallinity, amorphosity. The EXAFS study reveals the local environment of the ion as well as the existence of ion pairs in both crystalline and amorphous phases. It also helps to determine the bond length of ion-polymer interaction. NMR is another powerful technique to probe the immediate neighbourhood of the transporting ion, in terms of chemical shifts, line widths, relaxation times, self-diffusion coefficient, etc. Scanning electron microscopy (SEM) provides surface morphological information on the polymer electrolyte films. The thermal analysis of these materials using DTA/DSC reveals important insights regarding the degree of crystallinity/amorphosity, glass transition temperature ( $T_g$ ) and melting point ( $T_m$ ), etc.

The characterization of ion-transport properties of these materials is done as usual in terms of some basic ionic parameters, namely, ionic conductivity ( $\sigma$ ), ionic mobility ( $\mu$ ), mobile ion concentration ( $n$ ), ionic drift velocity ( $v_d$ ), ionic transference number ( $t_{\text{ion}}$ ), etc measured using a variety of experimental techniques. The conductivity measurements are usually carried out by impedance spectroscopic (IS) ac techniques. The impedance values:  $Z'$  (real) and  $Z''$  (imaginary) are evaluated at various frequencies ranging from mHz to MHz and plotted as a complex impedance plot which clearly separates the different resistive contributions such as bulk, grain boundary and electrode/electrolyte interfacial resistance. The IS technique also provides a number of important insights related to a variety of interfacial phenomena. The ionic mobility ( $\mu$ ) and the ionic transference number ( $t_{\text{ion}}$ ) can be directly determined using the dc polarization transient ionic current (TIC) technique [143].  $t_{\text{ion}}$  quantitatively gives the extent of ionic contribution to the total conductivity. In a pure ionic conductor,  $t_{\text{ion}} = 1$ , while it varies between 1 and 0 in the mixed (ionic + electronic) systems. The cationic transference number ( $t_+$ ) is a key parameter to judge the performance of the electrolytes. The cationic transference number ( $t_+$ ) can also be determined alternatively using combined dc polarization and ac impedance measurements [24].

The other ionic parameters, namely,  $n$ ,  $v_d$ , can be evaluated by substituting the data obtained in the above measurements into the appropriate equations.

#### 3.3. Battery fabrication

The field of rechargeable battery technology has recorded spectacular progress in recent years, especially, the batteries based on  $\text{Li}^+$ -ion conducting SPEs. However, in spite of lithium batteries having a high electrochemical window favourable for high energy density applications, Li-metal, as an anode, suffers from many serious drawbacks, namely, high reactivity, unsafe in ambient environment, etc. Nevertheless, these shortcomings have recently been greatly reduced by the use of intercalating/layered materials as electrodes. Some widely used electrode materials are  $\text{LiCoO}_2$ ,  $\text{LiCo}_x\text{Ni}_{1-x}\text{O}_2$ ,  $\text{LiMn}_2\text{O}_4$ ,  $\text{V}_2\text{O}_5$ ,  $\text{V}_3\text{O}_8$ ,  $\text{LiFePO}_4$  (as cathode),  $\text{LiC}_6$ ,  $\text{Li}_{3-x}\text{Co}_x\text{N}$ ,  $\text{KC}_8$ ,  $\text{SnO}_2$ ,  $\text{Li}_3\text{Sb}$  (as anode). The cathode and anode films are fabricated by spreading the materials on metal foils with the help of polymer binder solvents and supported by



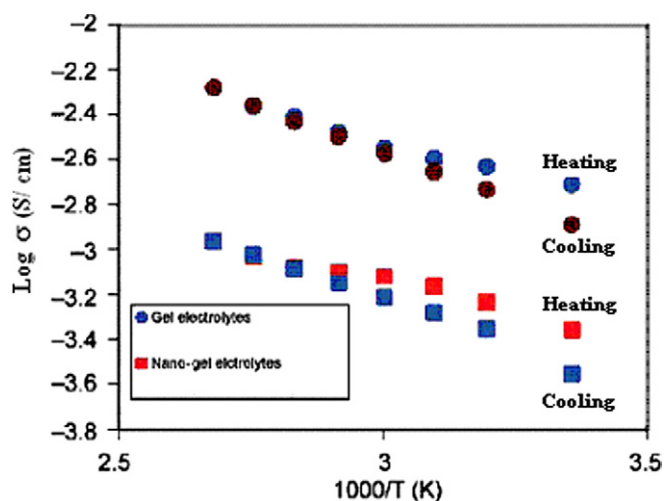
**Figure 7.** (a) Schematic cross-section of a thin film lithium battery structure; (b) general structure of thin film lithium battery; (c) schematic diagram of basic construction of polymer-based batteries. The thin membranes are flexible and can be arranged into several desired geometries [144].

electron conducting materials such as carbon, acetylene black, etc. The advancements in the lithium polymer electrolyte battery materials research would expectedly account for the development of new light-weight/shape-flexible/high energy density/cyclic efficient/safe/rechargeable all-solid-state batteries which would have outstanding commercial impacts in the near future especially as power sources for EVs. An all-solid-state lithium thin film battery is fabricated, in principle, by laminating a  $\text{Li}^+$  ion-polymer electrolyte membrane interposed between composite plastic anode/cathode materials in the form of a tape which can be rolled or folded into a variety of finished shapes, as shown in figure 7. To characterize the electrochemical performance of the batteries, cyclic voltammetry, charge/discharge potential profile under different loads and cyclic response are studied at varying thermal conditions.

#### 4. Recent development in materials designing

The objective of developing new generation ambient  $\text{Li}^+$ -ion polymer electrolyte batteries has recently diverted the attention of some of the research groups from nano-composite to nano-gel polymer electrolytes. The conventional gel electrolytes, one of the five broad categories mentioned in section 2, although exhibiting high ambient conductivity suffer from a number of drawbacks, namely, poor mechanical stability, increase in interfacial impedance due to rapid growth of passivation layer at the metal electrode/electrolyte interface, gas evolution, etc [29, 145–149]. However, many of these major problems can be excellently tackled by incorporating nano-sized ceramic filler particles into polymer gel electrolytes, but at the cost of a slight decrease in the conductivity value. Nevertheless, the conductivity of nano-gel

electrolytes remains almost stable even after several thermal cycles while that of the conventional gel electrolytes decreases rapidly due to solvent evaporation. Hence, it appears that nanoparticles act as a physical/chemical barrier to prevent the evaporation of solvent from the system [29, 145–150]. Figure 8 shows representative  $\log \sigma$  versus  $1/T$  plots for a conventional gel and a corresponding nano-gel containing 5 wt% synthetic fluoromica (layered silicate nanoparticles) [29]. Although the room temperature conductivity values of the polymer composite gel electrolytes are significantly high, due to the use of liquid components, namely, organic carbonates (EC/PC), there always exist significant problems of flammability and volatility associated with these systems [151, 152]. To overcome these discrepancies, nonflammable and nonvolatile ionic liquids have been used which allow the formation of much safer polymer gel electrolytes especially for Li-ion solid state batteries [153–158]. Ionic liquids are room temperature molten salts typically consisting of bulky, asymmetric organic cations and inorganic anions. The important attributes of ionic liquids include a wide electrochemical window, high ionic conductivity and high thermal stability [155, 159]. Webber and Blomgren [155] have enumerated the advantages of ionic liquids for lithium ion and related battery systems. More significantly, some ionic liquids with a certain combination of cation and anion have recently been reported as being electrochemically stable in the presence of lithium metal. These include quaternary ammonium salts [160, 161], pyrrolidinium salt [160, 162, 163], piperidinium salts [160] and some multi-substituted imidazolium salts [164, 165]. A significant number of studies appeared in the literature reporting the use of room temperature ionic liquids as promising electrolyte solvents for lithium ion batteries and other solid state electrochemical devices, namely, supercapacitors, fuel cells, etc [166–170].

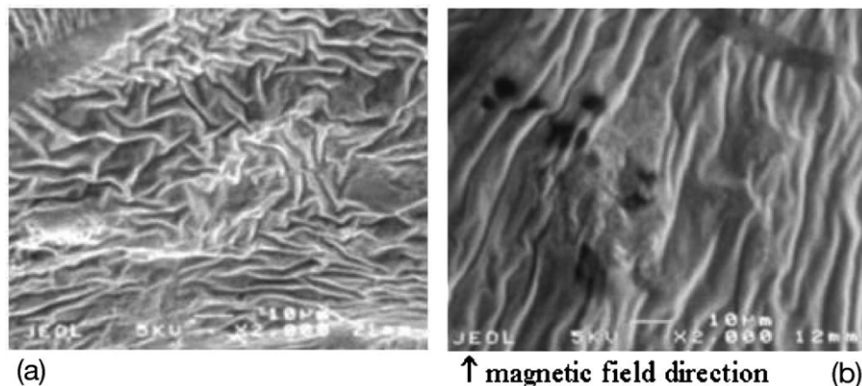


**Figure 8.** Arrhenius plots for gel (1 M  $\text{LiCF}_3\text{SO}_3$  in PVdF-co-HFP containing EC/PC) and nano-gel electrolytes containing 5 wt% synthetic fluoromica (reprinted from [29] by permission of the Royal Society of Chemistry).

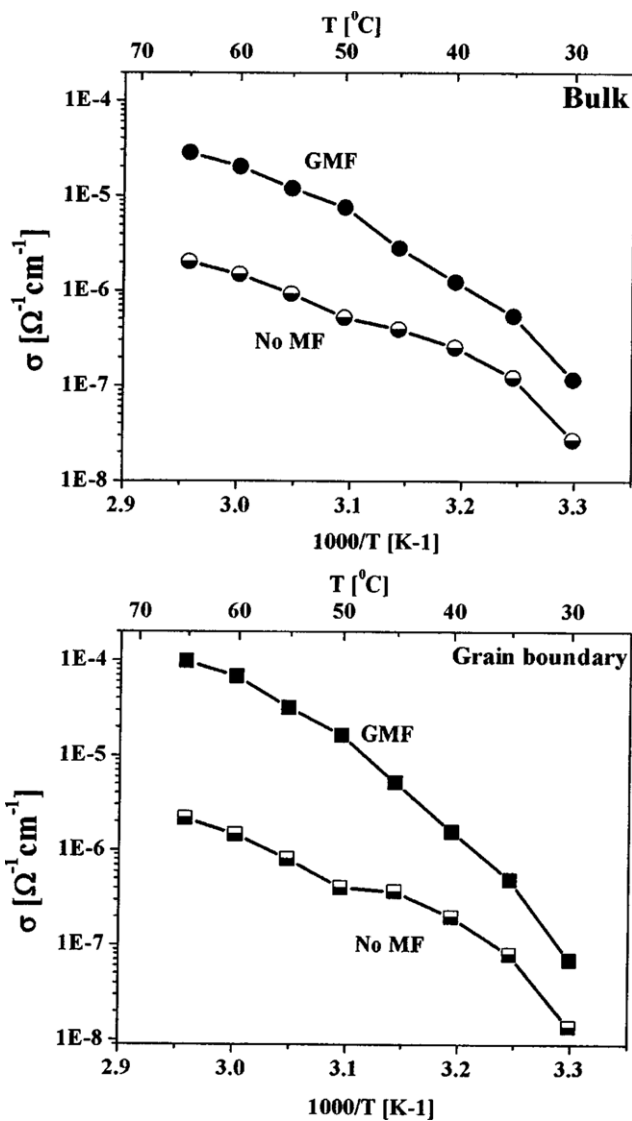
In recent years, an entirely new concept has evolved in the field of SPEs which has overturned the old views completely. According to the old concept, it was widely accepted, as a thumb rule, that enhancement in the ionic conductivity at room temperature could be achievable in SPEs only when the polymer host contains a large amorphous region or a low degree of crystallinity and low glass transition temperature ( $T_g$ ) [13–16]. As a general belief, the amorphous phase of the polymeric host supports high ion transport in SPEs. Based on this, a variety of approaches had been adopted to suppress the crystallinity and/or enhance amorphosity in the polymer (namely, PEO) host. However, despite all efforts, the maximum achievable conductivity in SPEs remained still around  $10^{-4} \text{ S cm}^{-1}$  to the maximum at room temperature. Ion conduction in SPE is a complex process and predominantly governed by the long-range ion motion, local motion of polymer segments and intra–inter-chain ion transport between coordinating sites. The intra-chain conduction is the inter-helix jump leading to bulk conductivity while inter-chain is related to grain boundary conduction and both contribute to overall conductivity in SPE. In general, SPEs are synthesized by solution cast/hot-press techniques and the electrolyte membranes have preferential plane ( $xy$ ) orientation of PEO helices. This, in turn, leads to higher longitudinal ( $xy$ -planar) conduction than orthogonal ( $z$ -perpendicular) conductivity. However, for practical battery applications, perpendicular ( $z$ -direction)-conductivity is crucial. Very recently, it has been reported that orthogonal (perpendicular) conductivity can be increased by altering the structure of SPEs. This is done by aligning the polymer helices by stretching the membrane either mechanically or magnetically (i.e. casting the film under a strong gradient magnetic field (GMF)). The effects of magnetic stretching are more pronounced in polymer electrolyte membranes dispersed with magnetic nano-filler particles. It has been observed that the stretch-induced effect led to an increase in the degree of crystallinity and, subsequently, to significant enhancement in both intra- and inter-chain ion conduction [171, 172]. As a matter of fact,

it can be thought that the aligned crystalline PEO chains are energetically more favourable for fast ion transport than the tangled chains in amorphous/disorder PEO. This has been looked at as ‘a complete overturn from the old views’ [22]. Figure 9 shows SEM micrographs of SPE:  $(\text{PEO})_3 : \text{LiI} + 9 \text{ v/v } \% \text{ Fe}_2\text{O}_3$  membranes cast with no magnetic field (No MF) and under strong GMF [171]. One can clearly note an orthogonal ordering in the direction of the magnetic field. Figure 10 shows representative  $\log \sigma$  versus  $1/T$  plots for ceramic-free SPE:  $(\text{PEO})_3 : \text{LiI}$  films cast with No MF and under GMF [171]. These clearly demonstrate the effect of magnetic stretching on intra/inter chain conduction. Both the bulk (intra-chain) and GB (inter-chain) conductivity increased substantially in SPE membranes cast under GMF. Conductivity enhancement is more pronounced in the magnetic nano-filler dispersed SPEs cast under GMF. In addition to this, a considerable increase in the cation transference number has also been reported in the magnetically stretched films. In as-cast SPEs films, predominantly having high amorphosity, both the ions may be mobile. Furthermore, in the magnetic stretching SPE membranes the solid electrolyte interfacial (SEI) resistance has also been observed to get lowered. Figure 11 shows the SEI resistance of  $(\text{PEO})_7 : \text{LiI} + 9\% \text{ Al}_2\text{O}_3$  membranes cast with No MF and under GMF [171]. Both the increase in cation transference number and decrease in SEI resistance are of great significance as far as the battery applications of SPEs are concerned.

Another novel approach has been suggested recently for designing high ionically conducting polymer electrolyte membranes. Accordingly, the static/ordered environment of the crystalline SPE favours relatively high cationic transport than that in equivalent amorphous SPEs above  $T_g$  [22, 173]. The crystalline SPEs are formed using low MW polymers (namely, PEO) by imposing certain restrictions on EO/salt compositions. For example, predominantly crystalline SPEs such as  $(\text{PEO})_3 : \text{LiCF}_3\text{SO}_3$  and  $(\text{PEO})_6 : \text{LiX}$  (iso-structural compounds where  $X \equiv \text{PF}_6, \text{AsF}_6, \text{SbF}_6$ ) can be formed by dissolving/complexing the salt in low MW PEO ( $\sim 10^3$ ) with compositions corresponding to three and six ether oxygen, respectively, per lithium ion [174]. Equivalent mixed crystalline but predominantly amorphous SPEs can be created using high MW PEO ( $\sim 10^5$ ). Figure 12 shows  $\log \sigma$  versus  $1/T$  plots of crystalline as well as amorphous SPE:  $(\text{PEO})_6 : \text{LiSbF}_6$  [22]. One can obviously visualize that the conductivity of the crystalline SPE is more than an order of magnitude higher as compared with that of its amorphous counterpart particularly in the lower temperature region.  $\sigma$  values in both the phases remained stable during wide variations in the temperature. Although the change in concept from amorphous to crystalline polymer electrolytes is an important milestone in the field of SPE materials, the room temperature conductivity values achievable in these systems are too low ( $\leq 10^{-7} \text{ S cm}^{-1}$ ) for potential battery applications. Hence, alternative ways are to be explored to raise the conductivity values. Very recently, it has been suggested that a partial replacement (up to 5 mol wt%) of complexing salt anions by appropriate larger isovalent ions can bring substantial enhancement in the conductivity. For

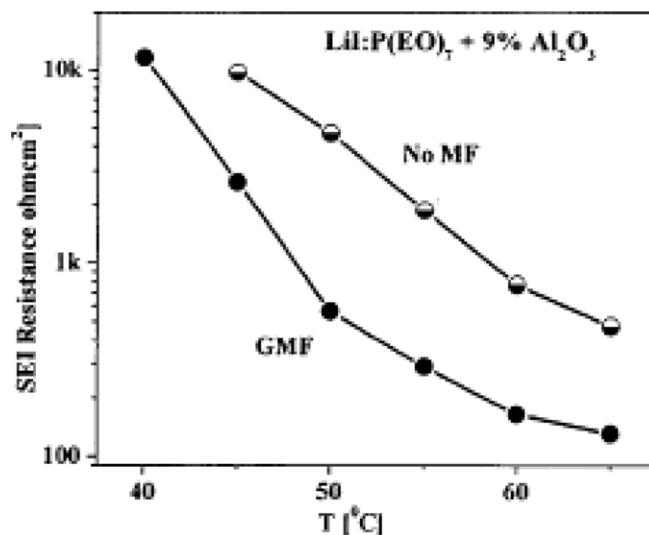


**Figure 9.** SEM cross sectional micrograph of SPE:  $(\text{PEO})_3 : \text{LiI} + 9\% \text{ (v/v) Fe}_2\text{O}_3$  films: (a) typical cast with No MF, (b) under GMF (reprinted from [171] by permission of ECS—The Electrochemical Society).

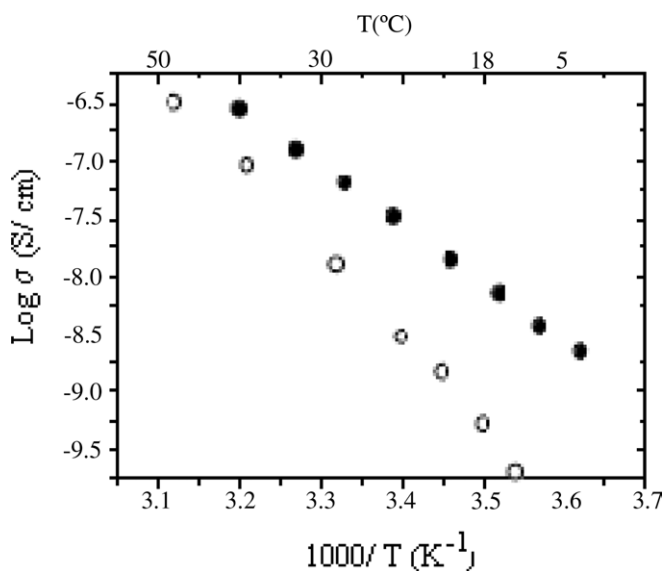


**Figure 10.** Log  $\sigma-1/T$  plots for SPE:  $(\text{PEO})_3 : \text{LiI}$ : (a) cast with No MF, (b) under GMF (reprinted from [171] by permission of ECS—The Electrochemical Society).

example, the conductivity of crystalline polymer electrolyte:  $(\text{PEO})_6 : \text{LiAsF}_6$ , increased by 1.5 orders of magnitude when 5 mol(%) of  $\text{AsF}_6^-$  ions were replaced by isovalent  $\text{N}(\text{SO}_2\text{CF}_3)_2^-$  (TFSI) ions [173]. Higher mol% replacement



**Figure 11.** Plot of solid electrolyte interface (SEI) resistance versus temperature for the cell:  $\text{Li}/\text{SPE}/\text{Li}$  (reprinted from [171] by permission of ECS—The Electrochemical Society).



**Figure 12.** Log  $\sigma-1/T$  plot of SPE:  $\text{PEO}_6 : \text{LiSbF}_6$ , amorphous ( $\circ$ ) and crystalline ( $\bullet$ ) (reprinted from [22] by permission of Nature Publishing Group).



of TSFI ions led to a two-phase solid-liquid composite for low molecular weight PEO.

## 5. Conclusion

Although the SPEs have a much lower room temperature ionic conductivity than those comprising organic salt liquids, their safety is an advantage. The SPEs, especially NCPes, show great technological potential for developing all-solid-state electrochemical devices, namely, thin film rechargeable batteries in all possible shapes and sizes. Presently, most of the commercial batteries are based on Li-ion conducting polymer electrolytes. However, these systems are not absolutely free from many serious concerns. What we need today are completely clean/green/safe electrochemical power sources. Hence, in the field of thin/flexible film all-solid-state battery technology the future relies on polymer electrolytes which are environment-friendly/least hazardous to our planet Earth.

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