

Trends in polymer electrolytes for secondary lithium batteries

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Abstract

The polymer electrolytes are promising materials for the ever-growing need for high energy density power sources for power and traction applications. With an emphasis on lithium batteries, the field of polymer electrolytes has gone through a sort of three stages; dry solid systems, polymer gels, and polymer composites. The ‘polymer gels’ and the ‘polymer composites’, the former incorporating organic solvents, have shown room temperature conductivities as high as 10^{-3} S cm⁻¹. The ‘dry solid systems’ presently suffer from poor ionic conductivities ($\sim 10^{-5}$ S cm⁻¹ at 20°C), but are safer than the former due to absence of any organic solvent which can cause environmental hazards. In the area of electrode systems, one can notice quite good performances by the organo-sulfur polymers as cathode materials and poly(*p*-phenylene) as an anode material. Specific energies as high as 180 W h kg⁻¹ have been demonstrated in cells containing these polymers. Examples of various test cells based on the above types of polymer electrolytes incorporating lithium metal, intercalation type electrodes, and polymer electrodes are reviewed. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

So far no rechargeable lithium battery using a solid polymer electrolyte is commercially available in the market. Thus research is being focused world-wide on the development of high power and high energy density secondary lithium batteries with a major concern to performance, safety, and reliability. Applications of lithium batteries in automotive industries, portable devices, and aerospace applications is presently the subject of interest, both to the battery developer and the manufacturer [1–4]. Depending on the type of the cathode, anode, and the electrolyte used in the battery one can expect a range of energy densities. With the use of a polymer electrolyte in lithium batteries, high specific energy and specific power, safe operation, flexibility in packaging, and low cost of fabrication can be expected. Although specific energy as high as 150 W h kg⁻¹ can be achieved in lithium-ion batteries using liquid electrolytes [5], a value more than twice than that achievable from Ni-batteries, polymer

lithium-ion batteries with more than 180 W h kg⁻¹ have already been demonstrated [4].

At present, various research units and private companies such as, PolyPlus, Moltec, and Ultralife Batteries in the US and Maxell in Japan are actively involved in developing polymer lithium batteries both for small and large scale applications. The PolyPlus Battery in the US, for example, is developing room temperature lithium polymer battery which would have specific energy as high as 500 W h kg⁻¹. In a prototype cell working at 90°C and using a lithium intercalated disulfide polymer as the cathode, specific energy as high as 100 W h kg⁻¹ was observed [6,7]. The discharge/charge cycles were almost reproducible for over 350 cycles. Moltec, on the other hand, have reported an AA-sized battery based on organo-sulfur cathode with 180 W h kg⁻¹ [8]. Ultralife Batteries have reported a solid polymer battery based on intercalation type electrodes giving 125 W h kg⁻¹, working at room temperature, and showing a performance of more than 500 charge/discharge cycles [9].

One of the main purposes to develop polymer lithium batteries is for traction applications. Based on the survey on demand for alternative fuel vehicles made by Turrentine and Kurani in the US in 1995 [10], consumers agreed to buy electric vehicles (EV) which would run for at least

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Table 1
The United States Advanced Battery Consortium (USABC) criteria for EV battery [12]

Battery property	Unit	Mid term (~ 2000)	Long term (~ 2010)
Power density	W l ⁻¹	250	600
Specific Power	W kg ⁻¹	150–200	400
Energy density ^a	W h l ⁻¹	135	300
Specific density ^a	W h kg ⁻¹	80–100	200
Life	years	5	10
	cycles	600	1000
Price	\$/kWh	< 150	< 100
Normal recharge time	h	< 6	3–6
Operating environment	°C	–30–65	–40–85

^aC/3 discharge rate.

200 kms. per battery. This was accepted mainly on the grounds of environmentally friendliness of an EV. It is only recently that details of EV in the US are communicated to the people through mail and telephone and internet communications [11]. It was found that some people rejected the idea of an EV mainly because of the need of home recharging and shorter driving range per battery. Nevertheless, the concept of zero emission and high reliabilities of an EV would still prove encouraging for an environmentally conscious person. Table 1 indicates the USABC (The United States Advanced Battery Consortium) criteria for an EV battery.

2. Some general considerations

2.1. Basic properties of polymer electrolytes

Although, tremendous research activities by Sony leading to commercialization of lithium batteries incorporating liquid electrolytes took place over the last decade [13], many advantages of solid polymer electrolytes over their liquid counterparts such as organic solutions and inorganic and molten salts can be seen [14]. The possibility of internal shorting, leaks, and producing combustible reaction products at the electrode surfaces, existing in the liquid electrolytes, is eliminated by the presence of a solid polymer electrolyte. Nevertheless, the polymer electrolytes should exhibit ionic conductivities, at least, of the order of 10⁻³ to 10⁻² S cm⁻¹ at room temperature and play the role of a separator, played by the liquids. The polymer should also allow good cycle lives, low temperature performances, and good thermal and mechanical strengths in order to withstand internal temperature and pressure buildup during the battery operation. The polymers, in general, being light-weight and non-combustible materials can be fabricated to requirements of size and shape, thus offering a wide range of designs. Since stable thin films of the polymers can be easily made, high specific energy (low-mass) and high specific power (less volume) batteries

can be expected for use in electric devices and EV. Internal voltage drops may be low, about 50 mV at 10 mA cm⁻², when films as thin as 40 μm are made [15,16].

The field of polymer electrolytes has gone through three stages: ‘dry solid systems’, ‘polymer gels’, and ‘polymer composites’. The ‘dry systems’ use the polymer host as the solid solvent and do not include any organic liquids. The ‘polymer gels’ contain organic liquids as plasticizers which with a lithium salt remain encapsulated in a polymer matrix, whereas the ‘polymer composites’ include high surface area inorganic solids in proportion with a ‘dry solid polymer’ or ‘polymer gel’ system. More detailed aspects of the systems with individual examples are discussed in separate sections below. The advancement of the field can be found in literature publications and reviews [15,17–25].

One of the important properties of a polymer electrolyte leading to its development activity is the ionic conductivity. Temperature dependence on conductivity of amorphous polymer electrolytes generally follows the Vogel–Tammann–Fulcher (VTF) equation

$$\sigma = AT^{1/2} \exp \left[E/(T - T_0) \right]$$

where, T_0 is the glass transition temperature of the polymer electrolyte measured by DSC, T is the temperature of measurement, A is the pre-exponential factor, and E is the activation energy which can be evaluated either from the configurational entropy theory or the free-volume theory, and hence relates to the segmental motion of polymer chains [26]. The ionic conductivity is usually measured by AC impedance techniques [27].

Another important property of the polymer electrolyte is the lithium ion transference number (t_{Li+}) which ideally for lithium battery applications should be unity. A value of t_{Li+} lower than 1 would tend to develop concentration gradients at electrode surfaces leading to limiting currents. Thus, both the parameters, ionic conductivity and lithium ion transference number are important in order to choose a polymer electrolyte for a practical lithium battery. The maximum power obtainable in a lithium cell can be related to the conductivity of the electrolyte, whereas, the maximum limiting current that can be drawn from the cell and the cycleability of the cell can be related to the t_{Li+} . The lithium transference number (and its associated diffusion coefficient) measurements are usually made using techniques such as concentration cell method [28,29], Tubandt method [30,31], ⁶Li NMR [32], and electrochemical [33,34], and electrophoretic NMR techniques [35,36]. The techniques have their advantages and disadvantages and differ by theoretical models used for interpretation of data. Analysis of some of the problems and limitations associated with some of the techniques have been described by Fritz and Kuhn [37].

An understanding to the interactions of the various species in the polymer electrolytes has made possible to

choose appropriate polymer hosts, complexing salts and salt concentrations so that the ionic conductivities are optimized. Evidence of salt dissolution into a polymer host is mainly based on spectroscopic methods such as IR and Raman [38,39]. The anion–cation and ion–polymer associations in both crystalline and amorphous phases have been studied using both these which monitor changes in the vibrational modes of the polymer host and the anions [40–43]. For example, in the case of lithium triflate (LiCF_3SO_3) [41] and lithium bis(trifluoromethane sulfonyl)imide [LiTFSI] complexes [42] with oxyethylene containing polymer chains, SO_3 symmetric stretching modes, CF_3 bending modes, and Li–O stretching modes were associated to ion–ion interactions and information on ion pairing and ion association was obtained [44].

X-ray and neutron diffraction methods have given detailed information on the structural aspects of coordination around the ions in crystalline phases of polymer electrolytes [45–47]. The EXAFS has revealed the local environment of the ion [48] in both crystalline and amorphous phases, including the existence of ion pairs such as $[\text{MX}]^0$, $[\text{M}_2\text{X}]^+$, $[\text{MX}_2]^-$, etc. and the determination of bond lengths of the ion–polymer interactions [49]. The EXAFS technique is more useful when theoretical models depicting the most probable situations are at hand so that fitting of the EXAFS spectrum of known structures similar to the chemical environment of the polymer electrolyte is possible.

2.2. Stability of polymer electrolytes

The electrochemical stability of an electrolyte is one of the essential parameters when rechargeable lithium batteries are concerned. The instability in the electrolyte is known to bring out irreversible reactions and capacity fading in the battery [50]. The stability commonly expressed as ‘electrochemical stability window’ of the polymer electrolyte (units of volts) should be the same as that of the electrode potential or higher so that overpotentials during re-charge are compensated by the higher stability window. For example, for a 4-V lithium battery a window of at least 4.5 V vs. Li/Li^+ in the polymer electrolyte is required for compatibility with a lithium metal anode and lithium-ion intercalating electrode materials (see Section 3.4).

Thermal and mechanical stabilities of a polymer electrolyte during charge/discharge cycles are vital for a safe and enduring battery. During charge and discharge, heat is known to get generated in the battery which increases the surface area of an existing passive layer at the electrode surface [51]. The heat can also melt and degrade the polymer electrolyte within the battery and cause internal short circuits. Increase in heat due to environmental factors during storage increases the self discharge reactions in the battery and shorten life.

2.3. Reactivity of lithium metal

Although in polymer electrolytes, lithium ion conductivities as high as 10^{-3} have been shown (see later sections), problems associated with the lithium battery electrodes still remain to be solved [15,52]. Lithium metal is quite well known to react with protic and aprotic solvents [53], causing passivation reactions at its surface [54]. This limits the charge transfer reactions at the electrolyte/electrode interface leading to deterioration in rechargeability of the battery [55]. The passivation reactions are usually initiated by the presence of organic solvents in the polymer electrolytes along with unstable anions of the salt resulting into their decomposition at electrode surfaces [56]. The reaction products of the anion tend to initiate reactions that can degrade the polymer chain [15]. In the presence of stable anions such as (LiTFSI) and lithium bis(trifluoromethane sulfonyl)methide (LiTFSM), the passive layer would mainly consist of decomposition products of the solvent. In the presence of carbonates in the electrolyte, passive layers consisting of Li_2CO_3 and LiHCO_2 are usually formed on the surface of the lithium metal anode [57].

The passivation reactions seem to be more serious in cells containing polymer electrolytes than those with liquid electrolytes; the former having a tendency to lose itself from the interface during cycling of the cell [5]. With the liquid electrolyte, one would expect the electrolyte surface to get regenerated due to fluidity in the liquid medium. The passive layer (and the polymer electrolyte) inhomogeneity at a lithium metal electrode surface results into variations in surface potentials leading to the commonly inferred ‘dendrite’ formation. Most of the cell failures have been found to be accompanied with this dendritic growth of lithium at the electrode/electrolyte interface during cell cycling [54]. As an attempt to minimize this problem, various methods of fabrication of the electrodes have been investigated with much considerations to the need of having intimate contacts between the polymer electrolyte and the electrode. In the case of solid polymer electrolytes, this is achieved by incorporating the electrolyte into the electrode matrix during its fabrication [15], whereas in the case of liquid electrolytes this is less a problem as the liquid electrolyte can easily soak the pores of the electrodes. Apart from increasing interfacial contact with the electrode, the polymer electrolyte also acts as a pore filler and a binder to the electrode mass.

Fig. 1, in a schematic drawing, shows the phases present between the electroactive material, conductive filler, and the electrolyte. The intimate contact at the electrolyte/electrode interface would tend to stabilize the interface and reduce interfacial resistance. To some extent, the adhesive property of polymers at electrode surfaces have an advantage over powdered electrolytes such as ceramics and other crystalline electrolytes. In the case of the later, the use of high compaction pressures during

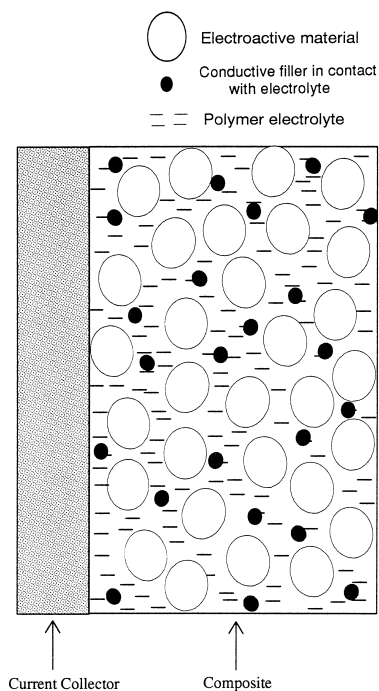


Fig. 1. Schematic diagram of phases between electroactive material, binder, and the electrolyte.

fabrication of the battery components is a means of increasing the electrolyte/electrode contact [58].

Techniques such as Fourier-Transform Infrared Spectroscopy (FTIR), XPS, scanning electron microscopy (SEM)[59,60] and impedance spectroscopy [61–64] have been widely used to follow respectively the morphological and electrochemical changes in the passive layers. Such techniques have indicated the formation of a first discharge passive layer to protect the lithium electrode from further attack during further cycling of the battery. The capacity losses during the first discharge are large and reduce the electrode utilization, whereas subsequent cyclings of the battery maintain the capacity of the lithium metal electrode.

2.4. Intercalation electrodes

In recent times, less-reactive electrode materials such as metal oxides, sulfides, carbon, graphite, and organic polymers which intercalate lithium ions have substituted the lithium metal in secondary lithium batteries incorporating liquid electrolytes containing pure or mixed organic solvents [13,65,66]. These batteries with such electrodes are presently classified as ‘rocking-chair batteries’ or ‘lithium-ion batteries’ and research on this technology still continues [14,66–69]. In a most common cell, the electrodes (commonly called ‘insertion’ or ‘hybrid’ electrodes) comprise of lithiated carbon as the anode, and a lithium intercalated metal oxide such as LiNiO_2 , LiMn_2O_4 , or LiCoO_2 as the cathode [13,61,70]. In the field of polymer lithium batteries, interest in order to find such cathodes

and anodes still continues. However, most of the electrode types commonly used in the lithium and lithium-ion batteries incorporating the liquid electrolytes have also been investigated for polymer electrolytes [5,71,72]. Some good examples of cells incorporating intercalation type electrodes with polymer electrolytes can be found in the review by Novak et al. [66].

The electrochemically active polymers are novel materials for possible applications in polymer lithium batteries so that an ‘all plastic battery’ is obtained. These materials are used in batteries in their doped (oxidized or reduced) state. Various examples of test cells using the electrochemically active polymers for polymer electrolytes with performance values are listed in the review by Novak et al., along with the synthesis and applications of electrochemically active polymers as electrode materials for rechargeable lithium batteries [66].

3. Dry solid polymer electrolytes

3.1. PEO-based electrolytes

In 1973, the first measurements on conductivities of poly(ethylene oxide) (PEO) complexes with alkali metal salts were made by Wright et al. [73,74]. It was after Armand that the potential of these new materials were realized for future battery applications [75]. PEO with high molecular weight of about 5×10^6 and 80% crystallinity was usually employed as the polymer host to form complexes with lithium salts. Apart from the ability of the sequential oxyethylene group, $-\text{CH}_2-\text{CH}_2-\text{O}-$ in PEO to complex with lithium salts, polymer hosts containing sequential polar groups such as $\text{O}-$, $-\text{NH}-$ and $-\text{C}-\text{N}-$ in the polymer chain were also found to dissolve lithium salts [76].

The lithium salt complexed-poly(ethylene oxide) (PEO) [77] and -poly(propylene oxide) (PPO) [78] are the most widely investigated ‘dry solid polymer’ electrolyte systems in all solid state lithium batteries. The main reason to choose these two polymer hosts is because they form more stable complexes and possess higher ionic conductivities than any other group of solvating polymers without the addition of organic solvents. Complex formation in PEO_n -salt (n = number of ether oxygens per mole of salt) is governed by competition between solvation energy and lattice energy of the polymer and the inorganic salt [79]. Low lattice energies of both the polymer and the complexing salt have been found to increase stabilities in the resultant polymer electrolyte [79].

As a function of concentration of lithium salt in PEO, a general trend of lowering both the conductivities and lithium transference numbers was observed as the concentration was increased [80]. This was considered as due to hindrance to the motion of polymer chains accompanying ion mobility and formation of ion pairs which lowered the

amount of free lithium ions available for conduction [81]. The formation of positively and/or negatively charged ion triplets is also known to take place at higher concentrations and temperatures [82]. Using NMR techniques, the ion pair formation has been shown to form at high salt concentrations [32]. In PEO complexes, ion pairing was found to set in when cation:ether oxygens ratio was greater than 1:8, whereas for 1 cation:4 ether oxygens, ion aggregates were generally formed [82]. This limited the maximum ionic conductivities obtainable in PEO complexes by limiting the amount of salt (or charge carriers) allowed in the host polymer.

PEO has been found to complex with lithium salts such as LiBr, LiI, LiCl, LiSCN, LiClO₄, LiCF₃SO₃, LiBF₄, and LiAsF₆, [76] out of which PEO LiCF₃SO₃ [83,84] and PEO-LiClO₄ [84,85] have been the most widely studied. Studies of crystal structures of PEO-LiCF₃SO₃, for example, have revealed the cation to remain encapsulated within the helix of the PEO chain with the anions stacked outside the helix [46]. Thus, the possibility of the anion to migrate within the polymer electrolyte does exist which would be detrimental to the performance of the lithium battery leading to self discharge and its possible degradation at the surface of the electrode. In order to minimize the anion migration, complexing salts containing large organic anions such as the LiTFSI and the LiTFSM were studied by Armand et al. [79]. The presence of the highly electron delocalizing anion in these salts was thought to plasticize the polymer chain making it more flexible. The polymer electrolytes containing these novel salts have shown much lower crystallinity, higher conductivity, and low anion transference number [86].

Since the ion mobility in the polymer electrolytes was found to be accompanied by polymer chain mobilities, conductivity and ion transport were restricted to the amorphous phase of the polymer electrolyte [87]. At about 100°C, above the melting point of PEO-lithium salt complexes, conductivities were three orders of magnitude higher than those at room temperature. This restricted the applications of PEO-based electrolytes in lithium batteries between 100°C and about 200°C, the upper limit of temperature involving the decomposition of the polymer complex.

In attempts to reduce the anion migration, complexes of PEO with aromatic anions such as phenols and naphthols were also prepared, but no ionic conductivities were reported [88,89]. Also, superacid salts of lithium having the general formula, C_nF_{2n+1}SO₃Li (n = 4, 8, and 10) were recently prepared by Nagasubramanian et al. for polymer electrolytes [90]. These salts were found to complex with PEO but showed much lower room temperature conductivities than the PEO-LiTFSI complexes. The room temperature conductivities reported were PEO-C₄F₉SO₃Li (10⁻⁶ S cm⁻¹), PEO-C₈F₁₇SO₃Li (~ 10⁻⁵ S cm⁻¹), and PEO-C₁₀F₂₁SO₃Li (10⁻⁶ S cm⁻¹). In another similar study, conductivities in PEO complexes with lithium salts of

benzimidazole were reported as 5 × 10⁻⁵ S cm⁻¹ at 100°C [91].

Venkatesetty reported the preparation of salts, lithium perfluoroalkyl sulfonimide (RSO₂NLiSO₂R) and dilithium perfluoroalkyl sulfonimide ((RSO₂N)₂Li₂), where R = C₄F₉ or C₈F₁₇ [92]. The room conductivities of complexes of both these salts with R = C₄F₉ with PEO were reported as in the range (2 to 5) × 10⁻⁶ S cm⁻¹, and those of dilithium salt with R = C₈F₁₇ as in the range 3 to 4 × 10⁻⁷ S cm⁻¹.

Attempts to impede the mobility of anions were also made by complexing anions such as Cl⁻ and I⁻ with aza-based compounds which apart from acting as anion receptors gave rubber like characteristics to the otherwise stiff polymer salt complexes (Fig. 2) [93]. Conductivities of such a complex, PEO₁₆-(LiCl-aza compound) were two orders of magnitude higher than the PEO₁₆-LiCl complex, measured in the temperature range 25–65°C. The higher conductivities were attributed to the lowering of crystallinity in the polymer complex in the presence of the anion receptor compound. Unfortunately, no results on the lithium ion transference numbers were reported, but one would expect the values to be high due to impediment of anion mobility resulting from their complexation with the aza compounds.

New structures with low crystallinity at room temperatures and hence with low glass transition temperature were synthesized, resulting into structures with graft polymers, block copolymers, and crosslinked polymer networks [15,94–96]. In most of the cases, PEO chain was used as the main polymer chain onto which the structural modifications were made [97,98]. Also polymers containing oligo-oxyethylene side chains, acting as lithium salt complexing sites, attached to main chain polymer backbones were synthesized [15]. The maximum conductivity at 20°C observed at an optimum chain length of the oligo-oxyethylene group was about three orders of magnitude higher than those of linear PEO-salt complexes [95].

Recently, amorphous, up to comb polymers based on methyl vinyl ether/maleic anhydride copolymer containing oligo-oxyethylene and stable upto 140°C were prepared by Ding et al. [99,100]. Room temperature conductivities of these polymers complexed with lithium salts were reported as close to 1.38 × 10⁻⁴ S cm⁻¹ at [EO]:[Li⁺] ratio of 15.5 [101].

Flexible polymers such as polysiloxanes (PS) [97,102], and polyphosphazenes (PPhz) [98,103] with different lengths and mixtures of etheric side chains were also used as polymer backbones. In the case of the PPhz-based block



Fig. 2. Chemical structure of aza-ether anion receptors [93].

polymers, the $-P=N-$ group (see Table 2) did not participate in the coordination of the cations, and thus helped to enhance the ionic conductivity of the electrolyte [98]. Enhancement of conductivity was also observed in the completely amorphous block copolymer, prepared by Nagoka et al., consisting of dimethyl siloxyl units in between medium length poly(oxyethylene oxide) units [104].

The room temperature conductivities of poly(bis-(methoxyethoxyethoxy)phosphazene (MEEP)_n-based polymers with LiX salts were found to be between 10^{-6} and 10^{-5} S cm⁻¹ [15]. The complexes were soft solids with an exception of LiAlCl₄ complexes giving mechanically sta-

ble free-standing films [105]. In the latter case, the conductivities were low and much depended on the salt concentration. Highly dimensionally stable polymer electrolytes were formed when bis-2(2-methoxy ethoxy) phosphazene (MEEP) was blended with a mechanically stable polymer such as PEO [105,106]. A conductivity value of 6.7×10^{-5} S cm⁻¹ at 25°C was reported for the fully amorphous 55 wt.% MEEP-45 wt.% PEO-(LiTFSI) complex [105]. This was three orders of magnitude higher than the PEO alone systems (10^{-8} S cm⁻¹ at 20°C) [107]. The MEEP in the polymer was considered to act as a network around the PEO-salt complex resulting into a highly mechanically strong solid mixture. In a similar study, Allcock et al.

Table 2
Conductivities of some Solvent-free polymer complexes

Polymer System	Polymer Host	Repeat Unit	Polymer Electrolyte (example)	Conductivity (S cm ⁻¹), 20°C.
LINEAR				
PEO	Poly(ethylene oxide)	$-\text{[CH}_2\text{CH}_2\text{O]}_n-$	(PEO) ₈ -LiClO ₄	10 ⁻⁸
POM	Poly(oxyethylene)	$-\text{[CH}_2\text{O]}_n-$	(POM) - LiClO ₄	10 ⁻⁸
PPO	Poly(propylene oxide)	$-\text{[(CH}_3\text{)CH}_2\text{CH}_2\text{O]}_n-$	(PPO) ₈ -LiClO ₄	10 ⁻⁸
POO	Poly(oxyethylene-oligo-oxyethylene)	$-\text{[(CH}_2\text{O)(CH}_2\text{CH}_2\text{O)}]_n-$	(POO) ₂₅ -LiCF ₃ SO ₃	3 x 10 ⁻⁵
Polysiloxane	Poly(dimethyl siloxane) (DMS)	$-\text{[(CH}_3\text{)}_2\text{SiO]}_n-$	DMS-LiClO ₄	10 ⁻⁴
Unsaturated Polymers (UP)	Unsaturated ethylene oxide-segmented	$-\text{[HC=CH(CH}_2\text{)}_4\text{O(CH}_2\text{CH}_2\text{O)}_n\text{(CH}_2\text{)}_4\text{]}_x-$ n = 3-5	UP-LiClO ₄ (EO:Li ⁺ = 32:1)	10 ⁻⁵
BRANCHED				
Comb branched ethers (PMEGE)	Poly[(2-methoxy)ethyl glycidyl ether)	$-\text{[CH}_2\text{CH}_2\text{O]}_n-$ CH ₂ (OCH ₂ CH ₂) ₂ OCH ₃	(PMEGE) ₈ -LiClO ₄	10 ⁻⁵
Comb-branched methacrylates (PMG _n)	Poly(methoxy poly(ethylene glycol) methacrylate	$-\text{[CH}_2\text{C]}_n-$ CH ₃ O ^o -O-(CH ₂ CH ₂ O) _x CH ₃	PMG ₂₂ -LiCF ₃ SO ₃ (EO:Li ⁺ = 18:1)	3 x 10 ⁻⁵
Block copolymers (cross-linked polymer networks)	(PEO-PPO-PEO)-SC SC=siloxane crosslinked	$\text{PEO-(CH}_2\text{)}_3\text{-Si(CH}_3\text{)}_2\text{-O-Si(CH}_3\text{)}_2\text{-(CH}_2\text{)}_3\text{-PEO}$ $\text{PEO-(CH}_2\text{)}_3\text{-Si(CH}_3\text{)}_2\text{-O-Si(CH}_3\text{)}_2\text{-(CH}_2\text{)}_3\text{-PEO}$	(PEO-PPO-PEO)-SC-LiClO ₄ (4:1 molar)	1.5 x 10 ⁻⁵
Polysiloxanes	PEO-grafted polysiloxane (PGPS)	$-\text{[SiO]}_n-$ CH ₃ CH ₂ CH ₂ PEO	PGPS-LiClO ₄	10 ⁻⁴
Polyphosphazenes (R ₂ P=N) _n	Poly[bis-2-(2-methoxyethoxy)ethoxy) phosphazene] (MEEP)	$-\text{[P=N]}_n-$ OCH ₂ CH ₂ OCH ₂ CH ₂ OCH ₃ OCH ₂ CH ₂ OCH ₂ CH ₂ OCH ₃	(MEEP) ₄ -LiBF ₄ (MEEP) ₄ -LiN(CF ₃ SO ₂) ₂ (MEEP) ₄ -LiC(CF ₃ SO ₂) ₂	2 x 10 ⁻⁵ 5 x 10 ⁻⁵ 10 ⁻⁴
POLYMER IN-SALT				
PPO	Poly(propylene oxide)	$-\text{[(CH}_3\text{)CH}_2\text{CH}_2\text{O]}_n-$	PPO-LiClO ₄ -LiBr-AlCl ₃	2 x 10 ⁻²

added small molecules comprising of cyclotriphosphazenes with linear or branched ethyleneoxy units to (MEEP)- LiCF_3SO_3 and observed higher conductivities than without the addition [108]. An increase in the conductivity was observed with increase in the small molecule concentration and was attributed to the ionic cross-linking by the small molecules leading to increase in the amorphous phase of the system.

Recently, new phosphazene-based polymer electrolytes consisting of poly(bis(pentylamino)phosphazene (PPAP) or poly(bis(hexylamino)phosphazene (PHAP) polymers complexed with LiClO_4 were prepared by ChenYang et al. [109]. Although, free standing films could be easily prepared from these polymer electrolytes, they showed poor room temperature conductivities of the order $10^{-7} \text{ S cm}^{-1}$.

Mechanical stabilities in polymer electrolytes were found in crosslinked polymer networks. Chemical cross-linking of low molecular weight PEO in presence of LiCF_3SO_3 or LiTFSM was done by Borghini et al. [110]. Conductivities were found to be improved with the addition of poly(ethylene glycol)dimethyl ether (PEGDME). Also networks mainly consisting of polyoxyethylene chains crosslinked via urethane [94] and siloxy linkages [111] were prepared. In a reverse case, crosslinking of PPhz via polyether linkages was done by Tonge and Shriver [112]. Rhee et al. prepared UV-cured polymer electrolytes by crosslinking polyethylene glycol diacrylates (PEGDA) and complexing with LiCF_3SO_3 salt [113]. The highest ionic conductivity at room temperature was reported as $1.7 \times 10^{-5} \text{ S cm}^{-1}$ for [EO]: $[\text{Li}^+]$ ratio of 8:1.

In general, the polymer networks were found to show maximum room temperature conductivities of the order of $10^{-5} \text{ S cm}^{-1}$, which were lower by about an order of magnitude as compared with materials before crosslinking [15].

Recent methods involving plasma-initiated polymerization have been used to obtain ultra thin films of polymer electrolytes with improved electrical properties [16,114]. Uniform, pin-hole free polymer electrolyte films have been deposited with a chemical gradient content along the film thickness [115]. Films of monomers doped with 10 wt.% LiCF_3SO_3 were plasma polymerized to obtain the polymer film, bis-[2-(2-ethoxyethoxy)ethoxy]methylvinylsilane (BEVS) with gradient in ionic conductivity [116]. The room temperature conductivity of the film at the top was found to be about an order of magnitude lower than that at the bottom indicating greater degree of crosslinking for the top side of the film which was proved by FTIR results.

As discussed above, compared with PEO-based polymer electrolytes, the room temperature conductivities in the modified 'dry solid polymers' were improved in many cases (see Table 2). However, linear and branched polymer electrolytes suffered from poor mechanical stabilities, whereas the networks showed poor ionic conductivities. The materials, therefore, could not be satisfactorily considered useful in lithium batteries.

3.2. Polyelectrolytes

In the polymer electrolytes both the anions and cations are mobile. By contrast, the polyelectrolytes comprise of charged groups covalently attached to the polymer backbone. This results in the free cation of being having long range ionic mobility. Sanchez et al. prepared a lithium salt of polyelectrolyte consisting of a perfluorosulphonated anion, a highly acidic group attached to the chain [117]. The acidic nature (high dissociation) and the flexibility of the anion on the chain (plasticising agent) promoted ion transport. The reported poor conductivities, of the order $10^{-5} \text{ S cm}^{-1}$ at 30°C , were attributed to the strong interaction of the lithium ion with the sulfonyl group.

Bannister et al. mixed an acrylate-based polyelectrolyte having pendant perfluorocarboxylate or sulfonate groups (Fig. 3a) with PEO [118]. The lithium ion conductivities reported at 100°C were of the order $10^{-5} \text{ S cm}^{-1}$. The lithium ion conductivities of PEO blended with a Nafion derivative shown in Fig. 3b, and prepared by Tsuchida and Shigehara, were an order of magnitude higher than those with the polymer shown in Fig. 3a at all temperatures [119].

Lithium ion transference numbers close to unity in the polyelectrolytes is expected due to the anion being attached to the polymer backbone. Kobayashi et al. reported lithium ion transference number of 1 in the copolymer of oligo(oxyethylene)mono-methyl ether (MEO) and lithium methacrylate [120]. The maximum ionic conductivities at room temperature for these materials were reported as in the order of $10^{-7} \text{ S cm}^{-1}$ for 15 mol% of the salt and were lower than that of the MEO- LiClO_4 complex itself ($3 \times 10^{-5} \text{ S cm}^{-1}$).

Ito et al. prepared polyelectrolytes consisting of lithium salts complexed with PEO oligomers ($M_w = 150\text{--}2000$) having sulfonate groups tied onto their chain ends (PEO- (SO_3Li^+)) [121]. The T_g of the polymer system was found dependent on the M_w of the PEO and amorphous phases were obtained below $M_w = 1000$. The room temperature conductivity for $\text{PEO}_{350}\text{-SO}_3\text{Li}^+$ was found to be $4.45 \times 10^{-6} \text{ S cm}^{-1}$ and a Li^+ transference number of 0.75. The conductivity of the electrolyte with PEO oligomers containing a sulfonate group only at one end was slightly higher than the one with both sulfonated ends (up to $M_w = 500$). Ito et al. also used benzene sulfonate groups (BSO_3) at the terminals of PEO and PPO oligomers [122]. A conductivity value of $2.95 \times 10^{-5} \text{ S cm}^{-1}$ at 50°C was reported for the $\text{PEO}_{550}\text{-BSO}_3\text{Li}^+$. Addition of PEO_{300} to

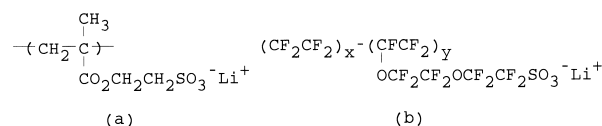


Fig. 3. Lithium ion conducting polyelectrolytes: (a) lithium poly(2-Sulphoethyl methacrylate) [118], (b) Nafion derivative 117 [119].

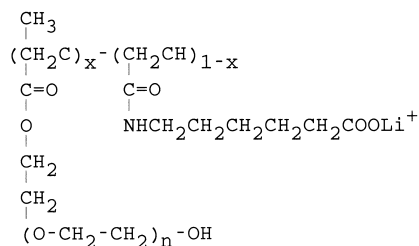


Fig. 4. Structure of poly(oligo-oxyethylene methacrylate-co-lithium acrylamidocaproate) [123].

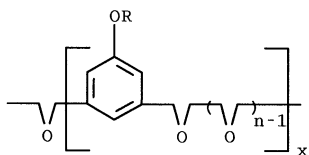
the $\text{PEO}_{350}\text{-BSO}_3\text{Li}^+$ was found to increase the conductivity 40 times than that in the $\text{PEO}_{350}\text{-BSO}_3\text{Li}^+$ [122].

PEO-based single Li^+ ion conductor, poly(oligo-oxyethylene methacrylate-co-lithium acrylamidocaproate) were prepared by Kim and Park (Fig. 4) [123]. They reported a maximum room temperature conductivity of $1.5 \times 10^{-7} \text{ S cm}^{-1}$ for an ionic content O/Li^+ of 30. From the glass transition temperature measurements on complexes with increasing cation size, they inferred ionic mobility to be mainly restricted by the ion-dipole interaction between the free cation and the PEO chain.

3.3. Others

Recently, Angell et al. studied new solid polymer electrolyte systems, called ‘polymer-in-salt’ systems in which the lithium salts of different anions were mixed with small quantities of the polymers, PEO and PPO [124]. The room temperature conductivities reported were as high as 0.02 S cm^{-1} for the mixture, $\text{AlCl}_3\text{-LiBr-LiClO}_4\text{-PPO}$. A difference in these high amount of salt containing systems from the conventional ‘salt-in-polymer’ systems is that the later have only one Li per about 10 repeat units of ether oxygens.

As discussed above and proved by NMR techniques [125], the ion-migration in polymer electrolytes has been widely accepted to take place through the amorphous phase of the polymer. In contrary to this, it was quite recently shown that in highly organized systems containing LiClO_4 complexes of the systems with general formula,



higher ionic conductivities were in line with degree of order. Unfortunately conductivity values ($10^{-6} \text{ S cm}^{-1}$ at 20°C) were poor for applications in lithium batteries [126]. Attempts to increase the degree of order, and hence conductivity are being pursued and ionic conductivities as high as $10^{-3} \text{ S cm}^{-1}$ at 60°C were recently observed in

systems incorporating space fillers in the side group [127]. These materials are termed as ‘low dimensional polymer electrolytes’ because of their two dimensional layered structure observed by X-ray analysis [126]. Since ion migration in these materials is restricted to one dimension, these materials were studied as highly stable Langmuir–Blodgett films deposited onto metal surfaces [128], and lithium salts were doped into the films similar to those in the bulk. The mechanical stability of such thin films and films prepared by solution casting seems sufficient for lithium battery applications.

Lauter et al. prepared similar materials in which the side chains consisted of oligo(oxyethylene) groups connected onto rigid rods of poly(*p*-phenylene) polymer [129]. These materials were found to complex with LiSO_3CF_3 and LiTFSI salts. X-ray analysis showed that the side chain matrix in the pure and complexed polymers was amorphous. Room temperature conductivities of the order $10^{-6} \text{ S cm}^{-1}$ were reported [129].

3.4. Electrochemical stability and electrochemical cells

As mentioned earlier, a polymer electrolyte is useful in a rechargeable lithium cell if it can withstand the potentials existing at the surface of the electrodes. The voltages of cathodes such as LiMn_2O_4 or LiCoO_2 are as high as 4.5 V, thus requiring the polymer electrolyte to be stable in the potential domain 0 and 4.5 V vs. Li^+/Li . In the case of polyether-based polymer electrolytes, stability upto 4 V vs. Li/Li^+ was observed [130,131]. As a function of temperature, $\text{PEO-LiCF}_3\text{SO}_3$ shows stability upto 3.77 V at 100°C , 3.30 V at 140°C , and 1.91 V at 170°C [132].

The following paragraphs discusses examples of the various electrochemical cells studied with the PEO-based solvent-free electrolytes comprising of lithium metal and lithium intercalation type electrodes, including the electroactive polymer electrodes. Cell properties such as specific energy, specific power, and coulombic efficiency are included in some of the examples.

From voltammetry studies at a platinum surface, the MEEP-based polymer electrolytes showed a stability window of over 4 V vs. Li/Li^+ [133]. Polymers comprising of blends of MEEP and PEO or PEDGA showed similar stability windows at stainless steel and gold electrode surfaces [105]. At a lithium metal surface, poly[bis(2,3-di-(2-methoxyethoxy)propoxy)phosphazene] (MEPP) was found to passivate the metal surface during cycling [134].

In a symmetrical cell $\text{Li}/(\text{PEO})_8\text{LiCF}_3\text{SO}_3/\text{Li}$ studied at 80° , Steele et al. observed a growth of a resistive passive layer at the electrolyte/electrode interface during storage of the cell [135]. The instability of the complexing salt LiCF_3SO_3 at the lithium metal electrode surface resulted into the passive film mainly consisting of lithium sulfite [136] and LiF [61]. The thickness of the film was found to be independent of the salt concentration [137]. Electrodes

consisting of lithium metal alloyed with metals such as Al and Sb, however, did not improve the interfacial stability of the salt [137].

A substitute for the lithium metal as a positive electrode is the intercalation type compounds which ideally should intercalate only lithium ions into their crystal lattices and co-intercalation of any anion would be a disadvantage to the reversibility of the electrode material structure. These electrodes are usually in the form of composites with the polymer electrolyte and a conductive filler such as carbon or acetylene black. The negative electrode is lithium metal, carbon, or an electrochemically active polymer.

PEO doped with lithium salts as a polymer electrolyte has been much investigated with lithium ion intercalation type positive electrodes such as V_6O_{13} [138,139], TiS_2 [140,141], and LiV_2O_5 [142]. Bonino et al. studied the cell, $Li/(PEO)_9-LiCF_3SO_3/V_6O_{13}$ and observed a voltage plateau of 2 V at current densities of around 1 mA cm^{-2} [138]. A practical specific energy of 200 W h kg^{-1} and specific power reaching 0.1 W g^{-1} were reported. Cycling of a similar cell was found to decline the electrode capacity due to increase in cell resistance resulting from morphological changes in the electrode [143]. The percentage utilization of the V_6O_{13} positive electrode in the cell $Li/(PEO)_8-LiCF_3SO_3/V_6O_{13}$ during cycling at 100°C was found to decline rapidly to around 55% in the first 10–20 cycles, thus giving only 100 cycles of performance [144]. From the studies of the cell $Li/(PEO)_8-LiCF_3SO_3/V_6O_{13}$ by Steele et al., it was concluded that PEO-based polymer electrolytes were suitable for operating temperatures of above 140°C , where appreciable capacity and electrode utilization could be obtained [135]. However, such high temperatures would be disadvantageous to the electrolyte because of its tendency to decompose.

West et al. investigated the cell $Li/P(EO)_{12}-LiCF_3SO_3/V_2O_5$ and observed lithium ion insertion of up to $2 \text{ Li}/V_2O_5$ at potentials above 1.5 V vs. Li/Li^+ [142]. At this depth of lithium insertion, the electrode was found to be stable, whereas at $1.8\text{Li}/V_2O_5$ the orthorhombic structure of V_2O_5 was found to collapse. The capacity retention of the electrode was not found satisfactory since only half the maximum capacity was available in the 20th cycle. Corrosion behavior of Al as a current collector was investigated by Chen et al. [139] in the cell, $Li/PEO-LiTFSI/V_6O_{13}$ who found Al to be more resistant to the polymer electrolyte than Cu or stainless steel. However pitting corrosion was observed in the Al after just 5 normal charge/discharge cycles at 100°C .

Cell studies using TiS_2 as a positive electrode were conducted by Gauthier et al. in the cells $Li/PEO-LiClO_4/TiS_2$, and $Li-Al/PEO-LiClO_4/TiS_2$. Cell voltages of about 1.8 and 1.4 V respectively were observed at about 80% of the electrode utilization at a C/8 discharge rate [140]. The cell delivered about 50% of the initial capacity at C/7 discharge rate [141]. Unfortunately, the cycle life of less than 100 cycles was poor for an en-

urable performance. However, changing the electrolyte from $PEO-LiClO_4$ to $MEEP-PEO-LiTFSI$, more than 200 cycles were obtained [105].

Mesocarbon microbead carbon was tested as a negative electrode material in combination with a Li metal positive electrode incorporating $P(EO)_8-LiClO_4$ as the polymer electrolyte [145]. A specific charge of 410 A h kg^{-1} for the carbon electrode was obtained. Using natural graphite carbon as the negative electrode in the same cell, a decrease in the specific charge was observed [145]. In the latter cell, the discharge/charge curves were flat [146], whereas those with mesophase pitch carbon fibers showed high slopes [145] with increasing voltage hysteresis between charge and discharge [147]. For comparison, Yazami and Deschamps showed the non-graphitized mesocarbon micro beads to give higher capacity than the graphitized one in the $C/P(EO)_8-LiClO_4/Li$ cell [55]. In the case of mesophase carbon fibers, the total relative amount of the lithium ion exchanged with the polymer electrolyte was found to increase with the crystallinity of the carbon fibers [148].

In the field of electrochemically active polymers as electrode materials, Novak et al. constructed a $Li/PEO-LiClO_4/PPy$ cell (PPy used as a composite with $PEO-LiClO_4$). They reported a specific energy of 55 W h kg^{-1} (based on weight of the composite electrode) and a coulombic efficiency of 92–99% [149]. In comparison with liquid electrolytes (typically 390 A h kg^{-1} with propylene carbonate/ $LiClO_4$) the specific charge of PPy was lower when polymer electrolytes such as $PEO-LiClO_4$ were used [150]. Cycle life of about 170 cycles at 60% depth of discharge was observed for the above $Li/PEO-LiClO_4/PPy$ cell [149]. Typically, PPy-PEO composite electrodes have shown cycle lives as high as 700 cycles [151]. Osaka et al. reported a cycle life of 1400 cycles for a similar cell at 80°C incorporating $P(EO)_{8-20}-LiClO_4$ as the electrolyte [152].

Self discharge of PEO-based Li/PPy cells is usually high [153], although capacities could be restored with subsequent charge [152,153]. At an operating temperature of 85°C , cells with PPy-PEO composite electrode and $PEO-LiClO_4$ electrolyte lost 50% of its charge within 4 h, and was completely discharged within a day [149]. But as the temperature was decreased, self discharge was slowed down [154]. Unfortunately, the lowering in operating temperature of the cell reduced the PPy electrode utilization [154]. The reason for the self discharge to be rapid at elevated temperatures was considered to arise from the mobility of the redox species formed at the $Li/PEO-LiClO_4$ interface [154]. In support of this, Armand et al. observed the formation of basic, nucleophilic species at the interface place resulting from reaction of lithium metal with the $PEO-LiClO_4$ electrolyte which further reacted with the radical cations of the PPy polymer [155]. Some improvements in self discharge at room temperature for the cell using poly(N-oxyalkylpyrrol) positive electrode and a

PEO-modified-LiClO₄ electrolyte was seen in which the cell lost 35% of its charge during storage of one week [156].

Some interesting results were observed with Li/P(EO)₂₀-LiClO₄/poly(bithiophene) (PBT) cell which showed about 300 life cycles operating at 70°C [157]. A doping level of 0.17 was attained in the PBT. Based on the weight of the PBT, a specific charge of 56 A h kg⁻¹ was obtained. Self discharge of this cell at 20°C was negligible (for a month test) but was high at an operating temperature of 70°C where conductivity of the solid electrolyte is known to be appreciable above its melting point (~60°C) [157]. At 70°C, the cell rapidly discharged from 3.7 to 3.35 V within 140 h and completely within a day [158].

Positive electrodes consisting of sulfur-containing polymers, for example those shown in Fig. 5, have been widely investigated with PEO-based electrolytes. Deggott used P(EO)₈-LiClO₄ electrolyte in combination with (CS)_n or (CS_x)_n as the positive electrode (P(EO)₈-LiClO₄ included) and Li metal as the negative [159]. A specific charge of 175 A h kg⁻¹ was obtained for the (CS)_n electrode, whereas the (CS_x)_n electrode gave specific charge of 310 A h kg⁻¹ and specific energies of 630 W h kg⁻¹ (*x* = 0.25) and 970 W h kg⁻¹ (*x* = 0.75). The cycling performances of this cell was poor. From the initial charge of 175 A h kg⁻¹ (based on weight of (CS)_n), only 100 A h kg⁻¹ was available in the second discharge after recharging with 745 A h kg⁻¹. Lower open circuit potentials were observed after the first discharge/charge cycle [159].

A cell Li/P(EO)₂₀-LiCF₃SO₃/McEE studied by Doeff et al. gave 120 A h kg⁻¹ and 240 W h kg⁻¹ of specific charge and specific energy respectively [160]. Changing the positive electrode from McEE to DMcT, the respective values were 110 A h kg⁻¹ and 330 W h kg⁻¹ [160]. Replacing the positive electrode McEE with EDT, increase in the specific charge (170 A h kg⁻¹) and specific energy (350 W h kg⁻¹) were observed [161]. Interestingly, utilization of the EDT electrode during discharge was high in thick cathode films and compared with DMcT and EDT electrodes, McEE showed poorest utilization [160]. The polymer EDT was highly insensitive to overcharging [160].

When used with the polymer electrolyte P(EO)₈-LiTFSI, the cell Li/DMcT (DMcT used in the form of a composite film with C and P(EO)₈-LiTFSI) operating between 77–93°C gave specific energy of 264 W h kg⁻¹, and specific power of 160 W kg⁻¹, and cycle life was about 350 cycles [161]. Maximum current densities of 250 μA cm⁻² were observed at 20°C. Cell operation at 100°C improved the

specific power (2400 W kg⁻¹), but reduced the specific energy (200 W h kg⁻¹) [162]. The DMcT electrode utilization was found to be strongly dependent on temperature (38% at 50°C, 75% at 93°C. and 96% at 100°C) [163]. Interestingly, the cells based on the DMcT cathodes were found insensitive to overcharge and overdischarge [6]. During discharge, the DMcT was found to undergo two stages, polymer to dimer and dimer to dithiolate monomer [162].

Paper-thin film type Li/PEO/DMcT cell was constructed with a PEO amorphous type electrolyte (poly(ethylene) glycol with oxymethylene links) [164]. An 80% DMcT utilization and specific energy of 140 W h kg⁻¹ was shown possible. A 30 W l⁻¹ power density was observed in a continuous discharge. The cells were found to recover rapidly from accidental overcharge and overdischarge and a maximum of 100 cycles were obtained.

3.5. Summary

In the first example of ‘dry solid’ polymer electrolytes, the PEO-based systems showed very low room temperature conductivities of the order of 10⁻⁸ S cm⁻¹. The PPO- and MEEP-based electrolytes showed some improvements, with increase in conductivities to 10⁻⁵ S cm⁻¹. However, branching of the linear polymers did not show drastic improvements in conductivities (between 10⁻⁵ and 10⁻⁴ S cm⁻¹), although the structures had much reduced crystallinity. Most of these systems, with improved conductivities, suffered from poor mechanical stabilities. A drastic increase in mechanical properties was observed when the branched polymers were cross-linked to form polymer networks, but showed slightly lower conductivities than their counterparts. In attempts to minimize the anion migration in the polymer electrolytes, polyelectrolytes with attached anion groups were prepared. Although the lithium ion transport number was close to unity in these systems, conductivities were only of the order 10⁻⁵ S cm⁻¹, which were mainly attributed to the polymer structures. More recently, the ‘polymer-in-salt’ type electrolytes have shown promising room temperature conductivities of the order 10⁻² S cm⁻¹, but unfortunately incorporate corrosive salts. Improvements in the salt combinations are needed, at the same time retaining the conductivity and mechanical properties. Present interest has been focussed on highly crystalline systems, similar to biological molecules, which allow migration of ions through channelized spaces within the molecular structure. The room temperature conductivi-

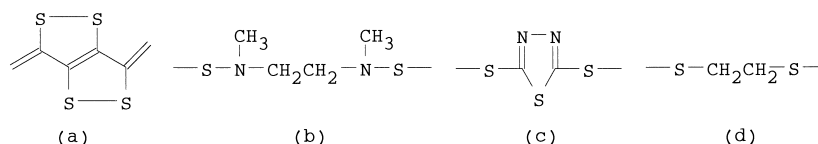


Fig. 5. Structure of monomer units of electroactive polymers used in lithium cells: (a) carbon-sulfur polymer (CS), (b) bis(2-mercaptoethyl) ether polymer (McEE), (c) dimercaptiothiadiazole polymer (DMcT), (d) 1,2-ethanedithiol (EDT) polymer.

ties of these systems are low (order of 10^{-5} S cm $^{-1}$), but values close to 10^{-3} S cm $^{-1}$ are expected with structural modifications.

The performances of electrochemical cells incorporating the ‘dry solid’ polymer electrolytes and lithium metal electrodes were not satisfactory, and cycle lives were as low as 200 to 300 cycles. The poor performance of the cells was mainly attributed to the poor conductivity of the electrolytes, along with the reactivity of the anion of the electrolyte towards the lithium metal electrodes. Thus, a search for stable and more environmentally friendly anions is seen necessary. Nevertheless, some promise in the performance of electrochemical cells has been shown by the intercalation type electrodes and polymer electrodes. Improved cycle lives as high as 1000 cycles, in the case of PPy as the cathode material have been reported. With cells operating at about 75°C, specific energy and specific power of around 250 W h kg $^{-1}$ and 170 W kg $^{-1}$ respectively have been shown by cells comprising of sulfur containing polymer electrodes.

4. Polymer gels

4.1. Introduction

In 1975, Feuillade and Perche demonstrated the idea of plasticizing a polymer with an aprotic solution containing an alkali metal salt in which the organic solution of the alkali metal salt remained trapped within the matrix of the polymer [165]. Such mixings have resulted into formation of gels with ionic conductivities close to those of the liquid electrolytes, arising from similar conductivity mechanisms

taking place in both the systems. However, one would expect slightly lower conductivities in the polymeric gels, if more viscous solvents are used, as compared to those used in the liquid electrolytes.

Since then, various polymeric hosts such as, poly(vinylidene fluoride) (PVdF) [166], poly(vinylidene carbonate) (PVdC), poly(acrylonitrile) (PAN) [167,168], poly(vinyl chloride) (PVC) [169], poly(vinyl sulfone) (PVS) [170], poly(*p*-phenylene terephthalamide) (PPTA) [171], and poly(vinyl pyrrolidone) (PVP), have been found to form electrolytes with conductivities ranging between 10^{-4} and 10^{-3} S cm $^{-1}$ at 20°C (Table 3) [15]. These systems are presently expressed in various terms such as ‘plasticized polymer electrolytes’, ‘polymer hybrids’, ‘gelionics’ and ‘gel electrolytes’. The electrolytes are easily prepared by heating a mixture containing the appropriate amounts of the polymer, solvent(s) and a lithium salt to about 120–150°C, a temperature above the glass transition temperature of the polymer, to form viscous clear liquids. Films of the gels are usually made by solution casting in hot state allowing the solution to cool under pressure of electrodes. Less-evaporating solvents, such as ethylene carbonate (EC), propylene carbonate (PC), dimethyl formamide (DMF), diethyl phthalate (DEP), diethyl carbonate (DEC), methylethyl carbonate (MEC), dimethyl carbonate (DMC), γ -butyrolactone (BL), glycol sulfite (GS), and alkyl phthalates have been commonly investigated as ‘plasticizer’ solvents for the gel electrolytes [15,172]. The solvents have been used separately or as mixtures.

The phenomenon of plasticization was found to increase the amorphous phase in the polymer system with a single glass transition temperature as low as -40°C , the latter

Table 3

Ionic conductivities of some gel polymer electrolytes and polymer composite electrolytes. Dimensionally stable gels consisting of PEG–PAN–PC–EC–LiClO $_4$ were prepared by Munichandraiah et al. [197]. Compared with gels PEO–PC–LiClO $_4$ and PAN–PC–EC–LiClO $_4$, the PEG containing gels showed lower room temperature conductivities, but higher mechanical stabilities

Polymer system	Polymer host	Polymer electrolyte	Conductivity (S cm $^{-1}$), 20°C
Plasticized			
Linear PEO	poly(ethylene oxide)	(PEO) $_8$ -LiClO $_4$ (EC:PC, 20 mol%)	10^{-3}
Crosslinked PEO	poly(ethylene oxide)	(PEO) $_8$ -LiClO $_4$ (PC, 50 wt.%)	8×10^{-4}
PVdF	poly(vinylidene fluoride)	PVdF-LiN(CF $_3$ SO $_2$) $_2$ (EC:PC, 75 wt.%)	1.5×10^{-3}
PEGA	poly(ethylene glycol acrylate)	PEGA-(LiClO $_4$:PO, 1 M)	10^{-3}
PEI	poly(ethylene imine)	PEI-LiClO $_4$	10^{-3}
PPTA	poly(<i>p</i> -phenylene terephthalamide)	PPTA-(PC:EC: LiBF $_4$, 25:25:0.8 mol%)	2.2×10^{-3}
Acrylates			
	ethylene glycol dimethacrylate (EGDMA)	EGDMA-(LiClO $_4$:PC, 1M)	2×10^{-3}
PAN	poly(acrylonitrile)	PAN-(EC:PC:LiClO $_4$), 38-33:21:8 mol%	10^{-3}
Composites			
Glass polymer composites		(0.564Li $_2$ S – 0.19B $_2$ S $_3$ – 0.25Li)-((PEO) $_6$ -LiN(CF $_3$ SO $_2$) $_2$) (18:13 vol.%)	10^{-4}
Gel polymer composites		PAN-(PC:EC:LiAsF $_6$)-zeolite	10^{-2}
Nanocomposites (ceramic composites)		(PEO) $_8$ -LiBF $_4$ -alumina (10% wt)	10^{-4}
Nanocomposites (ceramic composites)		PEG $_{200}$ -LiCF $_3$ SO $_3$ -silica, 20% wt.	1.5×10^{-3}

varying with the amounts of solvent and polymer containing in the gels. It was generally observed that upto 80% of solvent could be trapped into the polymer matrix. The high permittivity solvents allowed a greater dissociation of the lithium salt and increased the mobility of the cation. Much research work in the area of gel electrolytes can be found in literature reviews [15,79,173].

4.2. PEO-based gels

Plasticization of high molecular weight $\text{P(EO)}_n\text{-LiX}$ electrolytes with PC and/or EC was found to form soft solids with poor mechanical stabilities, although room temperature conductivities as high as the order of $10^{-3} \text{ S cm}^{-1}$ were obtained [174,175]. The poor mechanical stability was accounted to be mainly due to the solubility of the PEO in the solvents [175].

Cross-linking of polymers by methods such as, UV [176], thermal radiation [177], photo-polymerization [178], and electron beam radiation polymerization [179] was found to reduce the solubility of the polymers with the organic solvents and also helped to trap the liquid electrolyte within the polymer matrix. Low molecular weight PEO was cross-linked and plasticized with 50% PC by Borghini et al. [110]. This material showed good mechanical properties and conductivities of the order $10^{-4} \text{ S cm}^{-1}$ at 20°C were two orders of magnitude higher than the unplasticized amorphous cross-linked PEO-LiClO_4 complex. In general, the room temperature conductivities of gels based on polymers and copolymers prepared by crosslinking methods were found to be in the range of $10^{-5} - 10^{-4} \text{ S cm}^{-1}$ [110].

Plasticizers such as dioctyl-, dibutyl-, and dimethyl-phthalate were recently investigated for PEO-LiClO_4 complexes [180]. In comparison with the three plasticizer-based systems, lowest crystallinity in the gel containing the dioctyl phthalate (DOP) was observed showing the best room temperature conductivity of $9.67 \times 10^{-5} \text{ S cm}^{-1}$ for the composition $(\text{PEO})_8\text{-}(\text{LiClO}_4\text{:DOP}, 99.9\text{:}0.1 \text{ wt.}\%)$. However, the room temperature conductivities of the complexes containing the dibutyl phthalate and the dimethyl phthalate were slightly lower than those containing the DOP plasticizer.

4.3. PAN- and PVDF-based gels

The PAN-based [181–183] and PVdF-based [184] gel electrolytes are the most widely investigated polymer gel electrolyte systems and remarkable conductivities of the order of $10^{-3} \text{ S cm}^{-1}$ at 20°C have been obtained. A fully amorphous gel of PAN-LiClO_4 (1:0.2) in EC showed room temperature conductivity of $1 \times 10^{-3} \text{ S cm}^{-1}$ and an estimated activation energy of 86 kJ mol^{-1} [185]. Because of the absence of any oxygen atoms in the PAN polymer matrix, the PAN-based gels were found to have lithium ion transference numbers greater than 0.5 [186]. With a greater dissociation of salts such as, LiTFSI and LiTFSM in

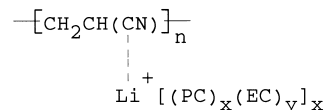


Fig. 6. Probable interaction of the lithium ion in gel electrolytes [188].

PAN-based gels, transference numbers as high as 0.7 could be obtained. The delocalization of electron density around the large organic anions in the salts is believed to promote greater dissociation and increase the transference number.

Strong polar groups in the polymer are undesirable because of the complexation of lithium ion by both the polymer matrix and the solvent [187]. A probable interaction of the lithium ion with the polymer chain and the solvent is shown in Fig. 6 for a PAN-based gel system [188]. Thus, the polymer in the gel electrolytes would mainly act as an encapsulating matrix with electrostatic interactions with the solvated lithium salt so that the lithium ion mobility is least hindered.

Yang et al. [185] studied a $\text{PAN-LiClO}_4\text{-DMF}$ gel in order to understand the interaction of the Li^+ ions with the PAN chain. Using FTIR they showed the Li^+ ions to form bonds with C=N groups of the PAN as well as C=O of the DMF which would support the structure in Fig. 6. Using the same technique, in $\text{PAN-LiClO}_4\text{-DMF}$, Wang et al. reported interactions between Li^+ ions and the oxygen and/or nitrogen atoms of DMF along with interactions between the O atoms of DMF and N atoms of the nitrile of PAN [189]. Unfortunately, no interactions between LiClO_4 and PAN could be detected with the use of the FTIR technique.

Jiang et al. recently studied PVdF-based gels consisting of EC, PC and a LiX salt [190]. As expected they found the presence of plasticizers EC and PC to significantly disorder the crystalline structure and reduce crystallinity in the gels than in the parent polymer host, PVdF. They also reported the mechanical strength of the resulting gel to be depended on the PVdF content, whereas the conductivity to be mainly influenced by the viscosity of the medium and the concentration of the lithium salt. Room temperature conductivities as high as $2.2 \times 10^{-3} \text{ S cm}^{-1}$ for the $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ salt containing mixture were reported [190].

Increase in gel properties were observed when mixtures of polymer hosts or copolymers were used in the gel preparation. Increase in gel properties were observed for PVdF co-polymerized with hexafluoropropylene (HFP). The PVdF-HFP co-polymer in the gel showed greater solubility for organic solvents, and lower crystallinity and glass transition temperature than the PVdF polymer alone in the gel [191].

4.4. Others

Wieczorek and Stevens studied blends consisting of a polyether, PMMA, and LiCF_3SO_3 [192]. The electrolytes showed a maximum room temperature conductivity of

$3 \times 10^{-5} \text{ S cm}^{-1}$. Morita et al. also prepared gels consisting of PMMA grafted with PEO and containing Li salts, and room temperature conductivities of the order 10^{-3} were reported [193]. Addition of crown ethers such as 12-crown-4 and 15-crown-5 to the PMMA-PEO-Li⁺ gel was found to increase the conductivity to some extent, whereas the Li ion mobility was found to increase significantly with the addition of the 15-crown-5 ether [193]. Lithium transference numbers greater than 0.5 were found in the gel electrolytes based on poly(methyl methacrylate) [194] and poly(tetrahydrofuran) [195]. The values were found to be dependent on the amounts of organic solvent present in the gel.

Blends of polymers, PVC and PMMA were studied using PC as the plasticizer and LiCF₃SO₃ as the salt [196]. Due to insolubility of PVC in the solvent PC, phase separation was observed. The inclusion of PVC into PMMA helped to increase the mechanical stability of the gel, but unfortunately decreased the lithium ion conductivity. The ions were found to preferentially move towards the plasticizer-rich phase or the PMMA-rich phase.

Dimensionally stable gels consisting of PEG-PAN-PC-EC-LiClO₄ were prepared by Munichandraiah et al. [197]. Compared with gels PEO-PC-LiClO₄ and PAN-PC-EC-LiClO₄, the PEG containing gels showed lower room temperature conductivities, but higher mechanical stabilities.

PVC-based electrolytes consisting of LiClO₄, LiTFSM, or LPF₆ salt and THF/PC mixture as plasticizer gave ionic conductivity of the order $10^{-4} \text{ S cm}^{-1}$ at 20°C with respective lithium ion transference numbers of 0.26, 0.40, and 0.45 [198]. Polymer gels consisting of PVC, LiTFSI, and solvents such as dibutyl phthalate (DBP) and dioctyl adipate (DOP) gave room temperature conductivities of the order $10^{-4} \text{ S cm}^{-1}$ [199].

Low molecular ethers such as poly(ethylene glycol) dimethyl ether (PEGDME) was used as a solvent for salts such as LiN(CF₃SO₂)₂, LiCF₃SO₃, and LiPF₆ to which poly(vinylidene fluoride)-hexafluoropropene copolymer was added as the encapsulating polymer matrix [200]. PEGDME was also added to a copolymer formed from triethylene glycol dimethacrylate (TRGDMA) and acrylonitrile (AN) and LiCF₃SO₃ salt. Room temperature conductivities in the range from 10^{-5} to $10^{-4} \text{ S cm}^{-1}$ were reported [201]. The conductivity was found to increase in line with the molar ratios of both AN:TRGDMA and (EO):LiCF₃SO₃ [201].

In the gel mixture consisting of poly(*p*-phenylene terephthalamide) (PPTA), polyethylene glycol (PEG), polycarbonate in PC-EC, and a lithium salt, conductivities as high as $2.2 \times 10^{-3} \text{ S cm}^{-1}$ at room temperature were observed at 0.8 M LiBF₄ salt per mole of PPTA content [171]. Above 1 M of the salt content, the conductivity was found to fall rapidly suggesting the ion conductivity to be due to LiBF₄ interaction at the amide bond sites of the PPTA [171].

In the gel electrolytes, ion pairing and ion aggregation are expected to take place similar to the systems without the presence of any organic solvent, although the effect would seem to be less in gels due to greater dissociation of the ions in presence of the solvents. Drogowska and Fawcett found the probability of ion pairing was greater in solvents with higher dielectric constant [202]. For example, LiAsF₆ ion pairing and triple ion formation was greater in 2-methyl tetrahydrofuran than in tetrahydrofuran (THF) [187]. Ion aggregation was also observed in plasticized polyelectrolytes studied by Kim et al. [203]. In a tough gel mixture of poly(methyl methacrylate co-lithium methacrylate), LiClO₄, and EC showing room temperature ionic conductivity of the order of $10^{-3} \text{ S cm}^{-1}$, the ion aggregation was considered to be responsible for the non-VTF behavior of temperature dependence on conductivity.

4.5. Electrochemical stability and electrochemical cells

A main disadvantage of gel electrolytes in lithium batteries is the tendency of their constituent organic solvents to react at lithium metal surfaces. Dominey has made an excellent comparison of the stabilities of various solvents and their mixtures in the presence of lithium salts and polymers as a means to establish stability windows for polymer electrolytes for applications in lithium batteries [187]. In his report, a few general remarks have been made. The stability range of the solvent and the polymer electrolyte are responsible for the lithium metal stability. Highly polar solvents such as PC or EC easily get decomposed at the lithium metal surface. However, in combination with less polar solvents such as DMC, stability increases drastically. Presence of any contaminant in solvents like 2-methyl THF reduces the reactivity of the solvent. Acetonitrile and higher nitriles are reported as not suitable in presence of lithium metal anode because of their high reactivity with the metal which initiates polymerization of the organic solvent [187]. Because of the high polarity of the solvents EC and PC, they have been much considered as plasticizers in gel electrolytes for lithium and lithium-ion battery studies, especially in the later type where the highly reactive lithium metal is replaced by the intercalation type electrodes.

Here, we describe some of the electrochemical cells investigated using the gel electrolytes. A Li/PEO-(EC, LiClO₄)/PAni cell investigated by Lang-sheng et al. performed for more than 250 cycles at 80% dept of discharge [204]. A specific charge of 48 A h kg⁻¹ based on the weight of the polymer electrode and coulombic efficiency of 98% for the PAni electrode were reported. However, the specific energy was only about 50 W h kg⁻¹ based on the weight of the polymer electrode [204]. The open circuit potentials of the cell and cells based on PAni cathode were mainly dependent on the method of synthesis of the PAni and its pretreatment [205].

The Li/V₆O₁₃ cells, based on PEO-gels, showed poor performances [206]. However, the addition of carbon dioxide into the electrolyte was effective in increasing the cycling efficiency to greater than 98% from about 80% [207]. The dendrite formation onto lithium anodes was reduced when CO₂ was passed through a PEO-based gel electrolyte before lithium was electro-deposited by a continuous cycling method [208]. The authors observed the decomposition products of CO₂ to form a protective layer on the metal surface and the presence of deposited polymer matrix was effective in suppressing the growth of dendrites [208]. The dendrite formation was also found to be reduced when thin films of the lithium metal were deposited by thermal vapor deposition onto the electrolyte [209].

A plasticized crosslinked random copolymer made of ethylene oxide and propylene oxide was studied by Aihara et al. in a 0.45-mm thick graphitized carbon/LiCoO₂ cell [210]. The cell was found to have an average voltage of 3.6 V and a discharge capacity of about 100 mA h. In a 0.3 C cycle test at room temperature, the battery showed capacity retention of about 90% of the initial capacity for 300 cycles.

PAN-based gel electrolytes have been widely investigated for lithium and lithium-ion battery applications since they show a wide electrochemical window of more than 5 V vs. Li/Li⁺ [186]. A window of 4.6 Volts vs. Li/Li⁺ was observed for PAN-EC-LiTFSI gel (82-9-9 wt.%). The LiTFSI salt in the gel was found to degrade at LiNiO₂ and LiCoO₂ cathodes, whereas the LiPF₆ salt was found to be stable [186].

PAN-EC-PC-LiTFSI electrolyte was incorporated in the cell, C/LiNiO₂ and test results at 0.25 mA cm⁻² showed a mid-discharge voltage of 3.0 V, specific energy of 337 W h kg⁻¹ and a coulombic efficiency close to 100% over 120 cycles [211].

Kakuda et al. studied PAN-LiClO₄-based gels in a Li/PPy cell. A poor shelf life for the cell was observed and was mainly attributed to the electrochemical instability of the electrolyte at the PPy cathode surface [212]. However, the morphology of the PPy electrode did not influence the charge/discharge cycling characteristics of the cell. A coulombic efficiency close to 90% was reported.

Using PAN:EC:LiTFSI as the electrolyte, the cell Li/PPy showed good cycleability at 0.3 mA h cm⁻² over 1200 cycles [186]. However, passivation at the lithium metal electrode was observed in which the type of lithium salt and salt concentration were directly responsible for the cycling behavior.

Passivation at lithium metal anode was observed for Li/LiCoO₂ cells consisting of PAN-EC-LiClO₄ (1:0.2) [213]. The internal resistance of the cell was dominated by the passive layer formed at the lithium/electrolyte interface.

Appetecchi et al. investigated cells, Li/LiCr-Mn₂O₄ and graphite/LiCr-Mn₂O₄ containing PAN-EC-PC-LiClO₄

as the gel electrolyte [214]. The capacity loss in the former cell was found to be less than 50% of the initial value for more than 1000 cycles, whereas in the latter cell, charge/discharge efficiency was close to 100% after the second cycle for about 1200 cycles. Large irreversible capacity losses were observed for both the cells in the first cycles due to passivation at the anode surface. In another study, the cell coke/PAN-EC-PC-LiTFSI/LiNiO₂ showed performance over 1000 cycles at 1.0 mA cm⁻² [215].

Recently, glycol sulfite (GS) was investigated as a new plasticizers for PAN-based gels [216]. During cycling of test cells, graphitized carbon fiber/PAN-LiClO₄ gel/LiMn₂O₄, the cell with gel containing GS showed much less capacity loss than that without the GS, although capacity loss due to decomposition of GS in the first cycles was found to be substantial [216].

The reversibility of the lithium ion in carbon-based anodes is shown to be related to the nature of plasticizer in the gel polymer electrolyte. For example, ethylene carbonate (EC) was found to be a more satisfactory plasticizer as it did not co-intercalate with lithium ions, unlike PC which was found to co-intercalate into graphite and destroy its structure (exfoliation), thus reducing the capacity of the anode during cycling [217]. It has been generalized that the capacity loss upon cycleability in cells containing the intercalation type electrodes is mainly attributed to the irreversibility of the intercalation reaction leading to degradation of the cells [218].

Alamgir et al. studied the cell PPPP/PAN-EC-LiClO₄/Li, where PPPP is pyrolyzed poly(*p*-phenylene) and reported specific charge of 610 A h kg⁻¹ and a coulombic efficiency of 99% [219]. However, a pronounced plateau of irreversible capacity was seen during first charge. Charging curves of subsequent cycles were smooth, but discharge curves of all cycles were sloping.

The presence of γ -butyrolactone (BL) in PAN-EC/PC-LiClO₄ showed increase in the electrochemical stability window from 4.3 to 5.8 V vs. Li/Li⁺ as compared with the system without the BL solvent [220]. A Li/LiMn₂O₄ cell containing the PAN-EC/PC/BL-LiClO₄ electrolyte showed more than twice the capacity than the cell without BL in the electrolyte, at -20°C with cycle life of more than 500 cycles at C/10 discharge rate [220]. Interestingly, at the end of the 500 cycles, the capacity loss was less than 50% of its initial value. Unfortunately, decline in the discharge voltage along with a gradual capacity loss was observed. Passivation at the lithium metal anode was found to take place after about 200 cycles resulting into increase in the interfacial resistance as measured by impedance spectroscopy [220].

The gels with electrochemical stability of 4.5 V vs. Li/Li⁺ comprising of PEG-PAN-PC-EC-LiClO₄, PEO-PC-LiClO₄ and PAN-PC-EC-LiClO₄ showed comparable lithium metal interfacial stabilities [197], whereas similar PVC-based cells were found to passivate lithium electrode at cycles as low as 22 cycles [221].

In the cells studied by Sureshini et al. based on PVC incorporating LiTFSI salt and DBP or DOP as plasticizing solvents, at 60°C, the stability domain of the electrolyte was found to be limited by the cathodic deposition and stripping processes of lithium and anodic oxidation of the polymer [199]. Both the electrode processes were related to the reaction of the plasticizers with the metallic lithium. PVC-based cells were also studied by Alamgir and Abraham [169]. A voltage window of ~ 4.5 V vs. Li electrode was obtained for Li/20%PVC–75%PC–5%LiClO₄/stainless steel system. However, passivation of lithium onto stainless steel (current collector) was observed after repeated cycles [221]. The performances with lithiated oxides seemed satisfactory (see Table 4).

Compared with PAN-based gels, the poly(methyl-methacrylate) (PMMA)-based gel electrolytes were found to have better interfacial properties towards the lithium electrode [222,183]. In the cell Li/PMMA gel/PPy, the PMMA/Li interfacial instabilities over storage time were found to gradually affect the discharge capacity of the cell [223]. However, in its overall performance, the cell showed more than 90% coulombic efficiency and constant discharge capacities for more than 1000 cycles. At high current densities, no dendrite formation at the lithium electrode was observed [223].

Oyama et al studied cells having lithium anodes and redox composite cathodes comprising of 2,5-dimercapto-1,3,4-thiadiazole (DMcT) and poly(aniline) (PAni) [224] or Cu(ClO₄)₂ [225,226] cathodes with acrylonitrile-methacrylate copolymer (AN/MA)-EC-PC-LiBF₄ as the gel electrolyte. The gel electrolyte was incorporated into the electrode composite ($\sim 230\%$ relative to DMcT). Using 25% PAni with DMcT, specific energies of more than 830 W h kg⁻¹ were observed and were reversible for more than 80 charge/discharge cycles at cathode specific charge of up to 300 A h kg⁻¹ [224,227]. Test cell, Li/AN/MA-EC-PC-LiBF₄/DMcT-(PAn or Cu) gave stable charge/discharge characteristics at 0.4 mA cm⁻² at operating temperatures of 0°C, 20°C, and 60°C [228]. A similar cell with gel electrolyte comprising of 20:1 acrylonitrile-methacrylate copolymer with LiCF₃SO₃ gave cathode specific energy of 303 W h kg⁻¹ at 0.1 mA cm⁻² discharge

[229]. Using carbon instead of PAni, the cathode specific energy fell to 235 W h kg⁻¹ at a discharge of 0.1 mA cm⁻².

The presence of LiBF₄ salt in the gel electrolyte in cell Li/DMcT-PAn (or C) has been found to increase current densities and cycle lives [230,231]. Addition of a substituted pyrrole polymer into the cathode composite improved the charging rate but did not affect the discharge rate capability [231]. The degradation of the electrode during cycling was slowed down with higher contents of PAni and C. The presence of *N*-methyl-2-pyrrolidone in the cathode composite (used during film casting of DMcT-PAni cathode and believed to have remained in the final cathode composite) showed large improvements in specific energy of the electrode [232]. Specific energies as high as 700 W h kg⁻¹ have been predicted from experimental evidence of cells based on Li anode and DMcT/PAni cathode [233].

The PVdF-PC-EC-LiX gels studied by Jiang et al. showed anodic stability up to 4 V on Al, 4.2 V on Ni, and 4.5 V on stainless steel vs. Li/Li⁺, and the cathodic stability as low as 0 V on both Ni and stainless steel vs. Li/Li⁺ [190]. Passivation at the PVdF-PC-EC-LiX/Li interface was observed, the resistances of which fluctuated over time. The fluctuations were attributed to the morphological changes in the passivation layer [183,234]. The passivation was minimum in the case of PVdF-PC-EC-LiTFSI electrolyte.

The nature of the current collector has been shown to influence the oxidative stabilities of gel electrolytes. Using cyclic voltammetry on PVdF-LiI-EC-PC gels, greater stability on stainless steel (~ 4.5 V vs. Li/Li⁺) than on Ni (~ 4.2 V) and Al (~ 4.0 V) was observed suggesting electrode corrosion to contribute to the apparent stability limit of the gel [234].

Passive layer formation at lithium electrode surface was also observed in the case of PVdF-PC-EC-DMF-LiX gel electrolyte [184]. The addition of crown ethers such as 4-crown-4 and 5-crown-5 to gel electrolytes such as PEO-PMMA was found to suppress the passivation rate at the lithium electrode surface [235]. Similarly, suppression in the decomposition of PC at a lithium electrode surface was shown in presence of diethylcarbonate (DEC), methylethyl carbonate (MEC) or dimethyl carbonate (DMC) [236].

Bellcore reported cells, Coke/LiMn₂O₄ based on PVdF-HFP copolymer matrix containing a lithium salt containing a solution of LiPF₆ in EC/DMC [237]. The cells demonstrated specific energy as high as 100 W h kg⁻¹ and capacities of about 35 mA h for more than 2000 cycles at room temperature. A maximum current density of 0.8 mA cm⁻² was observed for upto 800 charge/discharge cycles at 55°C. At -20°C , specific capacities of 2.5 mA h cm⁻² were obtained at power rates of C/5 [238].

Table 4 gives some examples of cells employing PAN, PVC, and PEO-based gel electrolytes [15]. It can be seen

Table 4

Percent capacity loss characteristics for some cells employing gel polymer electrolytes

Cell	Electrolyte	% Capacity loss ^a
C/LiMn ₂ O ₄	PAN-EC-PC-LiClO ₄	16
Li/LiMn ₂ O ₄	PAN-EC-PC-LiClO ₄	30
Li/LiMn ₂ O ₄	PAN-EC-PC-LiAsF ₆	35
C/LiMn ₂ O ₄	PVC-EC-PC-LiClO ₄	3.6
Li/LiMn ₂ O ₄	PVC-EC-PC-LiClO ₄	3.1
Li/V ₆ O ₁₃	PEO-EC-PC-LiCF ₃ SO ₃	30

^aAfter 50 cycles at 0.1 mA cm⁻²

that, as compared with the cells based on PAN-EC-PC-based gels, the PVC-EC-PC gels show the minimum percent capacity loss. The PVC-EC-PC-based gels are more reactive towards the lithium metal than the PAN-EC-PC-based gels [221], thus showing better compatibility with the LiMn_2O_4 cathodes.

4.6. Summary

In the polymer gel electrolytes, the incorporation of liquid electrolytes into homo- or co-polymer hosts has allowed room temperature conductivities as high as $10^{-3} \text{ S cm}^{-1}$. The mechanical stability of the gels is determined by the ratios of the polymer and solvent (plasticizer) in the gel. Highly mechanically stable gels with 10–12 wt.% of plasticizer and 70–80 wt.% of polymer, with room temperature conductivities between 10^{-4} and $10^{-3} \text{ S cm}^{-1}$ have been generally observed. Plasticizer solvents such as EC and PC have been much studied due to their high polarity and low vapor pressure, which also allow greater plasticizing effect to the polymer host. Most of the studied plasticizers have shown electrochemical instabilities at lithium metal electrode surfaces, and thus a search for new plasticizers is seen necessary. Due to greater dissociation of the lithium salt, much higher lithium ion transference numbers than in the solvent-free electrolytes (about 0.6) have been observed.

The PAN-based gels have been widely studied in cells comprising of the intercalation type electrodes. Specific energies of around 300 W h kg^{-1} have been reported in a C/LiNiO₂ cells. As compared with PAN and PEO-based gels, the relative capacity loss of cells containing the LiMn_2O_4 cathodes was found to be minimum with the PVC-based gel electrolyte. In C/DMcT cells based on PAN gel electrolytes, cycles lives of around 1000 cycles have been observed.

5. Polymer composites

5.1. Introduction

Weston and Steele first demonstrated the idea of incorporating electrochemically inert particulate fillers into polymer matrixes as a means to increase mechanical stability of the polymer [239]. Since then, with a view to making dimensionally stable polymer electrolytes for lithium batteries, high surface area particulate fillers such as ZrO_2 , TiO_2 , Al_2O_3 , hydrophobic fumed silica, and fiber glass were introduced into polymer matrices to obtain the so called ‘composite polymer electrolytes’ or ‘composite ceramic electrolytes’. Composite formation was also found to enhance the ionic conductivities of the electrolytes leading to their potential use in lithium batteries [239–241]. The

increase in conductivity has been mainly attributed to the decrease in the level of polymer crystallinity in presence of the fillers [242].

Increase in mechanical strengths have been generally observed in the composite electrolytes. Raghavan and Khan used reological techniques on fumed silica (methyl group terminated)-based composites containing PEG-LiX solutions [243]. The composites were found to be shear sensitive which resulted into dropping in its viscosity due to the presence of weak physical bonds between the silica particles. This shear-thinning behavior is considered as advantageous, allowing processing of these composites as thin-films [243].

Cho and Liu used glass as a filler for $\text{P(EO)}_6\text{-LiC}(\text{CF}_3\text{SO}_2)_2$ [244]. Room temperature conductivities as high as $10^{-4} \text{ S cm}^{-1}$ and good mechanical stabilities were observed for $x = 13\%$, in a $(100 - x):x$ system, where, $(100 - x)$ and x are respective volume percents of the glass electrolyte, $(0.56 \text{ Li}_2\text{S}-0.19 \text{ B}_2\text{S}_3-0.25 \text{ LiI})$ and the polymer electrolyte.

Similarly, Mustarelli et al. prepared a PEO-based polymer-glass matrix doped with lithium salts using sol-gel techniques [245]. In a PEO matrix made with glassy lithium triborate and LiClO_4 or LiBF_4 room temperature conductivities of the order $10^{-5} \text{ S cm}^{-1}$ were shown for $[\text{EO}]/\text{Li}^+$ ratio of 8 [245]. Completely amorphous complexes were obtained with the LiClO_4 salt whereas the LiBF_4 showed some crystalline phase.

Mechanically stable (MEEP)-LiX polymer electrolytes were prepared by trapping the electrolyte into porous matrixes of fiber glass to obtain a highly mechanically stable composite [245,246]. Brusatin et al. used sol-gel procedures to synthesize composites comprising of poly[bis(methoxy-ethoxy-ethoxy)phosphazene] (MEEP) and silica and increase in mechanical and electrical properties of the otherwise flowing polymer MEEP alone [247]. Room temperature conductivity of a LiCF_3SO_3 salt complex with the MEEP-silica composite was reported as $3 \times 10^{-5} \text{ S cm}^{-1}$ [247].

Krawiec reported a relationship between particle size of Al_2O_3 filler and conductivity [248]. The composites of PEO with LiBF_4 showed an increase in ionic conductivity from 10^{-5} for a micrometer sized Al_2O_3 to $10^{-4} \text{ S cm}^{-1}$ for a nanometer sized one.

Quite recently, composites based on gel electrolytes have also been prepared and improved room temperature conductivities have been shown in presence of the plasticizers. For example, the addition of fine particles of $\gamma\text{-Al}_2\text{O}_3$ to PEO- LiClO_4 complexes plasticized with dioctyl phthalate was found to increase the room temperature conductivity by an order of magnitude [249].

Ardel et al. studied the phenomena taking place at the grain boundary of $\text{P(EO)-Al}_2\text{O}_3$ -based composite electrolytes with and without the presence of plasticizers such as EC and PEGDME using impedance spectroscopy and (SEM) techniques [250]. With mere addition of Al_2O_3 ,

increase in grain boundary resistance and decrease in grain boundary capacitance were observed. However, bonding of the Al_2O_3 particles with the polymer was observed when the composites were hot pressed at 120°C and 600 kg cm^{-2} , thereby reducing the grain boundary resistance by 3- to 10-folds. The presence of EC or PEGDME decreased the resistance and increased the capacitance at the grain boundary by about ten folds. The presence of the solvents helped in the accumulation of Al_2O_3 on the surface of the polymer particles.

Composites containing particles (10 wt.%) of nano-scale TiO_2 or zeolites were prepared from gel electrolytes based on PVdF [251] and PAN [252] with PC/EC as the plasticizer solvents. The increase in ionic conductivity in the composite, (zeolite-PAN-PC, EC, LiAsF_6) from $10^{-3} \text{ S cm}^{-1}$ (zeolite free) to $10^{-2} \text{ S cm}^{-1}$ (with zeolite) was attributed to the suppression of the phase boundaries in the composite [251].

Composites containing highly porous hydrophobic fumed-silica ($\text{Si}(\text{OR})_4$) (see Fig. 7), LiX, poly(ethylene glycol) (PEG) and mono- and di-methyl terminated PEG (MW 200–400) were prepared by Fan and Fedkiw [253]. The composites showed gel like characteristics with the liquid electrolyte being immobilized into the pores of the silica. A maximum room temperature conductivity of $1.5 \times 10^{-3} \text{ S cm}^{-1}$ was reported for the composite containing silica with $\text{R}=\text{C}_8\text{H}_{17}$, di-methyl terminated PEG and LiTFSI salt [253].

In a similar attempt, trapping of liquid electrolytes was done by Wasiucionek and Breiter involving sol-gel acid catalysis of ($\text{Si}(\text{OR})_4$) in presence of organic solvents containing lithium ions [254]. Room temperature conductivities were of the order $10^{-3} \text{ S cm}^{-1}$ for the system with $\text{R}=\text{CH}_3$ and LiBF_4 or LiPF_6 solutions in EC/PC. With 0.2 M LiCl (MeOH (H_2O)) as the pore liquid, ionic conductivities were as high as $1 \times 10^{-2} \text{ S cm}^{-1}$ [254].

The idea of incorporating silica particles with surface modified large alkyl groups (R) is relatively new. The large alkyl groups allow an increase in inter-particle interactions (van der Waals interactions) and hence produce highly mechanically stable composites [255,256]. Much

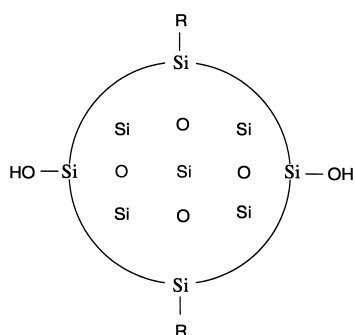


Fig. 7. Schematic diagram of a fumed silica particle with surface attached group $\text{R}=\text{C}_8\text{H}_{17}$ [253].

improved mechanical stabilities were observed in fumed-silica with attached polymerizable alkyl acrylate groups onto its surface which chemically cross-linked between adjacent silica particulates [256]. In general, polarity of the liquid phase within the silica pore and the size of the hydrophobic group in the composites showed large influence on the mechanical properties of the composites [243].

Using NMR techniques, Wu et al. reported liquid-like ionic mobility over temperature range $30\text{--}80^\circ\text{C}$ in a silica composite they prepared from hydrolysed silica precursor and lithium ion conducting liquid electrolyte [257]. Room temperature conductivity of the order $10^{-3} \text{ S cm}^{-1}$ was reported and temperature dependence on conductivity was found to follow an Arrhenius relation in the temperature range $30\text{--}80^\circ\text{C}$.

Composites consisting of low molecular weight PEO-LiX and silica were prepared by sol-gel processes of tetraethoxysilane in presence of poly(ethylene glycol)-sol-gel precursor [258]. Room temperature conductivity of the films were reported as in the order of $10^{-6} \text{ S cm}^{-1}$. Also composites of copolymers such as poly(ethylene oxide-b-amide-6) and poly(ethylene oxide-co-epichlorohydrin) with silica were prepared by sol-gel processes involving the hydrolysis followed by condensation of tetraethoxysilane [259] and conductivities at 100°C were about 1.5×10^{-4} and $3.5 \times 10^{-4} \text{ S cm}^{-1}$ respectively. Activation energies reported with and without inclusion of silica for the poly(ethylene oxide-b-amide-6)/ LiClO_4 were 9.7 and 37 K J mol^{-1} respectively. Apart from the lowering in the activation energies in presence of silica, lowering in the energy of activation was observed for the poly(ethylene oxide-co-epichlorohydrin)/ LiClO_4 system.

5.2. Electrochemical stability and electrochemical cells

Unfortunately, not much work has been carried out on electrochemical cells incorporating composite polymer electrolytes. It was in the earlier times that interfacial electrochemical stabilities towards lithium electrode in PEO- LiClO_4 electrolyte with the addition of fine $\gamma\text{-LiAlO}_2$ particulates was investigated [242]. Borghini et al. studied similar composites and found that passivation at lithium electrode surfaces to be reduced in presence of the inorganic filler [260].

The presence of hydrophobic fumed silica in a composite consisting of LiTFSI, polyethylene glycol dimethyl ether, and the silica showed an electrochemical stability window of 5.5 V [253]. Increase in the electrochemical stability window in presence of silica was also observed in the case of copolymer poly(ethylene oxide-co-epichlorohydrin)- LiClO_4 polymer electrolyte (5.5 V in presence of silica vs. 4.0 V without silica) [259].

Addition of ceramic materials such as zeolites ($\text{Na}_{12}[\text{Al}_{12}\text{Si}_{12}\text{O}_{48}]$) and alumina (Al_2O_3) to gel polymer

systems has shown to increase stability at the lithium metal interface [5,240]. The presence of zeolites in PAN-based gels was found to reduce the extent of passivation at lithium electrode surfaces [240]. In a Li/LiCoO₂ cell incorporating ceramic gel electrolytes (zeolite-PAN-PC-EC-LiAsF₆), current densities at 25°C as high as 0.5 mA cm⁻¹ with negligible capacity loss were reported [252]. In comparison with liquid electrolytes, lower voltage and capacity losses were observed. Also high electrochemical stabilities were observed for the Li/Li_xMn_xO₄ (or C) cells containing glass composite polymer electrolyte.

More recently the cell, Li/P(EO)₂₀-LiI-EC-Al₂O₃/FeS₂ was investigated by Strauss et al. [261]. The cell is interesting because of its high theoretical energy density of about 860 W h kg⁻¹ based on the 2.8 electrons exchanged per mole of FeS₂ and practical values of 175 W h kg⁻¹ have been made possible [262]. The FeS₂ cathode contains about 50 volume percent of the polymer electrolyte. The cell reaction



is accompanied by the intermediate phases of FeS₂ to finally give the product metallic Fe [263]. Due to these intermediate phases affecting the surface layer of the electrode the first discharge gave a slope in the voltage from 2.5 to 1.8 V. From the second discharge onwards a second voltage of 1.3 V was observed which was considered to be associated with a phase formed by a reaction between PEO and metallic Fe [261].

5.3. Summary

The incorporation of about 10 wt.% of an inorganic filler to 'dry' or 'gel' polymer electrolytes has been generally found to increase ionic conductivities by about an order of magnitude. This phenomenon of conductivity enhancement is still not clearly understood, but low interparticle resistance between inorganic particles has been observed. The order of room temperature conductivities in the composites range between 10⁻⁵ and 10⁻² S cm⁻¹. The highest conductivities of the order of 10⁻² S cm⁻¹ were reported in the case of composites based on the gel electrolytes and zeolites. In another type of inorganic composites, porous hydrophobic fumed-silica has been used as a medium to hold liquid electrolytes, and room temperature conductivities of the order 10⁻³ S cm⁻¹ have been reported. The presence of hydrophobic groups on the surface of the silica particles has been found advantageous in increasing the mechanical properties of the composites.

Not many electrochemical cells have been investigated with the use of inorganic composite electrolytes. However, the presence of an inorganic filler in the electrolyte has been found to increase the stability of the electrolyte and

also the interfacial stability towards the lithium metal electrode.

6. Conclusions and future aspects

Although the 'dry polymer' electrolytes have much lower room temperature ionic conductivities than those comprising of organic liquids, their environmental safety is an advantage. However, the cells based on PEO have shown good performances at temperatures between 70°C and 200°C, above the melting temperature of the crystalline phases, where the conductivity is appreciable. The gel electrolytes are promising because of their high room temperature conductivities. However, the PVC-based gels have shown poor stability towards the lithium metal electrode, but have shown good performance when used with LiMn₂O₄ cathodes. The anions of the lithium salt are known to decompose at lithium metal electrodes, and thus the synthesis of less reactive and more environmentally friendly anions for lithium salts is seen necessary. The polyelectrolytes, having the anion attached to their polymer backbones, will minimize self-discharge, salt-leakage, and disposal problems. Also the use of novel salts with large electron delocalizing anions aims at reducing the self-discharge problems. Composite ceramic polymer electrolytes have also shown promise by achieving high room temperature conductivities and work to obtain a partial or complete ceramic secondary battery seems to be the next step. The high conductivity of the order 10⁻² S cm⁻¹ in the composite based on PAN-gel/zeolite is the highest so far in the field of polymer electrolytes. Studies on electrochemical cells based on the composite polymer electrolytes are very few and much work is needed to explore these materials for lithium batteries. The recent work on highly crystalline polymers which allow a flow of ions through molecular channels seems interesting, but lacks detailed electrochemical characterization. Improvements in room temperature ionic conductivities in these systems are expected with structural modifications.

The use of electroactive polymers as electrode materials have taken the field of lithium batteries forward, and much encouraging results have been shown with the polymer electrolytes. Unfortunately, the cells containing the PPy cathodes have high self-discharge rates. However, the cells based on DMcT/Ani composite as cathodes have shown much promise for future battery applications, although problems such as discharge curves being sloping, especially at higher current densities still exist. Interestingly, the cells with the DMcT cathodes have been found to be insensitive to overcharge and overdischarge. A replacement for carbon (and lithium) has been recently shown by Alamgir et al. with the use of PPPP of high specific charge of 610 A h kg⁻¹ [219]. Improvement in the performance of cells containing the PPPP anode in combination with other

types of cathodes is seen necessary. Further tests related to self-discharge, temperature variation, safety, etc. of the cells based on the electroactive polymers still need to be done.

7. List of abbreviations

AN	Acrylonitrile
BEVS	Poly[bis-(2-(2-ethoxyethoxy)ethoxy)]-methylvinylsilane
BL	γ -butyrolactone
CS	Carbon-sulfur polymer
DBP	Dibutyl phthalate
DEC	Diethyl carbonate
DEP	Diethyl phthalate
DMC	Dimethyl carbonate
DMcT	Dimercaptiothiadiazole polymer
DMF	Dimethyl formamide
DOP	Dioctyl adipate
EC	Ethylene carbonate
EDT	1,2-Ethanedithiol polymer
EO	Ether oxygens
EV	Electric vehicle
FTIR	Fourier-transform infrared spectroscopy
GS	Glycol sulfite
HFP	Hexafluoropropylene
LiTFSI	Lithium bis(trifluoromethane sulfonyl)-imide
LiTFSM	Lithium bis(trifluoromethane sulfonyl)-methide
McEE	Bis(2-mercaptoethyl)ether polymer
MEC	Methyl ethyl carbonate
MEEP	Poly[bis-2(2-methoxy ethoxy ethoxy)]phosphazene
MEPP	Poly[bis(2,3-di-(2-methoxy ethoxy)propoxy)]phosphazene
MOE	Oligo(oxyethylene)mono-methyl ether
PAN	Poly(acrylonitrile)
PBT	Poly(bithiophene)
PC	Propylene carbonate
PEGDA	Poly(ethylene glycol)diacrylate
PEGDME	Poly(ethylene glycol)dimethyl ether
PEI	Poly(ethylene imine)
PEO	Poly(ethylene oxide)
PHAP	Poly(bis(hexylamino)phosphazene)
PMMA	Poly(methylmethacrylate)
POM	Poly(oxymethylenec)
POO	Poly(oxymethylene oligo-oxyethylene)
PPAP	Poly(bis(pentylamino)phosphazene)
PPO	Poly(propylene oxide)
PPTA	Poly(<i>p</i> -phenyl terephthalamide)
PPTA	Poly(<i>p</i> -phenylene terephthalamide)
PPy	Poly(pyrrole)
PS	Poly(siloxane)
PVC	Poly(vinyl chloride)

PVdC	Poly(vinylidene carbonate)
PVdF	Poly(vinylidene fluoride)
PVP	Poly(vinyl pyrrolidone)
PVS	Poly(vinyl sulfone)
THF	Tetrahydrofuran
t_{Li^+}	Lithium ion transference number
TRGDMA	Triethylene glycol dimethacrylate

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