

Review of gel-type polymer electrolytes for lithium-ion batteries

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Abstract

This review describes the advantages and characteristics of employing polymer electrolytes in solid-state lithium-ion batteries. Criteria for an ideal polymer electrolyte and the differences between polyelectrolytes are discussed. The emphasis of this article is on plasticized or gelled electrolyte systems. Hence, the review focuses on four plasticized systems which have received particular attention from a practical viewpoint, i.e., poly(ethylene oxide) (PEO)-, poly(acrylonitrile) (PAN)-, poly(methyl methacrylate) (PMMA)-, and poly(vinylidene fluoride) (PVdF)-based electrolytes. Some critical concepts and points associated with this emerging technology that still require attention are discussed in the final part of the review. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

The science of polymer electrolytes is a highly specialized interdisciplinary field which encompasses the disciplines of electrochemistry, polymer science, organic chemistry, and inorganic chemistry. The field has attracted ever-increasing interest, both in academia and industry, for the past two decades due to the potentially promising applications of such electrolytes, not only in all solid-state rechargeable lithium or lithium-ion batteries, but also in other electrochemical devices such as supercapacitors, electrochromic windows, and sensors [1–3]. The study of polymer electrolytes was launched by Fenton et al. [4] in 1973, but their technological significance was not appreciated until the research undertaken by Armand et al. [5,6] a few years later. These latter authors claimed that the crystalline complexes formed from alkali metal salts and poly(ethylene oxide) (PEO) were capable of demonstrating significant ionic conductivity, and highlighted their possible application as battery electrolytes. This work inspired intense research and development on the synthesis of new polymer electrolytes, physical studies of their structure and charge transport, theoretical modelling of the charge-transport processes, and the physical and chemical properties at the electrolyte/electrode interface. The rapid progress in

this field has been reported in numerous monographs and reviews [1–3,7–13].

In principle, a polymer electrolyte battery is formed by laminating a lithium metal (or a composite carbon) anode, a lithium-ion conducting membrane, and a composite cathode, as indicated in Fig. 1 [14]. The entire cell assembly can be produced as a continuous tape, or can be rolled or folded into its finished shape. The underlying charge–discharge mechanism [15–19] and the insertion electrode materials [20,21] of lithium-ion batteries have been extensively discussed elsewhere, and thus are not included in this review. The membrane plays a crucial role in a cell. The motivation and advantages for using such a polymeric membrane as the electrolyte component in a lithium cell are as follows.

(i) *Suppression of dendrite growth.* Although conventional separators serve well as the ionic conducting media in rechargeable lithium cells, they unfortunately possess many sufficiently large electrolyte-containing, interconnected pores such that continuous pathways can develop between the cathode and the anode and, thereby, encourage the formation and growth of lithium dendrites during charging periods. These dendrites lower the cycling efficiency and, ultimately, cause internal short-circuiting of the cells [22]. The use of continuous or non-porous polymeric membranes which provide few or no continuous free paths for electrolyte solution in which lithium dendrites propagate has been one of several successful approaches to suppressing the problem of dendrite growth [6,18].

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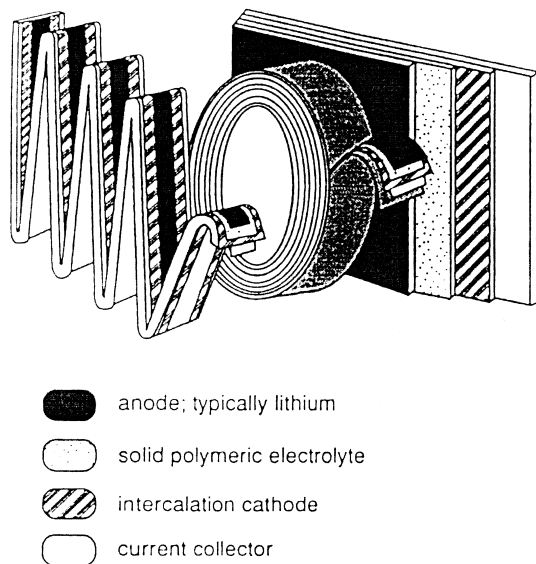


Fig. 1. Schematic diagram of basic construction of polymer-based batteries. The thin membrane composites are flexible and can be arranged into several desired geometries (after Ref. [14]).

(ii) *Enhanced endurance to varying electrode volume during cycling.* Polymer electrolytes are more compliant than conventional inorganic glass or ceramic electrolytes. This feature enables the construction of solid-state rechargeable batteries in which the polymer conforms to the volume changes of both electrodes that occur during charge–discharge cycling.

(iii) *Reduced reactivity with liquid electrolytes.* It is generally accepted that no solvent is thermodynamically stable towards lithium [22] and even carbonaceous anodes. Polymer electrolytes, due to their solid-like nature and much lower liquid content, are expected to be less reactive than their liquid electrolyte counterparts.

(iv) *Improved safety.* Solid-state construction of a polymer electrolyte battery is more tolerant to shock, vibration, and mechanical deformation. In addition, since there is no or little liquid content within the electrolytes, cells can be packaged in a vacuumed flat ‘plastic bag’ other than a rigid metal container which is prone to corrosion. This unique characteristic prevents build-up of internal pressure [23] and, hence, removes the possibility of explosion.

(v) *Better shape flexibility and manufacturing integrity.* Due to the need for smaller and lighter batteries, the battery shape factor has become one of the major design issues. A rectangular battery is often preferable to a conventional cylindrical battery since it occupies space more efficiently in consumer electronics such as cellular phones and laptop computers. A film-like, polymer electrolyte battery is quite promising from this aspect [24,25]. Another feature associated with polymer–electrolyte batteries is the manufacturing integrity; all elements, both the electrolyte and electrodes, of a cell can be laminated automatically via well-developed coating technology [26].

Although this novel class of materials is formally classified as ‘solid electrolyte’, the charge-transport mechanism is completely different from that in inorganic crystals, and actually resembles the ion transport in liquid media. This follows primarily from the fact that ions are transported in the polymeric host material which is not as rigid as the defect crystal of the classical inorganic solid electrolyte. In addition, chain motions or rearrangements of the polymer host virtually contribute to the ion transport. On the contrary, transport of ions are usually visualized as hopping between fixed sites within solid electrolytes, the positions of which do not change significantly with time. Ion-conducting polymers therefore present a special class of electrolytes with features intermediate between those of solid (defect crystals) and liquid (solutions, melts) electrolytes [27,28]. Table 1 compares the main properties of the nature

Table 1
Behaviour of cation-conducting electrolyte materials (after Ref. [29])

Phenomenon/environment	Electrolyte behavior		
	Polymer	Liquid	Solid
Matrix	Flexible	Mobile	Fixed
Position of ion sites	Changes as chains flex	None	Fixed; accessibility affected by temperature
Solution	Yes	Yes	Not usually
Solvation	By matrix: roll-on mechanism	Forms mobile solvated ions	No
Concentration of solute	Usually high	Often low	Usually does not apply
Participation of charged ion clusters	Often yes	Usually no, except in molten salts	No
Contribution from migration of neutral species	Important	Usually unimportant	No
High cationic transference number	Usually no	Usually yes	Often unity for cation conductors

of ionic conduction in polymer electrolytes, liquid electrolytes, and solid electrolytes [29].

From a practical point of view, polymer electrolytes for rechargeable lithium and/or lithium-ion batteries must satisfy certain minimal requirements [2,9,10], as follows.

(i) *Ionic conductivity.* Liquid electrolytes commonly used in ambient-temperature rechargeable lithium and/or lithium-ion batteries have ionic conductivities in the range 10^{-3} to 10^{-2} S cm^{-1} . They comprise solutions of lithium salts in non-aqueous organic solvents, such as mixtures of ethylene carbonate (EC)/propylene carbonate (PC), and tetrahydrofuran (THF)/2-methyltetrahydrofuran (2-MeTHF). Therefore, to achieve the performance level of liquid electrolyte-based systems which can be discharged at current densities of up to several mA cm^{-2} , polymer electrolytes should possess conductivities approaching or beyond 10^{-3} S cm^{-1} at ambient temperature.

(ii) *Transference number.* It is desirable that the transference number of lithium ions approaches unity in an electrolyte system. Many existing electrolyte systems, either liquid or polymeric, have transference numbers less than 0.5, i.e., no more than half of the ionic charge is transported via the movement of lithium ions [30–32]. In other words, anions and ion pairs are also important vehicles responsible for charge transport. A large transference number can reduce concentration polarization of electrolytes during charge–discharge steps, and thus produce higher power density.

(iii) *Chemical, thermal, and electrochemical stabilities.* Three properties regarding the stability should be evaluated. Since the electrolyte membrane is interposed between the cathode and the anode, its chemical stability must be such that no undesired chemical reactions occur when the electrodes come into direct contact with one another. In addition, in order to have an appropriate temperature range of operation, polymer electrolytes must have good thermal stability. Finally, they must also have an electrochemical stability domain extending from 0 V to as high as 4.5 V vs. Li/Li⁺ to be compatible with lithium and cathode materials such as TiS₂, V₆O₁₃, LiCoO₂, LiNiO₂, and LiMn₂O₄.

(iv) *Mechanical strength.* Manufacturability is overwhelmingly the most important factor to be considered when battery technology moves from laboratory to pilot or full production. Although many electrolyte systems can be fabricated as free-standing membranes and achieve various favourable electrochemical properties, their mechanical strength still requires further enhancement in order to allow manufacture by conventional large-scale coating processes.

To date, several types of polymer electrolytes have been developed and characterized, such as those based on poly(ethylene oxide) (PEO) [4–6,33–46], poly(acrylonitrile) (PAN) [47–60], poly(methyl methacrylate) (PMMA) [61–67], poly(vinyl chloride) (PVC) [68–72], and poly(vinylidene fluoride) (PVdF) [73–80]. Table 2 lists some polymers that have been investigated as hosts for polymer electrolytes. Although a large number of polymer electrolyte systems have been prepared and characterized, it is possible and convenient to group all the polymer systems into two broad categories, i.e., pure solid polymer electrolyte (SPE) and plasticized or gelled polymer electrolyte systems [9]. The first category is composed of lithium salts (e.g., LiClO₄, LiBF₄, LiPF₆, LiAsF₆, LiCF₃SO₃, LiN(CF₃SO₂)₂, LiC(CF₃SO₂)₃) dissolved in high molecular weight polyether hosts (e.g., PEO and PPO) which act as solid solvents. Polymer electrolyte systems of this category are generally produced in thin-film configuration by using solvent evaporation coating techniques. This class of electrolytes also includes copolymers made of polyether grafted polyether, polysiloxane, and polyphosphazene backbones. The ionic conduction mechanism of this class of polymer electrolytes is intimately associated with the local segmental motions of the polymer. The second category of polymer electrolyte is the so-called ‘gelled polymer electrolytes’ and is characterized by a higher ambient ionic conductivity but poorer mechanical properties when compared with pure SPE. Gel electrolytes are usually obtained by incorporating a larger quantity of liquid plasticizer and/or solvent(s) to a polymer matrix that is capable of forming a stable gel with the polymer host structure. In order to improve the mechanical

Table 2
Some selected polymer hosts and their corresponding chemical formulae

Polymer host	Repeat unit	Glass-transition temperature, T_g (°C)	Melting point, T_m (°C)
Poly(ethylene oxide)	$-(\text{CH}_2\text{CH}_2\text{O})_n-$	–64	65
Poly(propylene oxide)	$-(\text{CH}(\text{CH}_3)\text{CH}_2\text{O})_n-$	–60	– ^a
Poly[bis(methoxy ethoxyethoxide)-phosphazene]	$-\text{[N=P}(\text{O}(\text{CH}_2\text{CH}_2\text{O})_2\text{CH}_3)_2]_n-$	–83	– ^a
Poly(dimethylsiloxane)	$-\text{[SiO}(\text{CH}_3)_2]_n-$	–127	–40
Poly(acrylonitrile)	$-(\text{CH}_2\text{CH}(\text{CN}))_n-$	125	317
Poly(methyl methacrylate)	$-(\text{CH}_2\text{C}(\text{CH}_3)(\text{COOCH}_3))_n-$	105	– ^a
Poly(vinyl chloride)	$-(\text{CH}_2\text{CHCl})_n-$	82	– ^a
Poly(vinylidene fluoride)	$-(\text{CH}_2\text{CF}_2)_n-$	–40	171

^aAmorphous polymer.

properties of the gel electrolytes, components which can be cross-linked and/or thermoset may also be added to the gel electrolyte formulation.

The gel is a particular state of matter, neither liquid nor solid, or conversely both liquid and solid. To describe a gel is much easier than to define it because the precise definition of a gel must refer to the molecular structure and to the method of connectivity. Generally, a polymeric gel is defined as a system which consists of a polymer network swollen with solvent [81]. It must be understood that the solvent is dissolved in the polymer, not the other way around. Owing to their unique hybrid network structure, gels always possess, simultaneously, both the cohesive properties of solids and the diffusive transport properties of liquids. This duality enables the gel to find a variety of important applications that include polymer electrolytes.

Gels can be obtained as a result of either a chemical or a physical cross-linking process. When gelation occurs, a dilute or more viscous polymer solution is converted into a system of infinite viscosity, i.e., a gel. A gelled solution does not demonstrate any flow when a tube containing the solution is tilted. Chemical cross-linking, or covalent cross-linking, is a process associated with the covalent bonding of polymer chains by means of a chemical reaction to form a certain number of tie or junction points, as presented in Fig. 2a. Covalent cross-linking leads to the formation of irreversible gels. In such gels, the number of tie-points essentially does not change upon variation of the external conditions such as temperature, concentration, or stress. By contrast, the gel network formed via physical cross-linking is called the ‘entanglement network’. There are two main types of entanglements: ‘junction zones’

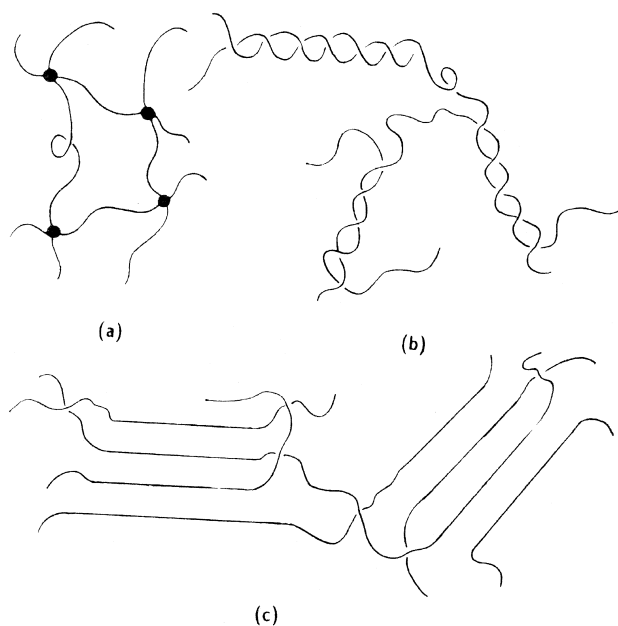


Fig. 2. Diagrammatic representation of a chemical gel network with junction points (a), and physical gel networks having junction zones (b) and fringed micelles (c), respectively (after Ref. [82]).

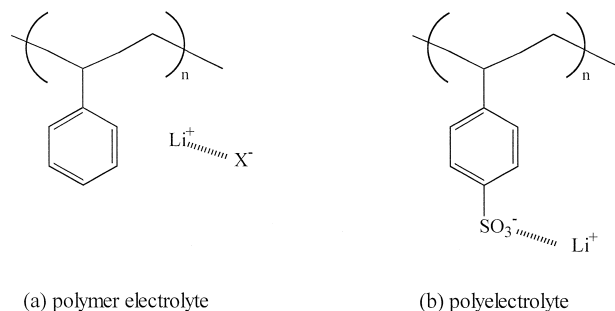


Fig. 3. Contrast between (a) a polymer electrolyte containing a salt LiX and (b) a polyelectrolyte in which the anion is attached to the polymer backbone via chemical bonds.

where the polymeric chains interact over a portion of their length (Fig. 2b), and ‘fringe micelles’ where the chains align in some regions to form small crystallites (Fig. 2c) [82]. Some other weak interactions, such as ion complexation, can also favour the formation of the physical gel network. Most gel electrolyte systems are prepared in this way.

This article does not intend to review all reported polymer electrolyte systems, but concentrates on four representative plasticized systems which have received much more attention from a practical viewpoint, i.e., PEO-, PAN-, PMMA-, and PVdF-based electrolytes. Prior to introducing each system, however, one important concept has still to be clarified. As noted earlier, since many polymer electrolyte systems exhibit transference numbers of no more than 0.5, the ionic conductivities of these electrolytes are established primarily through anionic transport.

To increase the cationic transference number, some researchers have synthesized polymers in which anions are covalently bonded to the polymer backbone, as exemplified in Fig. 3b. These polymers are called ‘polyelectrolytes’. By virtue of the anions being effectively immobilized, all ionic conductivity is due to cationic transport. Nevertheless, such materials are usually not sufficiently flexible and exhibit ambient-temperature conductivities only around or below $10^{-6} \text{ S cm}^{-1}$. In fact, polyelectrolytes have a unique advantage for applications such as batteries. Unlike polymer electrolytes, polyelectrolytes are not susceptible to the build-up of a potentially resistive layers of high or low salt concentration at the electrode/electrolyte interfaces during charging and discharging. Unfortunately, flexible polyelectrolyte films suitable for use in devices have yet to be prepared. Thus, although they belong to the category of ionically conducting materials, polyelectrolytes are beyond the scope of this review.

2. PEO-based electrolytes

PEO-based electrolyte is the earliest and the most extensively studied system. This system usually refers to

Table 3
Compositions and electrochemical properties of selected ALPE membrane samples (adapted from Ref. [44])

Sample	Composition (wt.%) ^a , PEO:PEGDME:(solvent), with $(n_{\text{EO}} + n_{\text{solvent}})/n_{\text{salt}} = 1/14$ and additional 10 wt.% γ -LiAlO ₂	Ambient-temperature conductivity (mS cm ⁻¹)	Transference number, t_{Li^+}	Anodic stability (V) vs. Li
ALPE 1	15:85:0	0.09	0.3	5.0
ALPE 2A-1 (DEC)	20:60:20	0.11	0.2	5.0
ALPE 2A-6 (DEC)	30:35:30	0.12	–	4.9
ALPE 3A-1 (DMC)	20:60:20	0.20	0.4	5.1
ALPE 4A-1 (EC)	20:60:20	1.90	0.3	4.9
ALPE 5A-1 (PC)	20:60:20	1.00	–	5.0

^aThe molecular weights for PEO and PEGDME are 4000000 and 500, respectively. The solvent used in each sample is listed in the first column.

solvent-free PEO/salt complexes. The electrolytes commonly exhibit conductivities which range from 10^{-8} to 10^{-4} S cm⁻¹ at temperatures between 40 and 100°C, which excludes practical applications at ambient temperature. This obstacle originates from, first, the high degree of crystallinity which is unfavourable for ionic conduction in these complexes and, second, the low solubility of salt in the amorphous phase [33]. Many valuable investigations have therefore focused primarily on the enhancement of the room-temperature conductivity, via various approaches such as using blends [34–36], copolymers [37], comb-branch polymers [38], and cross-linked ‘networks’ [39]. All these enhancements have been achieved either by reducing the crystallinity of polymers or by lowering the glass-transition temperature.

The most striking advancements in the ionic conductivity of polymer electrolytes have been attained through the incorporation of substantial amounts of plasticizers. In addition to reducing the crystalline content and increasing the polymer segmental mobility, plasticizers can result in greater ion dissociation which allows greater numbers of charge carriers for ionic transport. Low-molecular-weight polyethers and polar organic solvents are two commonly used types of plasticizers for these purposes.

Ito et al. [40] studied PEO–LiCF₃SO₃ complexes plasticized with PEG, which have the same repeat unit as PEO. The conductivity increases, approaching 10^{-3} S cm⁻¹ at 25°C, with decreasing molecular weight of the PEG plasticizer and with increasing PEG content. The conductivity enhancement at room temperature is attributed to the increase in the amorphous regions responsible for the ionic conduction. The PEG aids in ionic transport mainly by reducing crystallinity and increasing the free volume of the system. On the other hand, hydroxyl end-groups of PEG react with lithium metal [41], and such a system would not, therefore, be suitable for battery purposes. To avoid this problem, researchers have eliminated the troublesome hydroxyl end-groups of PEG by replacing them with less reactive methoxy ones [41,42]. For example, Kelly et al. [41] studied the same PEO–LiCF₃SO₃ complexes, but used mono- and di-methoxy PEG as plasticizers. Unfortu-

nately, the resulting systems, though electrochemically stable, are about one order of magnitude less conductive.

The use of crown ethers as plasticizers can also lead to the enhancement of conductivity. Nagasubramanian and Di Stefano [43] examined the effect of 12-Crown-4 on the conductivity and interfacial kinetics of PEO–LiX (X = CF₃SO₃, BF₄, ClO₄) complexes. They concluded that maximum conductivities are obtained when the 12-Crown-4 to Li ratio is kept at 0.003. With this ratio, the highest conductivity is obtained with PEO–LiBF₄, viz., $\sim 7 \times 10^{-4}$ S cm⁻¹. In addition, the 12-Crown-4-incorporated sample yields a lower charge-transfer resistance in a cell.

Recently, Appetecchi et al. [44,45] reported a noteworthy series of composite electrolytes based on PEO with the acronym ALPE (advanced lithium polymer electrolyte membranes). The novelty of these electrolytes resides in their particular composition which balances a combination of polymers (i.e., PEO and poly(ethylene glycol dimethylether) (PEGDME)), plasticizers (e.g., dimethyl carbonate (DMC), diethyl carbonate (DEC), EC, or PC), a selected lithium salt (e.g., LiN(CF₃SO₂)₂), and a ceramic filler (e.g., γ -LiAlO₂). The electrochemical properties of some selected ALPE samples are listed in Table 3. In addition to high ionic conductivities, the membranes are particularly characterized by a wide electrochemical stability window and stability towards the lithium metal. The improved stability of the lithium/electrolyte interface is attributed to the addition of dispersed γ -LiAlO₂ filler. Borghini et al. [46] showed that this phenomenon is also exhibited by simple (PEO)₈–LiN(CF₃SO₂)₂– γ -LiAlO₂ electrolytes.

3. PAN-based electrolytes

Except for PEO and its modifications, a number of polymer matrices which do not contain the –CH₂CH₂O– repeating unit either in the backbone or in the side-chain have been plasticized to obtain electrolytes for high ambient-temperature conductivity. Among polymer hosts such as PAN, poly(vinyl pyrrolidinone) (PVP), PVC, poly-

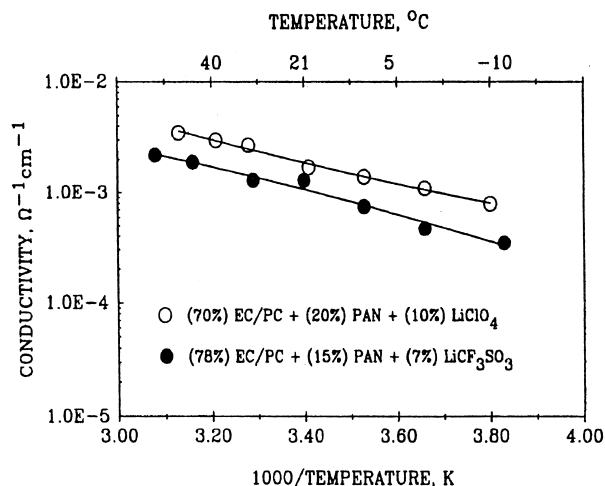


Fig. 4. Arrhenius plot of two electrolyte films prepared using PAN as the polymer matrix. The conductivities are presented for a series of temperatures between -10 and 50°C . The mole percentage of each electrolyte component is given in the legend to the curves (after Ref. [51]).

(vinylidene carbonate) (PVdC), and PVdF, PAN-based polymer electrolytes have been extensively studied.

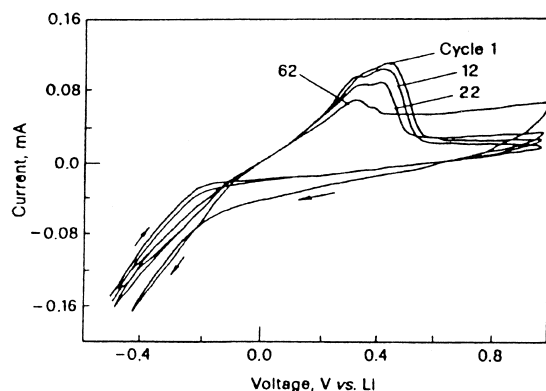
Watanabe et al. [47] used EC and PC to plasticize various LiClO_4 -polymer systems. Various polymers, including PMMA, polystyrene (PS), PVC, poly(vinyl acetate) (PVAc), PAN, and PVdF were investigated. Only PAN and PVdF allowed the formation of homogeneous hybrid films in which the salt and the plasticizer were molecularly dispersed. Next, the authors prepared solid electrolytes which comprised a plasticizer and LiClO_4 in PAN, and demonstrated that the conductivity correlated with the mole ratio $[\text{plasticizer}]/[\text{LiClO}_4]$ in the hybrid films [48,49]. The plasticizers were EC, PC, and *N,N*-dimethylformamide (DMF). An increase in the $[\text{plasticizer}]/[\text{LiClO}_4]$ ratio enhanced the conductivity—primarily as a result of increase in carrier mobility—to a maximum of about 10^{-4} to $10^{-5} \text{ S cm}^{-1}$ at 25°C . X-ray

diffraction patterns suggested that all PAN-based electrolytes are amorphous. Because the conductivity does not correlate well with the PAN content, it is concluded that the PAN host is inactive in the ionic transport mechanism, but simply a matrix of structural stability.

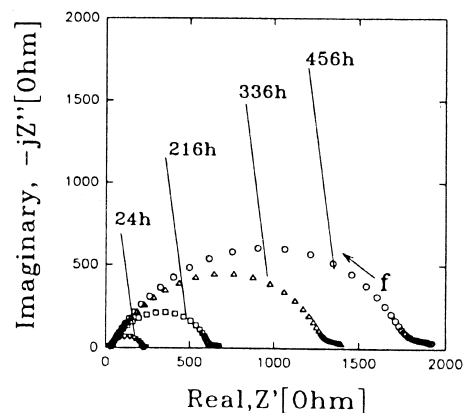
In later studies, Abraham and Alamgir [50,51] further elevated the conductivity of PAN-based electrolytes. A typical electrolyte comprises 38 m/o EC, 33 m/o PC containing 8 m/o LiClO_4 immobilized in 21 m/o PAN. It has a conductivity of $1.7 \times 10^{-3} \text{ S cm}^{-1}$ at 20°C and $1.1 \times 10^{-3} \text{ S cm}^{-1}$ at -10°C . The temperature dependence of the ionic conductivity of PAN-based electrolytes is indicated in Fig. 4.

The elevated conductivity is doubtless a favourable characteristic of gelled electrolytes based on PAN rather than on conventional SPE. Nonetheless, gel systems are essentially thermodynamically unstable. Gelled electrolytes may undergo solvent exudation upon long storage, especially under open-atmosphere conditions. This phenomenon, known as the ‘syneresis effect’, has been encountered in many systems [52,72]. When the effect occurs, the solvent will ooze to the surface of the electrolyte membrane, and the electrolyte gradually becomes turbid in appearance. This change results in a rise in the electrolyte viscosity, as well as a fall in the ionic mobility and, hence, a dramatic decrease in the ionic conductivity.

Besides good transport properties, compatibility with the electrode materials is also an essential parameter to guarantee acceptable performance in electrochemical devices. When a lithium or a carbon anode is contacted by an electrolyte, a thin layer of a third phase is formed between the two bulk phases. Croce et al. [52] reported that lithium metal electrodes may undergo passivation when in contact with PAN-based gel electrolytes. This was observed via cyclic voltammetry of aged cells (Fig. 5a) and long-term impedance analysis of symmetrical cells of the Li/electrolyte/Li type (Fig. 5b). The observed expansion of the



(a)



(b)

Fig. 5. (a) Cyclic voltammetry of a SS electrode using a 16PAN–23PC/56.5EC–4.5 LiClO_4 electrolyte. Lithium reference electrode. Scan rate: 10 mV s^{-1} . The number of subsequent cycles is indicated. (b) Time evolution of impedance of a Li/electrolyte/Li cell kept continuously under open-circuit conditions at room temperature. Electrolyte composition is the same as that in part (a) (after Ref. [52]).

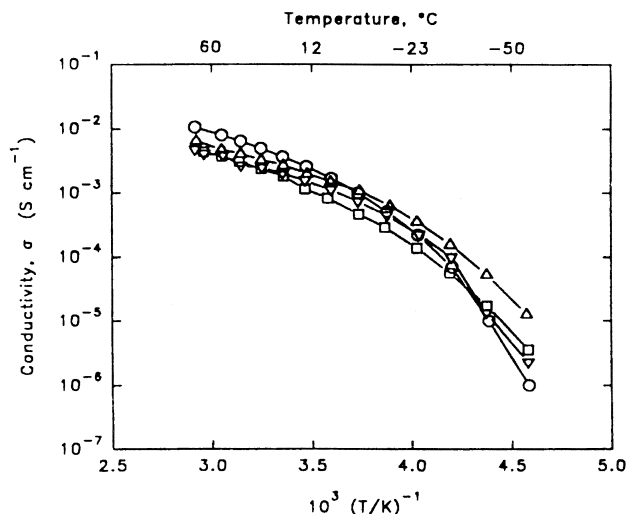


Fig. 6. Arrhenius plots of ionic conductivity for gel electrolytes of PAN-PC/EC-LiAsF₆ with (○) no zeolite, and 5 wt.% additions of zeolite, (□) 4 Å, 40 μm, (Δ) 10 Å, 40 μm, (▽) 10 Å, 2 μm (after Ref. [53]).

impedance semicircle implies that the lithium electrode is passivated with time.

Slane and Salomon [53] studied composite polymer electrolytes which consisted of zeolite powders dispersed in PAN-based gels with LiAsF₆. The advantages of incorporating zeolite are two-fold. One is the enhancement in ionic conductivity at low temperatures, as revealed in Fig. 6. Although PAN-based gel electrolytes have been found to be highly amorphous [49], the polymer chain rearranges

and aligns in a more ordered or crystalline state at lower temperatures. Additions of small amounts of zeolite particles will prevent this crystallization process, leading to the preservation of amorphous domains which are responsible for ionic conduction. Another way to improve the ionic conductivities of polymer electrolytes is the addition of a third solvent to form a ternary solvent mixture. Peramunage et al. [55] selected butylene carbonate (BC) and 3-methyl-2-oxazolidione (MEOX) to be the third co-solvent of EC/PC-LiAsF₆ electrolyte solution. They reported that an electrolyte composed of 21 m/o PAN:33.8 m/o EC:27.7 m/o PC:11.5 m/o MEOX:6.0 exhibits conductivities of 1.14×10^{-4} S cm⁻¹ at -40°C and 2.98×10^{-3} S cm⁻¹ at 25°C.

The other advantage is the improvement of the stability at interfaces with electrodes. Addition of 5 wt.% zeolite to the gels will effectively reduce the rate of growth of the resistive layer on the lithium surface (Fig. 7b). It is believed that this beneficial interfacial characteristic is based, in part, upon the water affinity of molecular sieves. The dispersion of ground zeolite traps impurities and prevents them from reacting at the interface. Another possible reason for the improved interface may be due to the composite film being more viscous than the gel electrolytes, thus preventing the flow of corrosive solvents to the interface [53].

A detailed discussion regarding the electrochemical stability of PAN-based electrolytes was first presented by Dautzenberg et al. [54]. The anodic and cathodic stability limit for a typical PAN-based electrolyte film is shown in

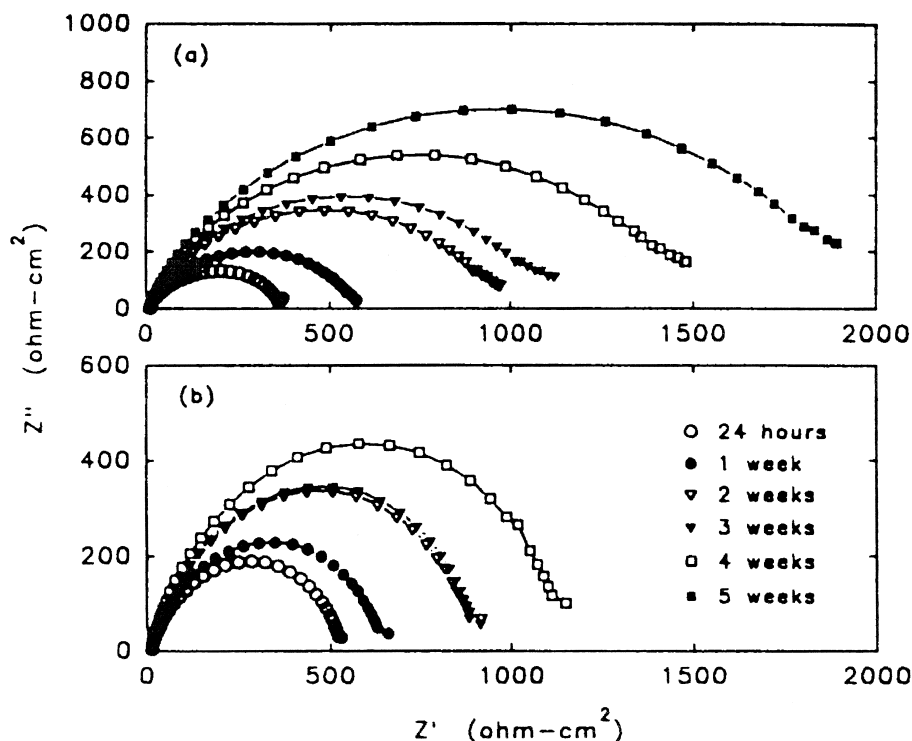


Fig. 7. Time evolution of impedance response of Li/PAN-EC/PC-LiAsF₆/Li cells: (a) gel, (b) composite with 5 wt.% zeolite powder, 10 Å, 40 μm (after Ref. [53]).

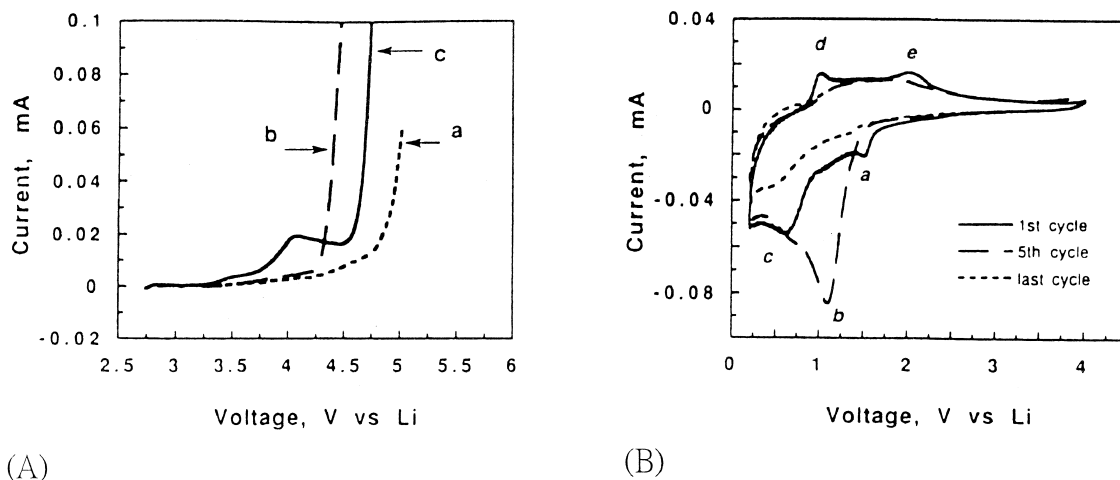


Fig. 8. (A) Anodic decomposition of 16PAN/23PC/56.5EC/4.5LiX gel electrolytes at room temperature. Curves a, b, and c correspond to samples containing LiClO_4 , LiAsF_6 , and $\text{LiN}(\text{CF}_3\text{SO}_2)_2$, respectively. Scan rate: 1 mV s^{-1} . Working electrode: SS 304. (B) Cyclic voltammetry in voltage range 0.2–4.0 V for sample in part (A) (after Ref. [54]).

Fig. 8. Salt concentration, PAN concentration, and the mixture ratio between EC and PC have no obvious effects on the anodic stability. The anodic stability is usually limited by the decomposition of PAN and the lithium salt. In contrast, the situation with cathodic stability is more complex. Fig. 8B indicates that the cathodic stability may be affected by the reduction of water (peak a), the anion groups (peak b), and the lithium (peak c) on the electrode.

Although the conductivities of PAN-based electrolytes approach those found in EC/PC liquid electrolytes, NMR line-width and spin-lattice relaxation time (T_1) measurements indicate that short-range ionic mobility is impeded by the presence of PAN [57], and the idea of inert PAN chains providing only dimensional stability can be discarded. There are many other reports on the transport mechanism of lithium ions through PAN gel electrolytes [58–60]. They basically support the notion that lithium ions experience strong interactions between plasticizers and polymer backbone. More investigations are needed, however, to gain a complete understanding of the transport mechanism in gel electrolytes which are complex composites.

4. PMMA-based electrolytes

The use of PMMA as a gelatinization agent in the electrolyte was first announced by Iijima et al. [61] in 1985. They reported that a conductivity of $10^{-3} \text{ S cm}^{-1}$ at 25°C was attained with 15 wt.% PMMA with an average molecular weight of 7000.

Bohnke et al. [62] dissolved PMMA, up to 20 wt.%, in a $\text{LiClO}_4(1 \text{ M})\text{-PC}$ electrolyte at room temperature to obtain a homogeneous and transparent gel. They reported that the resulting gel electrolyte possessed a conductivity of $2.3 \times 10^{-3} \text{ S cm}^{-1}$ at 25°C . The presence of the high-molecular-weight PMMA imparts a very high macro-

scopic viscosity ($\sim 335 \text{ Pa s}$) to the system without significantly diminishing the conductivity, i.e., the conductivity of the gel remains very close to that of a liquid electrolyte. They concluded that the PMMA acts primarily as a ‘stiffener’, that fast ion transport occurs through a continuous conduction path of PC molecules, and that the presence of PMMA does not affect the electrochemical stability of the electrolyte.

In later studies, Bohnke et al. [63,64] revealed that the ionic conductivity of the $\text{PMMA-LiClO}_4(1 \text{ M})\text{-PC}$ system decreases with increasing amount of polymer and lies between 5×10^{-3} and $5 \times 10^{-5} \text{ S cm}^{-1}$ at room temperature. On the other hand, the viscosity varies greatly, from 8×10^{-3} to $6 \times 10^6 \text{ Pa s}$, and results in a solid adhesive material. Experimental results showed that some change occurs in the conduction path of the gel around 30 to 35 wt.% of polymer. At lower concentrations of PMMA, the gelatinized electrolytes can be considered as a liquid electrolyte engaged in an inert polymer matrix, and there is a very small decrease in conductivity although the possibility of enhanced macroscopic viscosity still exists. Interactions between the conductive medium and the polymer are almost absent. On the other hand, for higher concentrations, some stronger interactions may be established between the polymer chains and the conducting electrolyte. These cause a dramatic decrease in conductivity and an increase in the activation energy of conduction. Although as high as $2.3 \times 10^{-3} \text{ S cm}^{-1}$ or above, the conductivities reported by Bohnke et al. were measured over viscous or concentrated polymer solutions.

Appetecchi et al. [65] examined PMMA-based electrolytes, prepared as thin films, which were plasticized by EC/PC- LiX ($\text{X} = \text{ClO}_4$, AsF_6 , or $\text{N}(\text{CF}_3\text{SO}_2)_2$). It was found that PMMA-based electrolytes exhibit similar conductivity behaviour with only a slight difference in the activation energy. Arrhenius plots showed that the elec-

Table 4

Lithium transference numbers and anodic stability of various gelled electrolytes at ambient temperature (after Ref. [65])

Sample	Molar composition (m/o)	Transference number, t_{Li^+}	Anodic stability (V) vs. Li
PMMA-PC/EC-LiClO ₄	30:19:46.5:4.5	0.4	4.6
PMMA-PC/EC-LiAsF ₆	30:19:46.5:4.5	0.6	4.8
PMMA-PC/EC-LiN(CF ₃ SO ₂) ₂	30:19:46.5:4.5	0.7	4.8
PAN-PC/EC-LiClO ₄	16:23:56.5:4.5	0.5	4.8
PAN-PC/EC-LiAsF ₆	16:23:56.5:4.5	0.6	4.5
PAN-PC/EC-LiN(CF ₃ SO ₂) ₂	16:23:56.5:4.5	0.7	4.6

trolites reach conductivities of the order of $0.5 \times 10^{-3} \text{ S cm}^{-1}$ at 60°C and that even at low temperatures (e.g., down to -20°C) the conductivity remains quite high (i.e., around $10^{-4} \text{ S cm}^{-1}$). Transference numbers for PMMA-based electrolytes are higher than those obtained for conventional PEO-based polymer electrolyte systems, as indicated in Table 4. In addition, various current-voltage curves obtained by sweeping a stainless-steel (SS) electrode in cells showed that PMMA electrolytes have an anodic stability higher than 4.5 V vs. Li⁺/Li (Table 4), and are thus compatible with high-voltage electrode couples such as Li-V₆O₁₃ or Li_xC₆-LiCoO₂.

Stallworth et al. [66] studied the same system by means of differential scanning calorimetry (DSC) and NMR spectroscopy. The DSC analysis revealed that only a single glass-transition temperature exists for an electrolyte membrane; this reflects the relatively homogeneous nature of the material. Although ionic conductivities of gels approach those of liquid electrolytes above the ambient temperature, NMR results indicate that the immediate environments of both the cations and anions differ significantly in the gel and in the liquid because the line-widths for ⁷Li - NMR spectra are significantly larger than those for the liquid counterpart. Moreover, because the main source of broadening of the central portion of a spectrum is short-range nuclear dipole-dipole interactions with protons in the solvating molecules, broadened line-widths usually imply the absence of microscopic liquid regions in the gel, which rules out the conclusions of Bohnke et al. [62].

5. PVdF-based electrolytes

PVdF (-[CH₂-CF₂]_n-) has been chosen as a polymer host by virtue of its various appealing properties. PVdF-based polymer electrolytes are expected to be highly anodically stable due to the strongly electron-withdrawing functional group (-C-F). Further, PVdF itself has a high dielectric constant ($\epsilon = 8.4$) for a polymer, which can assist in greater ionization of lithium salts, and thus provide a high concentration of charge carriers. The earliest examination of PVdF was undertaken by Watanabe et al.

[47] in 1981. It was found that PVdF can form homogeneous hybrid films with a lithium salt, EC, and/or PC in the proper proportions.

Tsuchida et al. [73,74] studied the plasticized PVdF system. They demonstrated that in systems with 30 mol% LiClO₄, plasticizers increase the conductivity in the following order: DMF > γ -butyrolactone > EC > PC > PEG 400 > PPG 1000. This trend reveals that the viscosity, rather than the dielectric constant of the plasticizers, is the controlling parameter. Thus, the conductivity of a polymer electrolyte depends strongly upon the ionic mobility within the material. Low-molecular-weight polyethers with low dielectric constants and high viscosities are the least effective in elevating the conductivity. Unfortunately, this work also indicated that the preferred PVdF compositions were capable of exhibiting a ionic conductivity above $10^{-5} \text{ S cm}^{-1}$ only at elevated temperatures, reportedly due to the inability of the membrane to remain homogeneous at or below room temperature.

Nonetheless, the most critical issue of the PVdF-based polymer electrolyte may be its interfacial stability toward lithium metal. In fact, fluorinated polymers are not chemically stable toward lithium owing to an interfacial reaction between lithium and fluorine which results in the formation of LiF and renders PVdF-based electrolytes unsuitable for batteries using lithium metal anodes. Choe et al. [75] confirmed this phenomenon via lithium plating/stripping experiments. The peak current decreased upon cycling and the working electrode was completely covered with a black powdery substance. Also, they reported that PVdF-based electrolytes plasticized with a solution of LiN(SO₂CF₃)₂ in PC had a conductivity of $1.74 \times 10^{-3} \text{ S cm}^{-1}$ at 30°C and oxidatively stable potential limits between 3.9 and 4.3 V vs. Li⁺/Li. Finally, they suggested that ionic mobility is the primary determinant of polymer electrolytes conductivity since this conductivity increases by about two to four orders of magnitude on incorporating plasticizing solvents into the SPE.

The outstanding studies of Gozdz et al. [76–78] and Tarascon et al. [79] in recent years deserve detailed description. Previously, hybrid polymer electrolyte films were usually made by dissolving a polymer matrix into a low-boiling solvent (THF, acetonitrile, etc.) together with a

non-aqueous Li salt electrolyte. The resulting viscous solution (consisting of polymer matrix, low boiling solvent and liquid electrolyte) was cast, and usually resulted in tacky and mechanically weak films. While the many hybrid electrolytes reported at the time exhibited high ionic conductivities, most of them suffered various deficiencies which prevented their use in practical cells. For example, their mechanical properties were often very poor and the films had to be hardened by either chemical or physical (high energy radiation) curing. Besides the need for cross-linking, the main shortcoming of the above process was that it had to be carried out in a completely moisture-free atmosphere because the moisture sensitive lithium salt was present at the initial stage. This resulted in high processing costs. Gozdz et al. successfully overcame these difficulties and developed reliable and practical rechargeable Li-ion plastic batteries. Rather than choosing commonly used gel electrolytes, they selected a copolymer of vinylidene fluoride with hexafluoropropylene (PVdF–HFP) which contained amorphous domains capable of trapping large amounts of liquid electrolytes, and crystalline regions which provided sufficient mechanical integrity for the processing of free-standing films and, thereby, eliminated the need for a cross-linking step. Further, to bypass the burden of assembling the cell in a moisture-free environment, Gozdz et al. used a Li salt-free plasticizer which was then substituted by the liquid electrolyte during the final stage of cell processing through an extraction/activation step.

More specifically, the system can be described as a heterogeneous, phase-separated, plasticized polymer elec-

trolyte/separator. There are at least four phases in the activated electrolyte: a semi-crystalline polymer with a relatively low degree of crystallinity (20–30%) which is not swollen, an amorphous part which is plasticized with the electrolyte solution, a large volume of nanopores, and interfacial regions of the nanoparticle filler (silica, alumina, titania) filled/coated by the liquid solution of the electrolyte, and the inorganic filler.

The most critical stages of Bellcore's process are the plasticization of PVdF–HFP copolymers, subsequent plasticizer removal, and the final reswelling in an electrolyte solution. Low-boiling solvents, such as diethyl ether or methanol, are successfully employed to remove dibutyl phthalate (DBP) from the polymer matrix, leaving a pore structure in the polymer layers which is then refilled with the liquid electrolyte during the cell activation process. The ability of previously extracted and dried PVdF–HFP/DBP laminates to reswell after immersion in organic electrolyte solutions is critical to their application in lithium-ion batteries. The larger the amount of trapped liquid electrolyte, the higher the ionic conductivity of the membrane. While quite efficient, the pore memory effect during the removal of DBP is not 100% efficient. Accordingly, the liquid electrolyte uptake during the activation step is slightly lower than the initial volume of DBP and results in electrolyte films with ionic conductivities of only 0.2 mS cm^{-1} (Fig. 9). To enhance further the electrolyte uptake and the ionic conductivity, inorganic fillers such as fumed silica are included in the polymer matrix. Electrolytes with excellent mechanical properties, up to temperatures of about 100°C , containing up to 60% of liquid

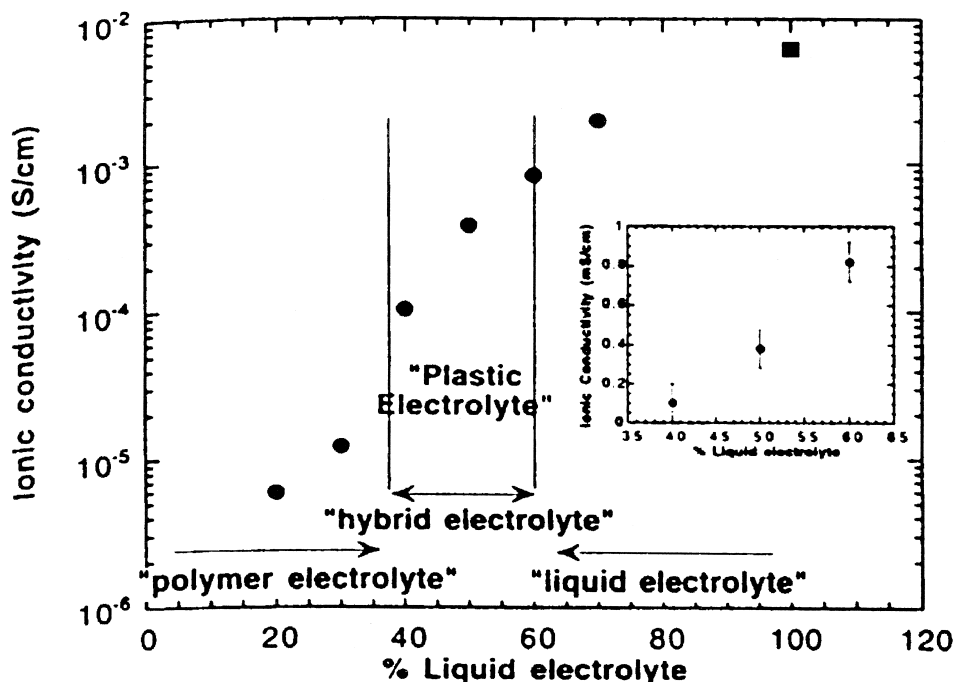


Fig. 9. Ionic conductivity of hybrid electrolyte films based on PVdF–12% HFP and 1 M LiPF_6 in EC/PC (after Ref. [79]).

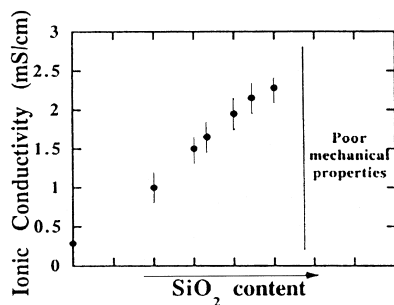


Fig. 10. Effect of inorganic filler on ionic conductivity of hybrid electrolyte films based on PVdF–12% HFP in 1 M LiPF₆ in EC/PC (after Ref. [79]).

electrolyte and having ionic conductivities of 3 mS cm⁻¹ have been prepared (Fig. 10).

Jiang et al. [80] studied electrolyte membranes which consist of PVdF, EC, PC, and LiX (X = CF₃SO₃, PF₆, or N(SO₂CF₃)₂). They found that the conductivity of the electrolytes was influenced by the viscosity of the medium and the concentration of the charge carriers, which are directly related to the weight ratio of PVdF/(EC + PC) and the type and concentration of the lithium salt. Room-temperature conductivities as high as 2.2 mS cm⁻¹ were obtained for some LiN(SO₂CF₃)₂-containing electrolytes. Cyclic voltammetry of the LiN(SO₂CF₃)₂-containing electrolytes showed anodic stability up to 4.0 V on Al, 4.2 V on Ni, and 4.5 V on SS, as well as cathodic stability down to zero volts on both Ni and SS. The stability of the lithium interface in the PVdF–EC/PC–imide polymer electrolyte has suggested that lithium anode batteries utilizing these electrolytes may have good shelf life at room temperature. The low lithium cycling efficiencies from cyclic-voltammetric experiments suggest, however, that PVdF–HFP based electrolytes may be better suited for primary than for secondary batteries when the anode is lithium metal.

6. Key technical issues

Ionic conductivity is certainly the most important concern for polymer electrolytes. After incorporating plasticizers, conductivities of various systems have been elevated by several orders of magnitude. From the numerous observations in recent years, it is easily concluded that ionic mobility plays the pivotal role in the improvement of the conductivity of polymer electrolytes, and that achieving a high ionic conductivity is no longer a major problem. This viewpoint is well accepted by the battery community.

Nonetheless, the use of substantial amounts of plasticizers in gel electrolytes might result in some problems which existed in original designs of liquid electrolyte-based lithium and lithium-ion batteries. Aside from these intrinsic problems, certain new problems might arise in gel

electrolyte systems. Thus, it is timely to point out several fundamental issues that must be considered in the future development of gel-type electrolytes.

6.1. Compositional compatibility and stability

Compositional compatibility and stability originate from the presence of a polymer component, and present unavoidable problems with a plasticized polymer electrolyte in contrast with a liquid electrolyte. The imposed constraints which arise from the incorporation of polymer into a liquid electrolyte solution are two-fold: one is the compatibility between the polymer and the organic solvent, and the other is the lower limit of the boiling point of organic solvent. If any of the requirements are not satisfied, gel electrolytes will experience a syneresis effect [52,72,82], as noted in the third part of this article.

A gelled polymer electrolyte membrane is usually made from a polymer, a lithium salt, and solvents which are binary or ternary. To facilitate dissolving the polymer at the preparation step and to obtain a homogeneous membrane, good compatibility between the polymer and the solvent should be guaranteed. Although ‘like dissolves like’ is the well-known underlying philosophy, this aspect can be further quantified from thermodynamic considerations.

The Gibbs free energy change of mixing, ΔG_m , is a fundamental parameter which describes the miscibility of two components for a physical process of dissolving a polymer into a solvent or solvent mixture

$$\Delta G_m = \Delta H_m - T\Delta S_m \quad (1)$$

where ΔH_m is the enthalpy change of mixing, T is the absolute temperature, and ΔS_m is the entropy change of mixing. Only when ΔG_m is negative can the solution process occur spontaneously. The term $T\Delta S_m$ is always positive since the dissolution of a polymer is associated with an increase in entropy. In addition, the entropy change of mixing, ΔS_m , is comparatively small with respect to that in a regular solution, as predicted by the Flory–Huggins theory for polymeric systems [83]. Under this situation, the solubility is determined by the sign and the magnitude of ΔH_m . On a quantitative basis, ΔH_m can be expressed as:

$$\Delta H_m = V_m \left[\left(\frac{\Delta E_1}{V_1} \right)^{1/2} - \left(\frac{\Delta E_2}{V_2} \right)^{1/2} \right]^2 \phi_1 \phi_2 \quad (2)$$

where V_m represents the total volume of the mixture, ΔE represents the energy of vapourization of the mixture to a gas at zero pressure, V is the molar volume, ϕ denotes the volume fraction of component 1 or 2 in the mixture, subscripts 1 and 2 denote the solvent and the polymer, respectively. The quantity $\Delta E/V$ represents the energy of vapourization per unit volume and is called the cohesive

energy density (CED), and the square root of CED is the solubility parameter, δ ;

$$\delta \equiv \left(\frac{\Delta E}{V} \right)^{1/2}. \quad (3)$$

Since the intermolecular forces are determined by the sum of the secondary forces, dispersion forces, polar forces, and hydrogen bonding, Hansen [84] has proposed to divide the total solubility parameter into three contributions:

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \quad (4)$$

where δ_d , δ_p , and δ_h are solubility parameters due to dispersion forces, polar forces, and hydrogen bonding, respectively. As for a solvent mixture, the overall solubility parameter can be estimated from the following equation:

$$\delta_{\text{mixture}} = \frac{\sum_i x_i \tilde{V}_i \delta_i}{\sum_i x_i \tilde{V}_i} \quad (5)$$

where x_i is the mole fraction and \tilde{V}_i is the specific volume of component i . A comprehensive survey of solubility parameters can be found in compilations by Burrell [85] and Barton [86].

According to Eqs. (2) and (3), the enthalpy change of mixing ΔH_m of the polymer solution depends on $(\delta_1 - \delta_2)^2$. The closer δ_1 is to δ_2 , the smaller ΔH_m will be, and hence the better the intersolvation between the solvent and polymer. Yet, 'perfect' affinity between these two kinds of component is not actually desired in a polymeric electrolyte solution mixture, since it will cause the mixture to remain highly viscous and never convert into a free-standing gelled membrane. More specifically, it is best to keep the absolute value of the difference between the solvent and the polymer at a small value, i.e.,

$$|\delta_1 - \delta_2| \leq \xi \quad (6)$$

where ξ is not an universal constant, but an empirical parameter which may vary in each system. A value ranging from 0.8 to 1.5 is theoretically reasonable. This condition could be realized, for completely amorphous polymers in particular, by adding a small amount of non-solvent into the parent polymer solution. As implied in Fig. 11, the solution will gel at a lower polymer concentration through a sol-gel transition boundary. Of course, the effect of lithium ions within the mixture is temporarily ignored in Fig. 11 for the sake of clarity.

On the other hand, polymer electrolytes require organic solvents with higher boiling points. Commonly employed organic solvents in liquid-type electrolytes are not necessarily appropriate for use in gelled polymer electrolytes since these volatile solvents with low boiling point will hinder the stability of a gel. The gel systems are essentially thermodynamically unstable and rapid solvent evaporation actually will accelerate the degradation of a gel. Although

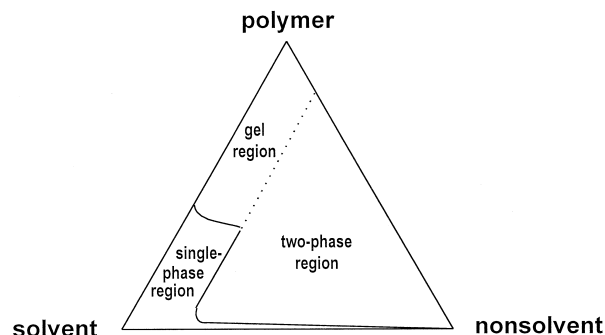


Fig. 11. Concentration phase diagram of a ternary polymer solution containing one-phase region, two-phase region, and gel region.

there is no definite threshold of the lower limit of the boiling point, 180°C appears to be reasonable.

6.2. Mechanical strength

To effect practical use of a polymer electrolyte, the electrolyte must: (i) remain structurally stable during manufacturing, cell assembly, storage, and usage; (ii) prevent flow from occurring within the cell to prevent self-discharge; (iii) be capable of preparation in an easy and repeatable manner. In other words, the mechanical strength is also one of the important factors while manufacturing polymer electrolytes. As noted earlier in this review, incorporating additive such as ceramic powder can strengthen the dimensional stability of electrolyte membranes. In addition to this method, some other feasible approaches are also introduced here.

The first type is the blended polymer electrolyte. The matrix of a such an electrolyte comprises at least a first phase adapted to absorb the electrolyte's active species and a second phase that is tougher and sometimes substantially inert. Systems such as PEO/PMMA [37], PVDF/HDPE [87], and PMMA/PVC [88] fall into this category. The second phase in the polymer blend may be selected from polyethylene, polypropylene, polytetrafluoroethylene, polystyrene, ethylene propylene diene monomer, nylon, etc. With respect to the relative amount of each polymer in the blend, it is contemplated that the matrix may comprise between 15 and 25 wt.% of the second component.

The second type is prepared via the chemical cross-linking method [39,89,90]. Most electrolyte systems today have been prepared by forming a temporary physical network. This is a method based, at least on the microscale, on phase separation. The disadvantage lies in the fact that a considerable volume fraction of the phase-separated materials does not contribute to ionic conductivity. Cross-links in a chemically cross-linked polymer electrolyte constitute, however, only a negligible volume fraction. Besides, it does not crystallize and can offer the advantage of good mechanical properties. An electrolyte of this type, therefore, seems to be the best choice to serve as a polymer electrolyte membrane.

The third type is based on the new concept of ‘hairy rod molecules’ [91], a scheme that overcomes the compatibility limitations of rigid and flexible polymer materials. These materials can hence be regarded as ‘molecular composites’ in which both components are dispersed on a molecular level. Rigid macromolecules in these materials serve as the reinforcing backbone moieties whereas flexible side chains provide the liquid matrix for ion transport. Lauter et al. [92] chose poly(*p*-phenylene) (PPP) as the rigid backbone attached with flexible oligo(ethylene oxide) (EO) side chains, which forms the liquid matrix in which lithium salts can be dissolved and in which ionic transport proceeds. Thermal analysis and X-ray investigations revealed that the self-rearrangement in these materials give rise to a superstructure in which the PPP backbones are arranged in layers which are separated by the liquid EO matrix, as shown in Fig. 12. This superstructure is responsible for the outstanding mechanical property. It can be described as a smectic B-type liquid-crystalline phase and remains stable up to temperatures well above 150°C. On the other hand, one disadvantage of the PPP-based polymer electrolyte is that its backbones may be electrochemically unstable since

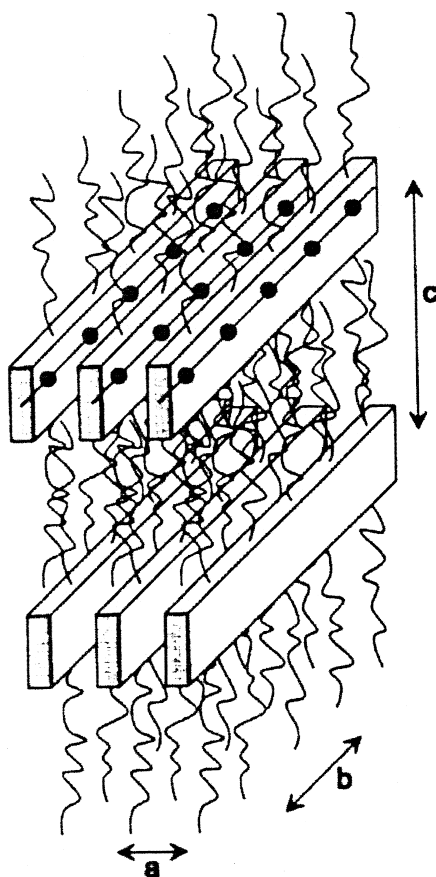


Fig. 12. Model of superstructure of PPP-reinforced SPE. PPP backbones (bars) are arranged in layers separated by the EO matrix. Layer distance increases with introduction of Li salt (after Ref. [92]).

they are able to undergo redox reactions owing to the π -conjugated electronic structure. Research in this area is still underway, but it indeed represents an interesting and valuable avenue of endeavour.

6.3. Electrochemical and interfacial stability

Finally, it should be noted that the electrochemical stability of the electrolyte still remains largely unresolved. Obviously, finding an electrolyte system which is stable to both metallic lithium (or lithiated carbon) and highly oxidizing cathode materials is not an easy task. Nonetheless, there are already promising research studies in this area [93–95]. For example, Xu and Angell [94] synthesized asymmetric noncyclic ethyl methyl sulfone (EMSF) as the electrolyte solvent and found that it can withstand a potential as high as 5.8 V vs. Li/Li^+ before the onset of oxidation. This excellent work has shed light on the practical application of some high-potential cathode materials such as the inverse spinel LiNiVO_4 [96].

Good stability at the electrode/electrolyte interface is the most critical criterion to be achieved before a reliable polymer electrolyte battery with long cycle-life can be realized. It is now well established that in lithium and lithium-ion batteries containing either liquid or polymer electrolytes, the anode is always covered by a porous passivating layer called the solid electrolyte interphase (SEI) [97–99]. For many electrolytes, this thin layer is formed from oxygen or water vapour that might be present in the cell before or after contacting the electrolyte and electrode materials, so the layer is often an alkali metal hydroxide or oxide, or a mixture of the two. The significance of the SEI cannot be over-emphasized and has been well recognized both by the scientific community and by industry. Research into the composition, formation mechanism, and growth kinetics of this passivating layer has been in progress since its discovery in 1979.

7. Summary

In brief, plasticized or gelled electrolytes are among the major polymeric electrolyte materials for solid-state lithium and lithium-ion batteries. The incorporation of substantial amounts of organic solvents has effectively improved the ionic conductivity of conventional SPEs. Four representative plasticized systems, namely PEO-, PAN-, PMMA-, and PVdF-based polymer electrolytes, have been the most widely studied. Some minor problems are associated with these electrolytes and need to be tackled, such as the compositional compatibility and stability, mechanical strength, and electrochemical and interfacial stability. Possible approaches and the underlying concepts for solving

these problems are discussed at the concluding part of this review.

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