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Lithium polymer electrolytes for novel batteries application: the review perspective

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Abstract

Beyond liquid electrolytes, the development of other electrolyte systems is needed to cover all needs for novel batteries suited for detailed usage. Lithium polymer electrolytes for next-generation batteries cover a broad range of emerging energy applications, including their further investigation of solid polymer ionic conductors. Possibility of transferring Li^+ cations through the unique polymer structure forces modifications of a solid polymer electrolyte. The host matrix is immobile, while long-range cation transport must involve dissociative steps where solvated cations are transferred between neighboring coordination sites, in combination with migration and diffusion of ion aggregates weakly coordinated to the polymer solvent. Most of the current models can be successfully applied to amorphous monophase systems. There are many concepts leading to the increase in flexibility, conductivity performance, and extended storage time for several months, which might be useful for even very demanding battery applications. This review provides readers with a comprehensive background for understanding current knowledge and opportunities for lithium polymer electrolytes.

Keywords Polymer · Electrolyte · Li-ion · Lithium · Battery

1 Introduction

Independent of the optimization of electrode materials (not discussed here), a lot of effort has been devoted to the development of electrolytes, tailored to specific electrochemical systems.

The role of electrolytes is two, or sometimes threefold:

1. Provide ionic contact between the electrodes which allows to close the circuit when the cell is working
2. Ensure electronic and spatial separation of the positive and negative electrode to avoid short-circuit and, as a result, self-discharge of the cell, which in some cases can be very spectacular (as the ones of high-power Li-ion cells)
3. In the case of electrochemical systems where electrode components are not the only reactants appearing in the overall cell reaction, the electrolyte is the source (storage) of the remaining ones.

2 Definition

Generally, polymer electrolytes are defined as "complexes" of electron-donor polymers with various inorganic or organic salts or acids. The main requirements for a polymer to be used as a matrix in polymer electrolyte systems are:

- the presence of a heteroatom (usually O, N, S) with lone electron pairs of a donor power sufficient to complex cations,
- appropriate distances between coordinating centers to insure the hopping of charge carriers and,
- sufficiently flexible polymer chain segments to facilitate the movement of ion carriers.

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In polymer electrolytes, ion transport occurs in a highly viscoelastic (solid) state. The most intensively studied polymer electrolytes are based on poly(oxa alkanes), poly(aza alkanes), or poly(thia alkanes). The present work contains the studies of polymer electrolytes based on low molecular weight poly(oxa alkanes)—polyethers and particularly on alkali metal salt complexes with poly(ethylene glycols) (PEG).

The interest in polymer electrolytes results from a variety of possible applications of these materials [1]. That has stimulated further investigation of solid polymer ionic conductors. Among them, the following seem to be of major importance:

- lithium and sodium polymer–ion batteries,
- fuel cells,
- electrochemical sensors,
- electrochromic windows or displays.

The properties of polymeric electrolytes should fulfill the requirements necessary for application in at least one of the above-mentioned devices. The most important and universal of these prerequisites are listed below:

- chemical and mechanical stability over a wide temperature range,
- electrochemical stability of at least 4 V versus Li electrode; especially important for battery applications
- the low activation energy for conduction
- high cation transport numbers
- good electrode–electrolyte interphase characteristics
- ease of sample preparation and processing.

The required conductivity depends on the intended application and cation transport number, but generally should be in the range of 10^{-3}-10^{-4} S cm^{-1} for batteries.

As one can imagine, it is demanding to find an electrolyte fulfilling all the requirements. Despite intensive research, there is still a considerable number of unsolved problems related to the fundamental understanding, synthesis, and application of polymeric electrolytes. This is a direct result of the phase structure of the materials. Even one of the simplest polymeric electrolytes, PEO-NaI, has a complicated phase diagram [2] (Fig. 1). The structure consists of an amorphous phase, a crystalline polymer phase, and at least one of a range of crystalline complex phases formed between the polymer and the salt. The contribution of each particular phase changes with temperature. Such a puzzling phase structure causes difficulties in the interpretation of ion transport phenomena in polymeric electrolytes. Therefore, the mechanism of conductivity in polymeric electrolytes is hard to establish.

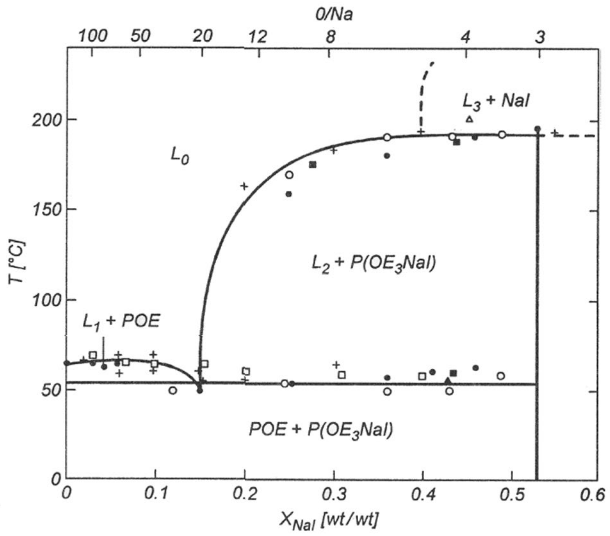


Fig. 1 Phase diagram of PEO-NaI electrolyte [Polymer Electrolyte Reviews—1 and 2 (J. R. Mac Callum and C. A. Vincent Eds.), Elsevier, London 1987 and 1989]

Several concepts have been proposed and summarized in review papers but none of them is generally valid for a wide range of materials. Berthier et al. [3] have shown that fast ionic transport takes place in the amorphous phase of the electrolyte. Here, ion diffusion coefficients are about three orders of magnitude higher than in the crystalline phase. This assumption by Berthier, concerning the crucial role played by the amorphous phase of the polymer in ion conductivity, forms the basis for some of the proposed conductivity mechanisms, such as free volume [4], configurational entropy [5] and dynamic bond percolation [1]. These models are mainly successful in quantitatively describing conductivity mechanisms for simple monophase amorphous electrolytes and are not valid for multiphase systems.

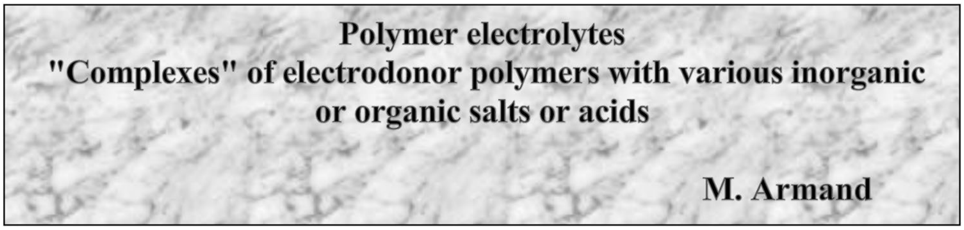
The flexibility of the amorphous polymer phase is of crucial importance for conduction since ionic and polymer segmental motions are coupled for good conductivity. Thus, a low glass transition temperature (T_g) for the amorphous polymer phase is a desirable property, along with the low crystallinity of the material. Unfortunately, the polyether–salt complexes which are the most widely studied systems are those which have high crystallinity at ambient temperatures. PEO poly(ethylene oxide) is still one of the most extensively studied polyether matrices due to its low cost, non-toxicity, relatively low melting point, reasonably low T_g, ability to dissolve a variety of lithium salts over a range of concentrations, and capacity to act as a binder for other phases. However, PEO is semicrystalline, which still inhibits the conduction of lithium ions [6].

The conductivities of plain PEO-based electrolytes are in the range of 10^{-7}–10^{-8} S cm^{-1}, which is too low for most applications. The amount of flexible amorphous phase increases as the temperature approaches the melting point of the crystalline polymer phase i.e., 65–68 °C. However, at temperatures exceeding the melting point the mechanical stability of electrolytes is much lower and membranes flow under any pressure applied in electrochemical devices resulting in short circuits.

Despite all the limitations mentioned above, semicrystalline PEO still has attracted the highest attention as the best highly viscous polymeric matrix. The main goal is to obtain a stable amorphous system containing a high amount of ethylene oxide molecular repeat units in the main or side polymer chain. The various modifications of PEO-based electrolytes can be divided into several categories:

- Preparation of amorphous polymer matrices in which the ether segments consist of 4–15 ethylene oxide monomeric units. These are long enough to effectively complex alkali metal cations but too short to show a tendency toward a crystallization. Such structures can be obtained by preparing copolymers with oxymethylene and/or oxypropylene units spread along the polymeric chain built of oxyethylene units. They can be also grafted or comb-like copolymers in which oligo(oxyethylene) units are attached to the main chain of high flexibility, e.g., poly(siloxane) [7, 8];
- Preparing electrolytes based on different polymer architectures (polyphosphazene [9, 10], poly(siloxane) [11], poly(oxypropylene)) whose crystallinity is much lower than the cristallinity of PEO [12, 13]. Another approach is the preparation of polymer blends and/or copolymers [10]. However, other issues are to be considered here, namely the stability of the polymer against low and high potential materials, dielectric constant, and donor number that have to be high-enough to enable salt dissociation;
- Doping the polymer matrix with light molecules, often of high dielectric constant and ability to dissolve the salt (organic carbonates, carboxylic esters, nitriles, glycols, etc.). This plasticization of the polymer leads to an increase in conductivity, however, causes deterioration of the mechanical properties that are of main interest in using polymer electrolytes [14–18]. To obtain more stable structures, such electrolytes are often reticulated through high-energy radiation. In addition—plasticizers embedded in the electrolyte can lead to the problems encountered in "classical" liquid electrolytes (evaporation, internal pressure, corrosion, flammability, etc.) [19, 20];
- Either charge carrier creation or migration can be limiting steps of the conduction phenomenon [21, 22], meaning that not only the polymeric matrix determines the conductivity but also the dopant salt. Severe aggregation of ions (formation of ion pairs, ionic triplets, and higher aggregates) [23] decreases the number of charge carriers and leads to the stiffening of the polymeric matrix due to bridging the coordination centers through the aggregates. This causes a drop in conductivity, combined with a drop in the cation transport number. To avoid that, new salts of very low lattice energy were developed and applied in electrolytes, where very weak Lewis bases were applied as anions (trifluoromethane sulfonate, bis(trifluoromethyl sulfonyl) imide, etc.
- There is a variety of ceramic materials that offer relatively high ionic conductivity at room temperature used as ceramic fillers [24–26]; however, applying them directly as electrolytes in commercial cells for mobile applications is not easy because they are brittle [27], hard to process and most importantly they cannot provide contact with the entire surface of porous electrodes made of powders as easily as polymers and liquids can do. Thus, the first approach was using the polymeric electrolytes as conductive binders for the ceramic ionic conductors added to the polymer in a form of powder.

Poly(oxyethylene) had been studied as the first candidate because of its availability and very favorable chemical and electrochemical properties. Although its complexes with simple alkali metal salts are not good enough to be applied in electrochemical cells working at room temperatures this material is still interesting to work with. Many different strategies for enhancing conductivity have been proposed ever since the first measurements have been done on PEO-salt complexes. However, a glance at the battery market gives a quick answer about the applicability of the results. Up to now the only dry polymeric electrolyte that has been applied in a commercial lithium battery is a plain poly(oxyethylene)–lithium bis(trifluoromethane sulfonyl) imide complex working at a temperature above the melting point. More exotic systems are difficult to be applied for several reasons. Due to the practical scope of this work, poly(oxyethylene) had been chosen arbitrarily as the polymeric matrix. Poly(oxyethylene) is stable enough to work with very low potential negative electrodes as well as with positive electrodes up to 4 V (4.2 V) vs. metallic lithium. The strategy of choice to improve the transport properties was the application of ceramic fillers since they are cheap, easily available in large quantities, non-toxic and stable in the cell environment, namely alumina and titania.



Polymer electrolytes
"Complexes" of electrodonor polymers with various inorganic or organic salts or acids

M. Armand

The “*lege artis*” polymer electrolyte is based on the dissolution of a salt in an ion-coordinating macromolecule such as poly(ethylene oxide) (PEO) with a high molecular weight of about 5×10^6 and 80% crystallinity.

These kinds of materials were first studied by Wright et al. in 1973 [28]. Recognition of the potential of such systems for practical applications and much of the early development are credited to Armand et al. [29].

The main reason to choose this polymer host is because of the formation of more stable complexes and the ability to possess higher ionic conductivities than any other group of solvating polymers without the addition of organic solvents. The oxygen atoms in this polymer have high electron-donor power and a suitable interatomic separation, enabling them to form multiple interpolymer coordinate bonds with cations. The low barriers to bond rotation allow segmental motion of the polymer chain, thus providing a mechanism for ion transport. Complex formation in PEO_n–salt (n—number of ether oxygens per mole of salt) is governed by a competition between the solvation energy and the lattice energy of the polymer and the inorganic salt. Low lattice energies of both the polymer and the complexing salt have been found to improve the stability of the polymer electrolyte [30].

PEO has been found to readily form complexes with lithium salts such as LiBr, LiI, LiCl, LiSCN, $LiClO_4$, $LiCFSO_3$, $LiBF_4$, and $LiAsF_6$ [31] out of which PEO–$LiCFSO_3$ [32, 33] and PEO–$LiClO_4$ [34] have been the most widely studied. Recently, the Li_2S_6-integrated PEO-based polymer electrolytes show an improvement in the Li^+ ion conductivity for all-solid-state lithium-metal batteries [35]. Indeed, the well-dispersed inorganic nanoparticles (nano-ZnO–PEO) exhibit a rather good lithium plating/stripping performance at 40 °C and the highest ionic conductivity (4.2×10^{-4} S cm^{-1}) at room temperature due to the polymer grafting and hybrid polymer approach [36].

Crystalline structures of PEO–$LiCF_3SO_3$, for example, have revealed that the cation remains encapsulated within the helix of the PEO chain; the anions are stacked outside the helix [37]. Thus, the possibility of migration of the anion within the polymer electrolyte exists. This would be detrimental to the performance of a lithium battery leading to excessive polarization due to concentration gradients, and possible anion degradation at the surface of the electrode. To minimize the anion migration, complexing salts containing large organic anions such as the LiTFSI and LiTFSM were studied by Armand et al. [30, 38] The presence of the high 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 lower anion transference numbers.

The most recent development in polymer electrolytes has been the synthesis and application of new salts employing anions with delocalized charge (otherwise known as Hückel’s anions). The name came from the transposition of the Hückel rule, predicting the stability of the aromatic systems. One of the most common examples of this type of anion is 4,5-dicyano-triazole (DCTA). This structure is completely covalently bonded and shows a very stable 6π (or 10π electron if CN bonds are involved in calculations) configuration. It can be produced from commercially available precursors and even more importantly, does not contain fluorine. Salts of this type were found to exhibit high (~ 300 °C) thermal stability. LiDCTA was successfully tested in PEO matrix systems proving to be a promising, improved electrolyte for lithium-ion batteries [39].

The structure of these anions ensures a weak interaction with the cation, which results in a significant improvement in the parameters associated with the transport of lithium ions when dissolved into the polymer. In combination with the simple synthesis, these salts are an attractive strategy to improve the operation of electrolytes (and cells with their use). It should be added that in the case of salts based on Hückel’s anions the trace moisture content is not disqualifying as is the case with electrolytes based on commercial $LiPF_6$.

Intensive crystallographic studies were related to the construction of the complexes of alkali metals containing 4,5-dicyanoimidazole derivatives. They showed that the solvates with acetonitrile exhibit the formation of structural motifs, in the form of complexes with dimeric structures [40]. This is rapidly developing research that is bringing a new level of understanding the solvation processes in battery electrolytes. Such knowledge combined with electrochemical studies enables the modeling of aggregation and transport processes in electrolytes. Understanding these phenomena will allow to improve the design of the electrolytes' salts in the future.

Another weakly coordinating imidazole derivative is LiTDI (lithium 4,5-dicyano-2-(trifluoromethyl)imidazolate). Following its rapid development, it is now in the commercialization stage, aiming for application in new types of lithium-ion cells. A major part of the research is the optimization of the electrolyte composition[41]. Reaching the highest ionic conductivities and ion transfer numbers, and in turn, the ability to work with modern cathodes and anodes is imperative to a successful, full-cell demonstrator.

The research efforts designed to obtain working half-cells for electrolytes with tricoordinate imidazole salt: trilithium 2,2′,2″-tris(trifluoromethyl)benzotris(imidazolate) (Li_3BTI), with a very high lithium-ion transfer number ($t^+ = 0.73$). Operation of several active materials (e.g., Si/C, $LiCoO_2$) vs. Li was demonstrated using Li_3BTI salt as an electrolyte [42]. While LiTDI development is more advanced at this stage [43, 44], LiPDI salt (lithium 4,5-dicyano-2-(pentafluoroethyl)imidazolate) is also investigated.

New salts were used in solid polymer electrolytes, their compatibility was demonstrated in the cell with metallic lithium and graphite, obtaining promising capacity parameters of 350 mAh g^{-1} and Coulombic efficiency of 98%.

Ultimately, the new salts and anions can be used as components of ionic liquids. So far, this has been presented only once in the literature, indicating high values of ionic conductivity (above 3 mS cm^{-1} at room temperature), low viscosity, a wide range of electrochemical stability, and non-flammability typical for ionic liquids [45]. Nevertheless, new approaches combining the use of ionic liquids and liquid metals for highly deformable mixed conductors are observed [46].

Currently, the market of electrochemical power sources is dominated by lithium-ion batteries. With the growing demand, the limited availability of this metal may become a problem [47] hence the necessity to look for new materials and solutions that can replace or supplement lithium. The natural candidate for replacing the metal lithium is a metal sodium [48]. It has a relatively low atomic weight, small ionic radius, and low standard redox potential (− 2.73 V vs. SHE), only slightly higher than the potential of lithium. In combination with practically unlimited resources, sodium is an excellent prospective material for use in battery cells.

The development of non-aqueous (liquid and solid) electrolytes dedicated to sodium-ion cells and demonstration of their ability to work with relevant electrode materials included:

- sodium 4,5-dicyano-2-(trifluoromethyl)imidazolate (NaTDI),
- sodium 4,5-dicyano-2-(pentafluoroethyl)imidazolate (NaPDI),
- sodium pentacyanopropenide (NaPCPI),
- sodium 2,3,4,5-(tetracyano)pirolate (NaTCP),
- sodium 2,4,5-(tricyano)imidazolate (NaTIM).

These new salts were also investigated in a polymeric matrix. Thanks to the implementation of the hot-pressing technique, it was possible to eliminate the use of solvents from the production of membranes, which allows to minimize the costs of the production and is much more environmentally friendly. Polymer electrolytes containing NaTCP-$P(EO)_n$ and NaTIM-$P(EO)_n$ showed maximum conductivity at $n = 16$, and $n = 20$ at 90 °C, respectively. NaTCP proved to be the most promising salt for use in polymeric electrolytes. The final materials exhibited very good mechanical properties and high ionic conductivity. NaTCP-$P(EO)_{16}$ showed ionic conductivity greater than 1 mS cm^{-1} at 70 °C. X-Ray diffraction data linked the electrochemical results with the unique non-covalent anion structure of this new class of battery electrolytes [49, 50]. Polymer electrolytes for next-generation batteries cover a broad range of emerging energy applications [51]. Recently, the lithium salt doped with single-ion conducting polymer electrolytes was assessed to enhance its ion conductivity [52]. On the other hand, there is a need for sustainable polymer electrolytes for post and lithium-ion batteries leading to the circular economy concept [53].

3 Classification

The conductivity of a polymer electrolyte is typically lower than the one of a comparable liquid electrolyte at any given temperature. Many new forms of polymer electrolytes have been developed to boost conductivity, and therefore different classifications are proposed. The term “polymer electrolyte” may now refer as a material from one of the following categories as classified by Fiona Gray:

1. A solvent-free system where the ionically conducting phase is formed by dissolving salts in a high molecular weight polar polymer matrix. This group consists of electrolytes which are primarily lithium-ion conductors.
2. A gel electrolyte is formed by dissolving a salt in a polar liquid and absorbing it into an inert, three-dimensional structured polymeric material to yield mechanical stability.
3. A plasticized electrolyte, similar to a gel electrolyte, is formed with the addition of small amounts of a high dielectric constant solvent to a conducting polymer electrolyte (#1 above) to enhance its conductivity.

4. An ionic rubber, which is a liquid electrolyte comprising a low-temperature molten salt mixture, is reduced to a rubbery condition by the addition of a small amount of high molecular weight polymer. On a structural level, these electrolytes have some factors in common with gel electrolytes.
5. A membrane ionomer and in particular, a proton-conducting polyelectrolyte e.g., the electrolyte having an ionic group incorporated into the polymer structure. This group exhibits high transference numbers for cations, which makes them more useful than other types of polymer electrolytes for applications [6].

Another classification has been proposed by Wright, and was based on mechanisms responsible for ion transport in polymeric electrolytes, e.g.,

1. The translation of lithium salts through liquid solvents in gels or hybrid materials of various kinds. These are solvent–containing systems in which a liquid electrolyte solution is either fully miscible with a single-phase swollen polymer matrix (gel) or is a two-phase system in which “free” liquid occupies micropores within a swollen polymer network (hybrid). Conductivity is essentially independent of the polymer segmental motion and typically around 1 mS cm^{-1} or higher at ambient temperature.
2. Solvent-free, salt-polymer complexed systems in which the ion couples with the motion of segments of the polymer chains above the glass transition temperature of the system. Typically, these are polyether–Li salt complexes in which both anions and cations are mobile within an amorphous, rubbery phase. Ionic conductivity is typically below 0.1 mS cm^{-1} at ambient temperature.
3. “Single ion” systems in which the lithium ion moves by a hopping process between anionic sites fixed to the polymer chain, or systems with reduced mobility of anions (solvent–containing or solvent-free). Ion conductivity is typically below 10^{-5} S cm^{-1} at ambient temperature.
4. Solvent-free, salt polymer complex systems in which ionic mobility is decoupled from the motions of polymer chain segments. Mobility through channeled structures involves minimal local segmental displacements. Conductivity is typically around 0.1 mS cm^{-1} at ambient temperature [54].

In this work, a different classification scheme is used. Lithium-conducting polymer electrolytes are placed into five classes according to the electrolyte composition and morphology. It is similar to the one originally proposed for lithium conductive systems by Scrosati and Vincent [55] and very similar to Gray’s.

Class 1: Amorphous macromolecular salt complexes

Materials of Class 1 are sometimes known as “dry” or “solvent-free” systems, typically based on polyether hosts. To avoid crystallization and to improve mechanical stability sophisticated polymer synthesis is often used. Molecular architectures based on random and block copolymers, comb-branched copolymers, interpenetrating networks, or liquid crystal-based systems are developed. Particular attention is paid to the synthesis of “single ionic conductors”, in which the anion is linked to the polymer backbone. In such systems, t_+ (cation transference number) is equal to 1, hence in a lithium battery, concentration polarization is prevented.

Class 2: Plasticized systems

A plasticizer is a small molecule material that may be added to enhance polymer segmental motion and flexibility and thereby improve the ionic conductivity of salts dissolved into the system. Generally, such polar liquids are added to the polymer electrolytes from Class 1. The addition of suitable organic solvents can increase conductivity 100 times. Degradation of mechanical properties can be offset by subsequent cross-linking of the system.

Class 3: Gel electrolytes

Gel electrolytes are formed by incorporating a nonaqueous electrolyte solution within an inactive structural polymer matrix. Since the plasticizers also interact with the ions (and indeed may preferentially solvate), coordinating macromolecules such as polyethers may be replaced by more inert polymers such as poly(vinylidene difluoride) (PVdF), polyacrylonitrile (PAN) (which is not totally inert), poly(methyl methacrylate) (PMMA), or vinylidene fluoride- hexafluoropene copolymers. These materials share some disadvantages associated with well-characterized reactions of liquid solvents with lithium metal and other negative electrodes used in secondary batteries. A more successful approach is to use plasticizing anions with extensive charge delocalization, such as bis(trifluoromethane sulfonyl) imido and carbon analogs.

Several specially designed additives have recently been reported, including a propylene carbonate molecule in which the methyl group has been substituted by $-(OCH_2CH_2)_3OCH_3$. The use of cyclic or linear, boron-based, and cyclic or linear aza-ether anion receptors [56], proposed for liquid lithium-battery electrolytes, may also be beneficial for Class 3 electrolytes.

The role of the solvent molecules is not fully understood since thermodynamic solvation and dissociation considerations are involved. These are in addition to dynamic mass-transport effects. The range of gel electrolyte systems that have been characterized and developed for practical cells is extensive [57].

Class 4: “polymer-in-salt,” or “rubbery” electrolytes

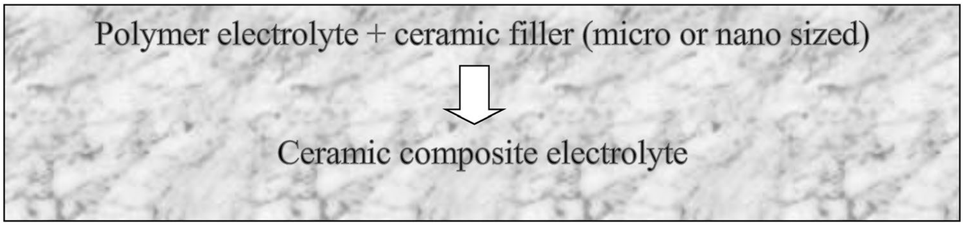
In such electrolytes, high-molar mass polymers are dissolved in low-temperature molten salt mixtures. These materials were developed by Angell and co-workers [58–60].

They combine the advantages of solid electrolytes, in which the cationic motion is decoupled from the matrix, with those of simple polymer electrolytes where the amorphous phase facilitates the ionic movement. The salt or salt mixture must have a low glass-transition temperature T_g, so that a rubbery material, rather than a glass, is formed when the polymer is dissolved in the fused salt. Unfortunately, most salts that have, or contribute to a suitably low T_g, tend to be very chemically reactive/corrosive or thermally unstable. Nevertheless, ambient temperature conductivity of 10 mS cm^{-1} has been demonstrated for certain salts.

Class 5: Composite polymer electrolytes

Class 5 comprises (i) dual-phase polymer systems [61] and (ii) mixed ceramic–polymer electrolytes [62]. Dual-phase polymer systems are based on two linked polymer blocks, one a “structural” element that provides mechanical stability and the other a “polar” element which can take up solvent together with any dissolved salt to produce ion-conducting pathways. Mixed latex dual-phase systems may involve, for example, styrene butadiene rubber as the supporting or structural phase, fused with acrylonitrile butadiene rubber as the polar element. Alternatively, a core–shell configuration may be produced in which the polar polymer block is formed around a mechanically strong nonpolar core.

Weston and Steele [63] first demonstrated the idea of incorporating electrochemically inert particulate fillers into polymer matrixes to increase the mechanical stability of the resulting material, with particles sized in tens of micrometers. Since then, a variety of high surface area particulate fillers (for example: ZrO_2, TiO_2, Al_2O_3, hydrophobic fumed silica, and fiber glass) was introduced into polymer matrices to obtain ‘composite polymer electrolytes’ or ‘composite ceramic electrolytes’.



4 Transport issues

4.1 Ionic transport

Although polymer electrolyte research and development has branched out significantly since its inception, the common mechanistic issues can best be understood regarding the Class 1 of Scrosati and Vincent that is concentrated polymer/salt complexes. Upon forming the complex, the glass-transition temperature (T_g) of the polymer normally increases by 50–100 K, and the material hardens, but it also increases in conductivity. The temperature dependence of the ionic conductivity of materials is usually analyzed using the Arrhenius phenomenological relationship of Eq. 1:

$$\sigma = \sigma_0 \exp\{-A/T\} \tag{1}$$

σ_0—preexponential factor, usually temperature-dependent.

In polymer electrolytes, on the other hand, the curve is best fitted to an expression of the form of Eq. 2:

$$\sigma = \sigma_0 \exp\left\{-B/(T - T_0)\right\} \tag{2}$$

T_0, normally called the *equilibrium glass-transition temperature*, is related to the (kinetic) experimentally measured glass-transition from DSC (Differential Scanning Calorimetry) but is typically lower by 30-50 K. This is normally called *VTF behavior* (after Vogel, Tammann, and Fulcher) and is applicable for diffusion in glassy and disordered materials.

The simplest understanding of VTF conductivity behavior is that diffusion can occur only when the diffusing particle moves from one free volume space to another. The availability of free volume is then indexed by the quantity $T - T_0$. One can trivially derive the VTF form of Eq. 2 based on an expansion of the free volume around the equilibrium glass-transition temperature T_0. The free volume model presents many difficulties, but it seems to be the simplest way to understand transport behavior in amorphous polymer electrolytes [1, 23, 64].

The free volume picture was successfully applied by Cheradane [1] to describe the temperature dependence of conductivity in polymer networks. It is also valid for simple monophase amorphous systems such as low molecular weight polyglycols or poly(propylene oxide) based polymeric electrolytes. Despite its simplicity (a one-parameter model), free volume cannot be applied universally due to the following limitations:

- the semicrystalline structure of polymer electrolytes,
- the incomplete dissociation of salts,
- the variation of T_g with the concentration of charge species and
- the fact that the model applies to polymers themselves rather than to ionic species.

There were several corrections to the free-volume picture described by Ratner [1]. However, none of them extends the applicability of the model.

One of the possible extensions of the free volume model is the configurational entropy theory derived by Adam and Gibbs [5]. In this approach, transport occurs by group cooperative rearrangements rather than by hole-to-hole jumping motions as in the free volume picture. The rearrangement probability is described by:

$$W = A\exp\left(\frac{-\Delta\mu s_c *}{kTS_c}\right) \tag{3}$$

where s_c* is the minimum configurational entropy required for the rearrangement, S_c is the configurational entropy at temperature T, $\Delta\mu$ is the free energy barrier per mole which impedes the rearrangement.

The configurational entropy model describes the motion of the polymer host in polymer–salt complexes, but not the conductivity itself. For the temperature dependence of conductivity, the empirical VTF equation is used. Contrary to the single-parameter free volume model configurational entropy is a two-parameter model. Since it was originally developed as a lattice model, first of its parameters counts the number of available lattice sites and the second—the number of distorted bonds. In comparison to the free volume model, configurational entropy theory gives a better description of the pressure dependence of conductivity, a more realistic picture of relaxation processes, and an introduction to kinetic ideas. Like the free volume theory, the application of configurational entropy is limited to simple, monophase amorphous systems. Using Pulsed Field Gradient NMR and impedance spectroscopy to study an amorphous oxyethylene–oxymethylene copolymer doped with $LiCF_3SO_3$, Vincent et al. [65, 66] showed that both conductivity and anion diffusion coefficients displayed a temperature dependence according to the VTF equation. The temperature dependence for the cation diffusion coefficient satisfies the Arrhenius equation. This, as stated by the authors, implies that cation transport is not governed by polymer chain movements. They have suggested a Grotthus-like transport of simple cation species through the exchange of cations between positively charged triplets and neutral contact ion pairs. Moreover, the authors pointed out that extrapolation of the results of investigations carried out on low molecular weight polyglycols to high molecular weight systems is limited in several respects. The main limitation is related to the measurements of the ions' diffusion coefficients since low molecular weight polyglycols themselves contribute to diffusion processes. All the above observations stress the limitations of the free volume and configurational entropy models.

Assuming some similarities between organic solvents and polymeric electrolytes Armand has developed an idea for treating a polymer host as an immobilized solvent [67]. According to this assumption, an increase in the polymer host polarity should increase the dissociation degree of a dopant, and hence an increase in the number of the charge carriers as well as the conductivity. However, the introduction of polar groups to a polymer host results in an increased T_g, which in turn impedes segmental chain motion and therefore the conductivity.

One very important concept in the mechanistic understanding of polymer ionics is the issue of strong *coupling* between transport (ion motion) and relaxation. When the host polymer relaxes more rapidly, ionic conductivity increases. Using the concept proposed by Angell [68] of a dimensionless decoupling ratio, R, where:

$$R = \frac{\tau_s}{\tau_\delta} \tag{4}$$

τ_s is the structural relaxation time and refers to viscosity or segmental relaxation, τ_σ is the conductivity relaxation time which is inversely proportional to the conductivity.

The strong coupling means that ionic movement cannot occur unless it is facilitated by polymer relaxation. As the polymer electrolyte cools toward the glass-transition temperature, structural relaxation is slowed, and therefore ionic conductivity decreases rapidly. These concepts suggest three ways to increase ionic conduction. The first is to add more salt or the degree of salt dissociation, thus increasing the prefactor σ_0 in Eq. 2 which is proportional to the number of mobile ions. The second is to decrease the glass transition temperature T_g, facilitating relaxation and, therefore, transport; and the third is to decouple the diffusion from relaxation that is, to create structures in which the ions can move without facilitation by structural relaxation [64].

4.2 Transport mechanism

While the free volume and excess entropy models are quasi-thermodynamic approaches that give impressive qualitative understandings of conductivity in polymer electrolytes [1], to gain a more microscopic understanding of the conduction process, a model called the dynamic bond percolation

(DBP) has been developed. It models the actual motion of individual ions and if successful, it could be of great value in correlating desirable properties such as ionic charge, charge density, polymer flexibility, temperature, and polymer–ion interactions with macroscopic transport measurements.

In a very dilute solution, the Kohlrausch equation (Eq. 5) and Nernst–Einstein equation (Eq. 6) relationship hold quite well.

$$\sigma = \sum_i \mu_i q_i n_i \tag{5}$$

$$\sigma = nq2D/k_\mathrm{B}T \tag{6}$$

where σ—conductivity, μ_i—mobility, q_i—charge, n_i—concentration of the ith ion, D—diffusion coefficient, k_B—Boltzmann constant, T—kelvin temperature.

Both equations fail to hold quantitatively in concentrated electrolytes (polymer electrolytes), but they give important indications of understanding and thereby optimizing the conduction.

In a static bond percolation problem, the so-called master equation can be described as:

$$P_i = \sum \left(P_j W_{ij} - P_i W_{ji}\right) \tag{7}$$

where $P_i = P_i(t)$—is the probability of finding the carrier at site i at time t, and $W_{ij} = W_{ji}$ is the rate (in units of s^{-1}) at which the carrier hops from site j to site i, $W_{ij} = 0$ with probability equal to $1 - f$, $W_{ij} = 1$ with probability equal to f.

Here f denotes the fraction of bonds (links between sites, not chemical bonds) which are open or available. $1 - f$ is the fraction of bonds which are occupied or unavailable; w is defined as the hopping rate. In a static image, the hopping rate is fixed at w or 0 for a particular bond ij. Polymer electrolytes are dynamically disordered systems, and a generalization has to be made. The simplest one relies on the introduction of a third parameter $\mathrm{P}^{\mathrm{eq}} = 1/N_\Gamma$, where N_Γ is the time of renewal which refers to the characteristic rate at which the bond may be opened or closed. This implies that a static picture can be easily transformed into dynamic problems by static equations. This is one of the most important strengths of the model. The possibility to discuss kinetic problems and the frequency behavior of conductivity are other strengths of Ratner's model. The difficulty of a direct connection of the parameters to the macroscopic properties of the system seems to be the main limitation of the DBP theory.

Ratner suggests that extension to more complicated semicrystalline electrolytes should be possible. In high molecular weight systems, the DBP model describes long-range transport for cations forming weak bonds with the ether oxygens of the polymer chain. In low molecular weight polymer systems, such as PEG, the self-diffusion of the polymer chain to which the cation is attached [65] gives an important contribution to cation transport. Finally, the different transport mechanism for anions and cations is due to the much weaker interaction of the anions with the ether oxygen.

To summarize, most of the current models can be successfully applied to amorphous monophase systems. There is a lack of a theory to describe conductivity in heterogenous polymeric electrolytes. Considering the variety of systems presented it seems to be rather difficult to construct a simple universal model which can be applied to all studied systems.

Semiempirical models like the Meyer–Neldel rule or the Almond–West formalism have been applied to describe conduction phenomena in composite polymeric electrolytes and their relation to the phase structure of the systems studied. The Effective Medium Theory (EMT) is widely used to describe various properties of heterogeneous systems. It has been applied by Wieczorek [69] to discuss conductivity mechanisms in composite polymeric systems. EMT models fit the theoretical considerations and experimental data quite well.

For presenting transport in polymer electrolytes, the coupling between polymer chain motion and ionic transport has been a dominant theme. In addition to Class 1 and Class 2 (polyelectrolytes), Classes 3, 4, and 5 were proposed to decouple the ionic transport from the host polymer relaxation. The processes by which this decoupling occurs differ. In composites under Class 5 [70–75], an interfacial transport process allows ions to move either on the surface of the ceramic grain or near the composite grain in a reduced crystallinity, lower density polymeric phase. Complex, multiphase polymer systems comprise the materials of increased interest because the added complexity in design can result in the independent optimization of several properties [76].

4.3 Association phenomena in polymer electrolytes

Although the macroscopic properties of composite electrolytes associated with an enhancement of ionic conductivity are widely discussed, a detailed microscopic picture of ionic conduction in these materials has not been achieved. Extensive experimental and theoretical studies have attempted to address the issues of ion complexation, ion pairing and clustering, ion exchange, and conductivity.

In a simple approach, the ionic conductivity of an electrolyte system can be described by the Kohlrausch relationship (see Eq. 5). However, the number of charge carriers available in a polymer electrolyte is determined by the type of salt and the host polymer. In a polymer electrolyte, cations coordinate to polar sites in the host polymer matrix, forming more or less stable bonds, while the anions normally are not solvated by the polymer host but occupy voids in the system [31]. Due to the relatively low dielectric constant of most polymer matrices, typically long-range Coulomb forces give rise to extensive ion-ion interactions and in general, several different types of ionic species can be present in the polymer salt complexes:

- "free" anions,
- solvated cations,
- solvent-separated ion pairs, contact ion pairs,
- triplets, and higher order aggregates.

Note that ion pairs are not charged carriers. Ion associations have been so far thoroughly studied for nonaqueous liquid electrolytes and low or medium molecular weight amorphous polymeric electrolytes based on polyether matrices [77–86]. As a result of ion association and ion-polymer interactions, which lead to an increased glass transition temperature, a lower-than-expected conductivity is observed, especially at higher salt content [6].

Since the host matrix is relatively immobile, long-range cation transport must involve dissociative steps where solvated cations are transferred between neighboring coordination sites, in combination with migration and diffusion of ion aggregates weakly coordinated to the polymer solvent. Ionic conduction mainly occurs in the amorphous regions of the polymer-salt complexes and local polymer segmental motion plays an important role in the transport mechanisms [87]. Strong coupling to the local dynamics of the solvent contributes to the complexity of the ion transport and, along with extensive ionic interactions present in solutions, distinguishes polymeric ion conductors from ordinary liquid electrolytes [88, 89].

Microscopic details of the ion-ion and ion-polymer interactions can be studied using vibrational spectroscopic techniques (i.e., Raman and IR) [90–106]. For example, in the case of PPG ion-polymer interactions are manifested as changes in spectral regions associated with polar sites of the host polymer, i.e., ether oxygens and hydroxyl terminal groups. Spectroscopic evidence of redissociation [1] as well as increasing ion aggregation [1, 99] with increasing salt concentration has been previously reported.

It should be mentioned that ab initio methodologies were successfully applied in this field, particularly to examine the relative local basicity and strength of interaction [107–111]. Several important results were obtained, including the finding that ion motion is not simply the diffusion of a single ion or ion cluster, but rather involves the rapid and random formation of different coordination environments around the mobile ions (similar to DBP discussed earlier). Because the diffusion coefficients deduced from conductivities are roughly 10^{-7} cm^2 s^{-1}, MD simulation of the actual ionic-transport problem in polymer electrolytes is demanding [64].

As the salt concentration increases, the average separation between dissolved ions decreases, and the extent of ion-ion interactions is expected to increase. Fuoss and Kraus [77] originally postulated the formation of ionic triplets with increasing concentrations of tetraisoamylammonium nitrate in dioxane-water solutions. When salt is added to low permittivity media, however, the relative dielectric constant increases. This is contrary to the decrease observed in aqueous solutions. If the increase in the permittivity value is rapid enough the fraction of dissociated ions may increase rather than decrease with increasing salt concentration. This is due to a reduced Coulomb interaction and the effect is referred to as "redissociation". Note that ionic species are not well defined in terms of the spatial separation of potential energies. For example, a concept has been proposed [78] that aggregates such as triplets should be defined in terms of short- and long-range molecular interactions rather than as "molecular" species.

At higher temperatures precipitation of salt has been observed in several electrolyte systems [1]. The dynamic equilibria governing ionic speciation generally shifts toward an increasing abundance of associated species at higher temperatures [90]. The work of Jacobsson and Lundin [112] indicates that the observation of increasing ion association with increasing temperature is fully attributable to volume changes.

Studies devoted to composite polymeric electrolytes based on semicrystalline polyether matrixes have been limited to a narrow salt concentration range (usually for polyether oxygen-to-metal cation ratios equal to 8 or 10) [113–115]. Assuming the crucial role of ion associations on the conductivity of electrolytes based on low permittivity solvents, it is important to know whether the effect of the filler leading to the conductivity enhancement is limited only to this narrow salt concentration range or can be extended over larger salt concentration ranges. To study the role of the filler, a comparison has been made between the conductivity vs. concentration relationship for the composite and the base salt-polymer solution. An increase in conductivity observed for composite systems can be discussed in terms of the formation and redissociation of contact-ion pairs and higher ionic aggregates.

It has been shown by Wieczorek et al. [116] that the conductivity of the PEO–$LiClO_4$ electrolytes changes upon the addition of various organic or inorganic fillers. The effect of a filler is to change the fraction of available oxygen sites which in turn results in changes to the formation of ionic aggregates. The region in which the enhancement of ionic conductivity is observed corresponds to a lowering of the fraction of contact ion pairs and higher aggregates; this is due to the placement of filler molecules in the vicinity of the coordination sphere of the Li^+ cations.

However, results published by Best [117] show that the addition of TiO_2 and Al_2O_3 to the 3PEG complexes lead to no change in the ionic association as a function of temperature. These authors were unable to discriminate between anion–cation-filler and polymer interactions at the time. These authors mentioned that only small volumes of the material are likely to be affected at the polymer electrolyte/ceramic interface. It may not be possible to detect these localized changes via Raman light scattering where the information arising from different environments is present as superpositions with a relative intensity being proportional to the actual scattering volume of the environment[118]. A SANS scattering data study of 3PEG-$LiClO_4$-TiO_2 nanocomposite polymer electrolytes show that the particles are not well dispersed but aggregate in the fractal, polymer-like structures[119]. Advanced comprehensive characterizations are in need, more than ever before, for solid-state lithium battery research [120].

For cations, their immediate environment is a result of ion pairing and Lewis acid–base interactions with oxygen atoms in the host polymer chains. This complexation generally results in a less mobile cation. This is also indicated by transference number measurements and simulations. Several theoretical methods including molecular dynamics, ab initio calculations, model calculations using DBP or its variants, and direct comparisons with such experimental methods as neutron scattering, light scattering, Raman scattering, infrared spectroscopy, ionic conductivity, and nuclear relaxation methodologies—have led to a deeper understanding of the mechanisms and some mechanism-based designs. Such advances as the use of low T_g hosts, the development of low-basicity anions, and the use of multiphase ionics to reduce coupling have been effective in increasing the performance capability of polymer electrolytes and have arisen from conceptual (or theoretical) ideas based on mechanistic models for transport.

4.4 Transference numbers

The transport number of an ion in an electrolyte is a fraction of the total charge carried in the solution by that ion [121]. It is defined as:

$$\sum_i T_i = \sum_i \frac{i_i}{i} = 1 \tag{8}$$

However, in the case of ion association, it appears impossible to distinguish between simple ions and other charged species. Instead of material transport, the total current is determined. Therefore, the value of the transport number relies on the transfer of all species containing the ion of interest, and not only the free ion. This quantity is called the transference number. The sum of the transference numbers for all possible charge carriers must also be equal to the unity

$$\sum_R t_R = 1 \tag{9}$$

A few techniques have been employed so far to measure the transference number. The most common are Hittorf/Tubandt [122, 123], AC impedance [124], DC polarization (probably the most popular) [125], NMR and radio tracers [126]. However, these techniques are not very useful for measuring solid polymer electrolytes due to their various limitations.

An idea was proposed by Newman [127] to measure a complete set of transport properties such as conductivity, salt diffusion coefficient, and cation transference number. The method is quite complicated experimentally, but in our opinion, provides complete information on the actual ion transport in the electrolyte. It is also interesting to note that because it considers the effect of ion associations, negative t values can be obtained.

The advantage of the Newman technique is that it does not require the solution to be dilute or ideal. According to Newman's theory, to describe completely the transport processes, it is necessary to measure $\frac{n(n-1)}{2}$ concentration-dependent transport properties, where n is the number of independent species in the solution. To describe a simple polymer system PEODME–$LiClO_4$ system, Li^+, ClO_4^- and PEODME were chosen to be three independent species ($n = 3$), regardless of the microscopic speciation. To determine individual transport properties, the following measurements are performed: conductivity—standard impedance measurement; salt diffusion coefficient—restricted diffusion measurement; cation transference number—concentration cell OCV measurements and symmetric cell polarization [128].

5 Methods of modification of polymer electrolytes

5.1 Filler addition

The incorporation of electrochemically inert fillers into polymer matrices is a well-known solution. Several methods for the modification of the structure leading to the enhancement of ionic conductivity of polymer electrolytes has been realized so far. For example, the addition of inorganic fillers is one of the most commonly used and effective methods of modification [31, 129, 130]. This process ensures better ionic conductivity, the possibility for better parameters of work in lower temperatures and improves the interface's stability.

A nanocomposite system is a PEO-based structure filled with ceramic filler (nanoscale inorganic oxides), for example, SiO_2, Al_2O_3, and TiO_2, superacid conducting zeolites lithium-based ionic glasses, and, more recently, piezoelectric ceramics like $LiNbO_3$ or $BaTiO_3$ [131]. It is one of the most effective methods for thermal, electrochemical, and mechanical stability improvement, as well as the way to reduce the tendency of crystallization. Also, better conductivity in these systems is observed, due to the small size of the added particles. The nanoscale (and mesoporous) characterization of fillers improves electrochemical stability windows and transport numbers [130].

5.2 Polymer networks

Polymers synthesized through cross-linking process led to the creation of new types of polymers which exhibit a much lower tendency to crystallize and better mechanical properties than linear ones. However, the mechanical properties must be balanced with the ionic conductivity parameters. It is achieved by proper polymerization method, for example, shown by Lu et al. ring-opening polymerization with diglycidyl ether of bisphenol-A (DEBA) as the supporting framework, which leads to improvement of the mechanical properties of the polymer. For better ionic transport, poly(ethylene glycol) diglycidyl ether (PEGDE) and diamino-poly(propylene oxide) (DPPO) are cross-linked throughout this framework [132]. The cross-linking method might be also applied to prevent polymer crystallization and promote faster segment migration. It was shown that using poly(ethylene glycol) (PEG), which cross-link with α-cyclodextrin (α-CD) to produce solid polymer electrolyte (SPE) is a good example of that property [133]. In this structure, PEG is responsible for Li^+ transport, but cross-linked α-CDs are not chemically bonded to the PEG, which can suppress the crystallization of PEG and ensures its mobility after cross-linking. It also enhances the ionic conductivity and durability of SPE. Li et al. have recently reported a nerve network-inspired solid polymer electrolyte (NN-SPE) for fast and single-ion lithium conduction [134], while semi-interpenetrating polymer network electrolytes with a spiro-twisted benzoxazine mitigates the short-circuiting phenomena caused by Li dendrite evaluation [135].

5.3 Polyethylene oxide modification methods

Polymer electrolytes, to effectively dissolve lithium salts and form a complex structure, should contain –O–, –C=O, –S–, –CN–, P– or another functional group. The very important parameter, which is the transmission of the lithium ions, is strongly connected to the amorphous region of the electrolyte. The crucial part of this section is the presence of the polar groups in the polymer electrolyte structure, for example –O– in PEO that allows the Li^+ to migrate in the structure driven by an electrical field. Lowering T_g of the polymer electrolyte increases the amorphous region and thus leads to better ionic transport [136]. However, the highest conductivity values for PEO are obtained, when its structure is fully amorphous, which is only a temporary state, due to its metastable structure, which is crystallizing in time and causes a decrease in conductivity. Also, the absence of the crystalline phase is undesirable, because of the worsening mechanical properties, for example, filmability and dimensional stability [131].

There is also a possibility to transfer Li^+ through the unique polymer structure, which is why modifications of a solid polymer electrolyte are desirable. Pure polyethylene oxide-based electrolytes are characterized by low ionic conductivity, especially in low temperatures (40–100 °C) [137]. To improve this parameter, the idea of using additives was applied to modify the structure of the polymer.

Synthesis of lithium complexes of PEO with $LiBF_4$, $LiCLO_4$, $LiCF_3SO_3$, $LiAsF_6$, lithium4,5-dicyano-1,2,3-trizolate and applying them with several additives is the possibility for PEO modification. A good example of the structural change is the addition of $LiAsF_6$, which forms with PEO a cylindrical channel, which enables Li^+ ion easy transfer [136]. Its 6:1 crystalline complexes (PEO_6–$LiAsF_6$), where the lithium ions are not coordinated by the anions, show not satisfy the ionic conductivity value. That is why, some improvement might be done by, for example, substituting the AsF_6^- ions in the crystal structure with the isovalent $N(CF_3SO_2)^{2-}$ ions [138]. What is interesting, with the higher salt content ($n < 6$), the crystalline aggregates are present and are responsible for the decrease of the conductivity and transport numbers, because of the formation of ion pairs and phase segregation [139].

Also, ionic liquids might be a part of the PEO-based gel electrolyte, which incorporates mostly pyrrolidinium, imidazolinium, and piperidinium ionic liquids. PEO-LiTFSI electrolytes were gelled with *N*-alkyl-*N*-methylpyrrolidinium and increased the conductivity and decreased the interfacial resistance with the lithium anode [131, 140].

A very interesting experiment was presented by Cha et al. [141], who researched systems with polyethylene oxide (PEO), poly(*N*,*N*-dimethylamino-ethyl-methacrylate) (PDMAEMA), $LiN(CF_3SO_2)_2$ (LITFSI) as the salt, and tetraethylene glycol dimethyl ether(tetraglyme) and EC + PC as plasticizers. These modifications are affecting the polymer membrane structure, thus influencing the conductivity to be higher, especially for the tetraglyme plasticized material.

5.4 Adding plasticizer

One of the modifications is adding a plasticizer, for example, PEG, which reduces crystallinity and increases the free volume in the system, thus providing better conductivity. However, due to the presence of hydroxyl end-groups, the interfacial properties worsened. There is also possible modification of this solution, for example, hydroxyl end-groups may be replaced by methoxy group [142]. Also, good examples of plasticizers applied in complexes are crown ethers or dibuthyl phthalate. Due to these changes a higher ionic conductivity, electrochemical stability, thermal stability, and high transference number might be obtained [137].

A novel example of the plasticizer that may be added to the PEO or PVdF-HFP membranes is succinonitrile. Good performance results were shown where LiTFSI and bisperfluoroethylsulfonylimide salt were also present in the system. Then the material's ionic conductivity is increased and excellent mechanical properties are shown [143]. Plasticized lithium ion conducting polymer blend electrolytes with chitosan and dextran can at definite conditions deliver a high-energy density and specific capacitance [144].

5.5 Synthesis path modifications

Polymerization technique change might facilitate a synthesis process and affect onto parameters of the membrane. Solid polymer electrolytes might be prepared by solvent casting, hot pressing, lamination, extrusion, or in situ polymerization [131]. One of the examples is a modification of the synthesis path using a polymer electrolyte membrane with bifunctional polyethylene glycol, creating a cross-linked network structure. Here a simple one-pot in situ reaction method was used (using the poly(ethylene glycol) (PEG), pentaerythritol tetrakis (3-mercaptopropionate) (PEMP), and lithium bis(trifluoromethane sulfonimide) (LiTFSI) as the raw materials) and led to obtaining better mechanical properties and reduced the interface impedance [145]. It also allows for upscaling and industrial production of polymer electrolytes, due to the easy synthesis path. It was observed that in-situ polymerization improves interface stability and contact properties. Other possibilities to facilitate the synthesis path are thermal and UV polymerization, which is characterized by its simpleness. This method is also environmental friendly and easy to use in in the industry [136].

5.6 Copolymerization

The structure determines the electrochemical parameters and mechanical properties of the polymer membrane. By mixing different types of polymers, new properties might be achieved. Block Copolymer Electrolytes (BCP) electrolytes are easier to control and are characterized by different properties, which made them very interesting for research and development. This technique allows the membrane to achieve properties that are impossible to occur if only one polymer is present in the structure, for example, high mechanical strength and good ionic conductivity. It is assured due to the presence of electron-rich groups, for example, PEO, PVC, PMMA, and more advanced structures like those proposed by Young et al. poly(styrene-*b*-ethylene oxide) (PS-*b*-PEO) block copolymer electrolyte doped with lithium perchlorate, which can obtain three different morphologies while changing volume friction [146]. When the molecular weight of the copolymers increases, also the presence of inhomogeneous local stresses in the block copolymer microdomains is higher, as well as the ionic conductivity of the copolymer. This phenomenon influences the ability of PEO chains to coordinate the lithium ions [147]. The next one might be an example described by Aldalur et al. comb polymer electrolyte designed by block polymerization of PEO and lithium bis(fluorosulfonyl) imide (LiFSI), which is characterized by strongly amorphous structure at room temperature and the T_g is -55 °C, which is much better result comparing to pure PEO, simultaneously showing good electrochemical compatibility with negative electrode [148]. Aromatic structures in BDP increased ionic conductivity, and ion mobility and ensured mechanical stability [149]. A suitable structure for application in lithium-ion batteries and seen as a promising solid electrolyte due to its properties is a star-shaped polymer, which is easy to modify due to the presence of many functional groups. These structures might even form 3D spherical shapes [136]. That kind of framework ensures additional free space for the movement of the segments and increases the ionic conductivity at room temperature, which is also supported by lithium salt dissociation. An example of that kind of structure is (HBPS-(PTFEMA-*b*-PPEGMA)$_{27}$) described by Xu et al. [150] Linear PS–PEO–PS is an example of a membrane, which is characterized by high conductivity and good mechanical properties [151].

5.7 Single ion conductors

In SPEs the migration of the lithium ions involves only a small part of the ionic transport through the membrane, the small volume of Li^+ and the tendency of binding of lithium ions with polar groups are significant in this process. In typical systems, double-ion conductor causes ions migration and thus the potential differences appear [152]. A larger volume of the anionic groups influences their faster migration and then leads to their accumulation on the anode. Thus polarization appears and a decrease in the conductivity and an increase of the impedance in the cell are present [153].

In searching for a solution to this problem, single-ion conductors were introduced. There are two main methods of modification that lead to achieving SIC. The first one is anchoring the anion to the polymer backbone, and the second one is the addition of the anion receptor into the polymer electrolyte system. It results in the interaction with the anion [136]. SIC is described by its lower than traditional SPEs ionic conductivity, however, it is selective, which is a huge advantage.

An example of that kind of system is a single ion polymer electrolyte based on an anionic block copolymer [P(STFSILi)-*b*-PEO-*b*-P(STFSILi)] reported by Bouchet et al. [154], presented by Porcarelli et al. poly(LiMTFSI)-*b*-PEO-*b*-poly(LiMTFSI) [155] and star-shaped single-ion conducting polymer (POSS–PEO–PSTF) researched by Cao et al. [156].That kind of polymer electrolytes are a quite new technology, which eliminates the polarization problems but is showing low conductivity. A very big disadvantage, which might be problematic in a big-scale application of single-ion conductive polymer electrolytes are poor cycle stability and a difficult synthesis process [136].

5.8 Plasticized systems and polymeric gels

A polymer electrolyte is generally a membrane that allows ionic transport between electrodes. One of its modifications is introducing gel polymer electrolyte or plasticized polymer electrolyte, which links the technology of liquid and solid electrolytes and is characterized by the features of both. These are multiphase systems content crystalline, amorphous/swollen, and liquid zones. The polymeric membrane is soaked in proper high-boiling solvents and/or plasticizers, which assures the solid character and the presence of liquid electrolyte characterization. The typical swelling liquids are polar and non-volatile ones (for example phthalates), or linear or cyclic organic carbonates like EC, PC, diethylcarbonate (DEC), dimethylcarbonate (DMC), g-butyrolactone and others [131].

The research about the gel polymer electrolytes started from poly(methyl methacrylate) (PMMA), which was an ideal matrix for lithium salts, however, the cycling efficiency was not acceptable and regarded huge excess of lithium inside a cell. Because of that the amount of solvent under consideration, also various salts and plasticizers, such us ($LiClO_4$, $LiAsF_6$, and $LiN(CF_3SO_2)_2$) modified the PMMA electrolyte [157].

Application of gel electrolyte was introduced in low-cost lithium-ion batteries comprising $LiFePO_4$/PEO-gel electrolytes/natural graphite system, which shows 80% of initial capacity after 180 cycles with C/2 rate. The coulombic efficiency of the first cycle was 70% and the reversible capacity was 111 mAh g^{-1}, presented by Zaghib et al. [158]. It shows that the compromise between gaining new technologies and the decrease of parameters is achievable and shows promising technology.

However, for searching for new opportunities and better results, other polymers were researched. Examples of the use of PVC and PVC-PMMA polymers were introduced [137], but nowadays the most common technologies are based on Poly(vinylidene fluoride) and linear poly(vinylidene fluoride-*co*-hexafluoropropylene) (denoted PVdF-HFP).

PVdF contains (–C–F) functional groups that stabilize its structure during the electrochemical reaction. The dielectric constant ($\varepsilon = 8.4$) provides good solubility of lithium salts and supports charge transfer. However, the linear poly(vinylidene fluoride-*co*-hexafluoropropylene) (denoted PVdF-HFP) is more suitable for electrochemical application and as a component of the membrane assures flexibility. Its structure inhibits Li dendrite growth and enables the formation of a highly uniform SEI layer on the lithium metal. The lithium metal battery with GPE has excellent safety properties and good electrochemical performance (the cell retains 99.3% of the initial discharge capacity after 200 cycles at 0.3 C) [132].

There are several methods of a GPEs synthesis. Conventional ones are based on the production of a dry membrane, which is then swollen by the liquid electrolyte. Casting and the Bellcore technology are the prime methods of the past technologies for GPEs. Traditionally free-standing film fabrication of PVdF-based copolymers was used. Then phase separation (phase inversion) has been proposed, which affects the synthesis of the highly porous membrane, which provides morphology easy to control. It also allows for a use of a great number of liquid electrolytes [131, 159]. However, that kind of approach leads to the loss of the cell's performance and there is a huge risk of enhanced solvent evaporation in case of a high working temperature, leading to a conductivity decrease consequently. The number of liquids in the structure must be optimized to balance the mechanical and electrochemical properties as the best-performing combination.

A novel one is based on an initiator-free one-pot synthesis strategy for PVdF-HFP based membranes. The reaction is based on a ring-opening polymerization reaction, which leads to the synthesis of a compact 3D network gel polymer electrolyte (3D-GPE). This method provides good mechanical strength, ionic conductivity, and effective suppression of Li dendrite growth. Another idea is to incorporate ionic liquids inside the GPEs structure, which might be characterized by good flexibility, satisfying conductivity performance, and ready to be stored for even 4 months. They are also forming a stable SEI layer, which is a great advantage [131].

One of the interesting methods of the synthesis of GPEs, which modifies the properties of a membrane is UV crosslinking. Due to the different irradiation times, the membrane was described by specific conductivity and mechanical properties [160].

5.9 Complexing agents

The next important chapter in the development of novel polymer electrolytes was to obtain a single-cation conductive system without affixing the anion to the polymer chain (which leads to a stiff polymer matrix with high T_g and low conductivity overall). Studies on the use of anion receptors in polymer electrolytes were quite limited. Papers dealing with this subject were based on either theoretical predictions [161] or studies on the addition of certain boron compounds, as well as aza-ether structures with electron-withdrawing groups to oligoethers. The new types of ionic conducting polymers with grafted anion receptors based on aza-ether structures have been described by McBreen [162–165]. Calix[4]arene derivatives with various types of active groups were studied giving lithium transport numbers close to unity [166, 167]. However, this effect was only observed for large molar fractions of the supramolecular additive which acted as a steric hindrance and caused an overall lowering of the electrolyte conductivity. Some of these limitations were overcome when calix[6]pyrrole (C6P) was used as an anion-trapping group [168].

Anion receptors based on boron compounds were applied to the solutions of lithium salts in an electrolyte based on low molecular weight solvents [169, 170] as well as in gel polyelectrolytes [171]. Boron-based aza-ether compounds (borane, borate complexes) have been studied by McBreen and co-workers using near-edge X-ray absorption fine structure spectroscopy (NEXAFS), and by Zhou and MacFarlane who used ^{7}Li and ^{11}B NMR[172]. These studies showed that the degree of complexation of Cl^- or I^- anions strongly depends on the structure of the boron compounds. They also showed a dramatic enhancement in ionic conductivity in these electrolytes.

Wieczorek's group analyzed the properties of triphenylborane (Ph_3B) [173] in PE systems and it lead to an increase in lithium transference number. The effect of this additive was discussed for various triphenylborane/LiX ($X = I^-$, ClO_4^-, BF_4^-, $CF_3SO_3^-$, $(SO_2CF_3)_2N^-$) molar ratios. A possible mechanism for anion-triphenylborane interactions is postulated based on conductivity and FT-IR spectroscopy results [174]. This effect was followed by specific fingerprints in infrared and Raman spectra that confirmed complex formation. Some novel boron-organic compounds have been also proposed to verify their stability and application as anion-trapping agents [175]. Adding additives to the electrolyte has been shown to increase the cell voltage and boost the anode efficiency in the Mg–air battery [176]. Here, lithium-rich layered oxides by the HEPES-assisted co-precipitation method can be provided for next-generation lithium-ion batteries due to their high specific capacity [177].

5.9.1 Crystalline polymer electrolytes

The common knowledge is that the ionic conductivity of the crystalline phase is much lower than that of the amorphous phase [3]. Crystalline polymer–salt complexes were considered to be essentially insulators until the discovery of ionic conductivity in PEO_6:LiXF_6 ($X = P$, As, Sb) [178]. Bruce et al. reported that, for some anions and Li:O ratios of 1:6 and 1:8, the crystalline phase can exhibit comparable, or higher conductivity than its amorphous analog [178–181]. Seneviratne et al. studied the amorphous PEO_6:$LiSbF_6$ experimentally and showed that the amorphous phase has a very similar polymer backbone conformation to that of the crystalline complex, with only a loss of long-range order [182].

However ionic conductivity of pristine crystalline PEs formed by $LiXF_6$ salts dissolved in PEO is still too low for applications [138, 183–186] supported by theoretical studies. in this field[187]. On reducing the molecular weight below 500 Da, a rich variety of crystal structures is observed [183, 188–192]. Several salt/small-molecule complexes, e.g., $(G4)_{0.5}$:$LiBF_4$, G3:$LiAsF_6$, G4:$LiAsF_6$, show appreciable levels of ionic conductivity, greater than the undoped PEs (G = glyme unit, –CH_2–CH_2–O–In addition, G3:$LiAsF_6$ and $(G4)_{0.5}$:$LiBF_4$ exhibit high values of the cation transport number, t_+: 0.80 and 0.66, respectively. As in the case of PEs, it is the specific structural features that determine conductivity and t_+ values. Higher conductivities and cation transport values are found in small-molecule electrolytes whose structures feature convenient pathways for the cations to move.

5.9.2 Polymer-in-salt

An effective approach to obtain polymer electrolytes with pure cation conductivity in a solvent-free configuration appears to be the synthesis of so-called polymer-in-salt solid electrolytes, (PISSEs) in which a large quantity of salt is mixed with a small amount of polymer [193, 194].

Poly(acrylonitrile), poly(1-vinyl pyrrolidone) and poly(*N*,*N*-dimethyl acrylamide) were mostly used as polymer matrices [195–197]. The highest ambient temperature conductivity exceeding 10^{-6} S cm^{-1} was reported for the poly(acrylonitrile)–lithium triflate system. Creating polymer-in-salt solid electrolytes where the lithium salt contents exceed 50 wt% is a viable technology to enhance ionic conductivity at room temperature of SPEs, which is also suitable for scalable production. Recent advances in polyacrylonitrile (PAN)-based PISSEs and polycarbonate derivative-based PISSEs were published by Yi et al. [198] This draws a parallel to recent reports about increasing salt concentration in classical electrolytes above a threshold (typically > ~3–5 M depending on the salt–solvent combination), which drastically changes the solvation environment of the ions and at sufficient concentration results in an ion-dominant solution known as “solvent-in-salt electrolytes” (SISEs) [199].

5.9.3 Highly concentrated electrolytes

Research on highly concentrated electrolytes traces back to 1985 when a saturated $LiAsF_6$-PC electrolyte was shown to inhibit solvent co-intercalation into a layered compound ZrS_2[47, 200]. Then in 2002 successful Li^+ intercalation in graphite was demonstrated by Jeong et al. using a 1:2 LiBETI-PC electrolyte where the corresponding dilute electrolyte (1:8) causes graphite exfoliation[201]. This was attributed to the changed solvation structure of Li^+, where all solvent is coordinated with the ions. Since 2010, similar experiments were done by Yamada et al. for LiTFSI and LiFSI in various solvents [202–205].

5.9.4 Hybrid ceramic polymer electrolytes

We also directed our interests toward a new group of lithium PEs based on the hybrid organic–inorganic matrix. The material is obtained by the reaction between the organometallic precursor—methylalumoxane (MAO) and olygooxyethylene molecules. The aluminum-oxide core of the MAO molecule is built from three four-member Al_2O_2 rings and two six-member Al_3O_3 rings. This molecule contains in its outer shell twelve methyl groups bonded to aluminum atoms. Systems based on the MAO organometallic precursor can be divided into three main groups[196, 197]. In the first one, the product of the reaction of monocapped oligoether (of various M_w being in the range 350–1000 g mol^{-1}) with MAO was used as the only constituent of the polymeric matrix. In this case, the samples were characterized not only by changing the molecular weight of the organic compound but also by varying the number of Al–CH_3 moieties undergoing the reaction with the –OH groups. The second group of electrolytes was obtained in a reaction of a branched system with PEG molecules containing two –OH moieties—in this situation PEG acted as a cross-linking agent. Contrary to the first case where a viscous liquid was formed, in the latter case, the consistency of the sample varies from liquid through rubbery to brittle solid depending on the M_w of the organic compounds and the sample composition. In the third case, a polymer blend was obtained by mixing PEGDME ($M_w = 500$ g mol^{-1}) with the product of a reaction of MAO with PEGME ($M_w = 350$ g mol^{-1}). In this case, the first olygoether compound did not contain in its structure any free –OH moieties and, in consequence, did not take part in chemical interactions with the MAO molecule and acted as a plasticizer. In all cases, three lithium salts ($LiClO_4$, $LiCF_3SO_3$ = LiTf, and $LiN(SO_2CF_3)_2$ = LiTFSI) were added to the system leading to the creation of a new type of hybrid organic–inorganic composite polymeric electrolyte. It’s set apart from typical composite electrolytes because the organometallic precursor forms a nanosized Al–O cage of an unprecedented, small size via reaction with the polymer matrix itself. In consequence, the composite material has well-dispersed, ultra-small size grains with well-defined structures and strong interaction between the ceramic core and polymer matrix. This system was characterized by electrochemical, thermal, and mechanical properties which can be easily tailored by an appropriate choice of branching and cross-linking olygoglycols, molecular weight, and the molar ratio between nano-cores and both reactants [206]. FTIR experiments reveal enhanced salt dissociation in the electrolyte containing MAO and it can be further correlated with improved cationic transference numbers measured for electrolytes containing LiTf and LiTFSI. The thermal stability of the system was increased by more than 50 °C compared to olygooxyethylene electrolytes (from 256 up to 308 °C). The T_g—FTIR studies of the decomposition products of electrolytes containing MAO led to the conclusion that MAO additives prevent the release of the extremely toxic gaseous product—hydrofluoric acid. MAO may participate in the catalytic decomposition of the salt or the bonding of the gaseous product, hence the operational safety of the electrolyte in terms of thermal decomposition is improved upon MAO addition.

5.9.5 Reversed-phase system

An interesting concept for polymer electrolytes is a so-called reversed phase, or polymer-in-ceramic systems [207, 208]. The essence of the concept was the combination of mechanical strength specific to ceramic materials with the flexibility of polymeric materials, along with the high conductivity of low molecular weight polymer electrolytes. Instead of adding dispersed ceramic grains into a 3D polymer matrix, a 3D porous ceramic piece is filled with a polymeric electrolyte. In this case, it is possible to decouple the mechanical strength of the material from the ionic transport properties of the polymeric phase and avoid wetting issues common for ceramic electrolytes. The interesting observation here was that ordered pore structures lead to ordered polymer structures, possibly along the lines of the crystalline polymer structures discussed earlier. The ease of production of Al_2O_3 membranes, along with their excellent mechanical strength may make this a viable approach for commercial cells where stopping Li dendrite growth is of utmost importance.

6 Summary

The definitions and basic information on polymer electrolytes are given above. Then several classes of polymer electrolytes are presented.

Of course, scientific progress has caused significant variations from this classical division, where hybrid systems, new composites, etc. have appeared.

This review does not exhaust the breadth of literature about polymer electrolytes. Various other concepts have been reported over the years, many of which are a combination of the different classes outlined in this study. It is worthwhile to remember that most of the work in this field uses the functional approach, which considers the properties of materials in holistic terms. It means that apart from electrochemical properties alone, other important factors are considered, like environmental issues, the safety of the final battery, price, scalability of production, and the possibility of prototyping and larger scale manufacturing of complete battery cells.

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Declarations

Conflict of interest The authors have no competing interests to declare that are relevant to the content of this article.

References

1. G.G. Cameron, Br. Polym. J. **20**, 299 (1988)
2. C.A. Vincent, Prog. Solid State Chem. **17**, 145 (1987)
3. C. Berthier, W. Gorecki, M. Minier, M.B. Armand, J.M. Chabagno, P. Rigaud, Solid State Ionics **11**, 91 (1983)
4. M.H. Cohen, D. Turnbull, J. Chem. Phys. **31**, 1164 (1959)
5. G. Adam, J.H. Gibbs, J. Chem. Phys. **43**, 139 (1965)
6. F.M. Gray, *Polymer Electrolytes* (Royal Society of Chemistry, London, 1997)
7. Z. Floriańczyk, W. Krawiec, T. Listoś, W. Wieczorek, J. Przyłuski, Synth. Met. **35**, 249 (1990)
8. Z. Florjańczyk, K. Such, W. Wieczorek, J. Macromol. Sci. Part A **29**, 853 (1992)
9. P.M. Blonsky, D.F. Shriver, P. Austin, H.R. Allcock, J. Am. Chem. Soc. **106**, 6854 (1984)
10. Z. Floriańczyk, K. Such, W. Wieczorek, M. Wasiucionek, Polymer (Guildf). **32**, 3422 (1991)
11. L.J. Lyons, B.A. Southworth, D. Stam, C.-H. Yuan, R. West, Solid State Ionics **91**, 169 (1996)
12. G. Silva, Solid State Ionics **93**, 105 (1996)
13. Z. Florjanczyk, E. Zygadlo-Monikowska, D. Raducha, K. Such, W. Wieczorek, Electrochim. Acta **37**, 1555 (1992)
14. Y.-G. Lee, J.-K. Park, S.-I. Moon, Electrochim. Acta **46**, 533 (2000)
15. G. Girish Kumar, N. Munichandraiah, J. Electroanal. Chem. **495**, 42 (2000)
16. X. Qian, N. Gu, Z. Cheng, X. Yang, E. Wang, S. Dong, Mater. Chem. Phys. **74**, 98 (2002)
17. M. Morita, M. Ishikawa, Y. Matsuda, J. Alloys Compd. **250**, 524 (1997)
18. H.M.J.C. Pitawala, M.A.K.L. Dissanayake, V.A. Seneviratne, B.-E. Mellander, I. Albinson, J. Solid State Electrochem. **12**, 783 (2008)
19. D. Golodnitsky, Solid State Ionics **85**, 231 (1996)
20. M. Morita, F. Araki, K. Kashiwamura, N. Yoshimoto, M. Ishikawa, Electrochim. Acta **45**, 1335 (2000)
21. M. Siekierski, W. Wieczorek, Solid State Ionics **60**, 67 (1993)
22. D. Almond, A. West, Solid State Ionics **9–10**, 277 (1983)
23. R. Dupon, B.L. Papke, M.A. Ratner, D.H. Whitmore, D.F. Shriver, J. Am. Chem. Soc. **104**, 6247 (1982)
24. J.B. Goodenough, H.-P. Hong, J.A. Kafalas, Mater. Res. Bull. **11**, 203 (1976)
25. L. Sebastian, J. Gopalakrishnan, J. Mater. Chem. **13**, 433 (2003)
26. A. Hooper, J. Phys. D. Appl. Phys. **10**, 1487 (1977)
27. H.-P. Hong, Mater. Res. Bull. **11**, 173 (1976)
28. D.E. Fenton, J.M. Parker, P.V. Wright, Polymer (Guildf). **14**, 589 (1973)
29. M. Armand, M.B. Chabagno, S.M. Duclot, in *Int. Meet. Solid Electrolytes Thomas Dickinson. 1979. [Papers] Second Int. Meet. Solid Electrolytes Univ. St. Andrews Scotl. Sept. 20–22 1978* (n.d.)
30. P. Donoso, W. Gorecki, C. Berthier, F. Defendini, M. Armand in *Proton Conductors: Solids, Membranes and Gels - Materials and Devices*. Chemistry of Solid State Materials, Series Number 2 (n.d.)
31. F.M. Gray, in *Solid Polymer Electrolytes*, ed. by F.M. Gray (VCH, New York, 1991) (n.d.)
32. S.M. Zahurak, M.L. Kaplan, E.A. Rietman, D.W. Murphy, R.J. Cava, Macromolecules **21**, 654 (1988)
33. A. Vallée, S. Besner, J. Prud'Homme, Electrochim. Acta **37**, 1579 (1992)
34. P.W.M. Jacobs, J.W. Lorimer, A. Russer, M. Wasiucionek, J. Power Sources **26**, 503 (1989)
35. R. Fang, B. Xu, N.S. Grundish, Y. Xia, Y. Li, C. Lu, Y. Liu, N. Wu, J.B. Goodenough, Angew. Chem. Int. Ed. **60**, 17701 (2021)
36. S. Nematdoust, R. Najjar, D. Bresser, S. Passerini, J. Phys. Chem. C **124**, 27907 (2020)
37. P. Lightfoot, M.A. Mehta, P.G. Bruce, Science (80-) **262**, 883 (1993)
38. D. Benrabah, D. Baril, J.-Y. Sanchez, M. Armand, G.G. Gard, J. Chem. Soc. Faraday Trans. **89**, 355 (1993)
39. M. Egashira, B. Scrosati, M. Armand, S. Béranger, C. Michot, Electrochem. Solid State Lett. **6**, A71 (2003)
40. M. Dranka, L. Niedzicki, M. Kasprzyk, M. Marcinek, W. Wieczorek, J. Zachara, Polyhedron **51**, 111 (2013)
41. L. Niedzicki, E. Karpierz, A. Bitner, M. Kasprzyk, G.Z. Zukowska, M. Marcinek, W. Wieczorek, Electrochim. Acta **117**, 224 (2014)
42. T. Trzeciak, L. Niedzicki, G. Groszek, P. Wieczorek, M. Marcinek, W. Wieczorek, J. Power Sources **252**, 229 (2014)

43. L. Niedzicki, G.Z. Żukowska, M. Bukowska, P. Szczeciński, S. Grugeon, S. Laruelle, M. Armand, S. Panero, B. Scrosati, M. Marcinek, W. Wieczorek, Electrochim. Acta **55**, 1450 (2010)
44. P. Wieczorek, A. Bitner-Michalska, L. Niedzicki, E. Żero, G.Z. Żukowska, K. Edstrom, W. Wieczorek, M. Marcinek, Solid State Ionics **286**, 90 (2016)
45. L. Niedzicki, E. Karpierz, M. Zawadzki, M. Dranka, M. Kasprzyk, A. Zalewska, M. Marcinek, J. Zachara, U. Domańska, W. Wieczorek, Phys. Chem. Chem. Phys. **16**, 11417 (2014)
46. J. Asada, N. Usami, H. Ota, M. Watanabe, K. Ueno, Macromol. Chem. Phys. **223**, 2270015 (2022)
47. M. Marcinek, J. Syzdek, M. Marczewski, M. Piszcz, L. Niedzicki, M. Kalita, A. Plewa-Marczewska, A. Bitner, P. Wieczorek, T. Trzeciak, M. Kasprzyk, P. Łężak, Z. Zukowska, A. Zalewska, W. Wieczorek, Solid State Ionics **276**, 107 (2015)
48. A. Plewa-Marczewska, T. Trzeciak, A. Bitner, L. Niedzicki, M. Dranka, G.Z. Żukowska, M. Marcinek, W. Wieczorek, Chem. Mater. **26**, 4908 (2014)
49. A. Bitner-Michalska, G.M. Nolis, G. Żukowska, A. Zalewska, M. Poterała, T. Trzeciak, M. Dranka, M. Kalita, P. Jankowski, L. Niedzicki, J. Zachara, M. Marcinek, W. Wieczorek, Sci. Rep. **7**, 40036 (2017)
50. M. Armand, P. Johansson, M. Bukowska, P. Szczeciński, L. Niedzicki, M. Marcinek, M. Dranka, J. Zachara, G. Żukowska, M. Marczewski, G. Schmidt, W. Wieczorek, J. Electrochem. Soc. **167**, 070562 (2020)
51. G. Cui, Y. Tominaga, Macromol. Chem. Phys. **223**, 2200013 (2022)
52. L.C. Loaiza, P. Johansson, Macromol. Chem. Phys. **223**, 2100419 (2022)
53. J.C. Barbosa, R. Gonçalves, C.M. Costa, S. Lanceros-Méndez, ACS Omega **7**, 14457 (2022)
54. P.V. Wright, MRS Bull. **27**, 597 (2002)
55. B. Scrosati, C.A. Vincent, MRS Bull. **25**, 28 (2000)
56. H.S. Lee, X.Q. Yang, J. McBreen, Z.S. Xu, T.A. Skotheim, Y. Okamoto, J. Electrochem. Soc. **141**, 886 (1994)
57. M.B. Gray, F.M. Armand, in *Handbook of Battery Materials*, ed. by J.O. Besenhard (Wiley-VCH, Weinheim, 1999) (n.d.)
58. C.A. Angell, K. Xu, S.-S. Zhang, M. Videa, Solid State Ionics **86–88**, 17 (1996)
59. M. Forsyth, J. Sun, D.R. Macfarlane, A.J. Hill, J. Polym. Sci. Part B Polym. Phys. **38**, 341 (2000)
60. W. Xu, K.S. Siow, Z. Gao, S.Y. Lee. Solid State Ionics **112**, 161 (1998)
61. S. Ichino, T. Takeshita, Y. Rutt, J.S. Nishi, Polym. Netw. Blends 5 (1995)
62. G.B. Appetecchi, F. Croce, B. Scrosati, J. Power Sources **66**, 77 (1997)
63. J. Weston, B. Steele, Solid State Ionics **7**, 75 (1982)
64. M.A. Ratner, P. Johansson, D.F. Shriver, MRS Bull. **25**, 31 (2000)
65. J. Shi, C. Vincent, Solid State Ionics **60**, 11 (1993)
66. C.A. Vincent, Electrochim. Acta **40**, 2035 (1995)
67. M. Armand, M. Gauthier, in *High Conduct. Solid Ion. Conduct. Recent Trends Appl.* (1989)
68. M. McLin, C.A. Angell, J. Phys. Chem. **92**, 2083 (1988)
69. W. Wieczorek, *Compos. Polyether Based Electrolytes* (Oficyna Wydawnicza PW, 1995)
70. Y. Dai, S. Greenbaum, D. Golodnitsky, G. Ardel, E. Strauss, E. Peled, Y. Rosenberg, Solid State Ionics **106**, 25 (1998)
71. C. Capiglia, Solid State Ionics **118**, 73 (1999)
72. G. Nagasubramanian, A. Attia, G. Halpert, E. Peled, Solid State Ionics **67**, 51 (1993)
73. J. Fan, S.R. Raghavan, X.-Y. Yu, S.A. Khan, P.S. Fedkiw, J. Hou, G.L. Baker, Solid State Ionics **111**, 117 (1998)
74. K. Nairn, Solid State Ionics **121**, 115 (1999)
75. P.V. Wright, Y. Zheng, D. Bhatt, T. Richardson, G. Ungar, Polym. Int. **47**, 34 (1998)
76. D. Ostrovskii, L.M. Torell, G. Battista Appetecchi, B. Scrosati, Solid State Ionics **106**, 19 (1998)
77. R.M. Fuoss, C.A. Kraus, J. Am. Chem. Soc. **55**, 2387 (1933)
78. S. Petrucci, E.M. Eyring, J. Phys. Chem. **95**, 1731 (1991)
79. A. Ferry, P. Jacobsson, J.R. Stevens, J. Phys. Chem. **100**, 12574 (1996)
80. A. Ferry, J. Phys. Chem. B **101**, 150 (1997)
81. A. Ferry, M. Tian, Macromolecules **30**, 1214 (1997)
82. J.R. MacCallum, A.S. Tomlin, C.A. Vincent, Eur. Polym. J. **22**, 787 (1986)
83. I. Albinsson, B.-E. Mellander, J.R. Stevens, J. Chem. Phys. **96**, 681 (1992)
84. M. Salomon, M. Xu, E.M. Eyring, S. Petrucci, J. Phys. Chem. **98**, 8234 (1994)
85. M. Xu, E.M. Eyring, S. Petrucci, J. Phys. Chem. **99**, 14589 (1995)
86. F. Gray, Solid State Ionics **40–41**, 637 (1990)
87. C.S. Harris, D.F. Shriver, M.A. Ratner, Macromolecules **19**, 987 (1986)
88. A.L. Tipton, M.C. Lonergan, M.A. Ratner, D.F. Shriver, T.T.Y. Wong, K. Han, J. Phys. Chem. **98**, 4148 (1994)
89. J.J. Fontanella, M.C. Wintersgill, M.K. Smith, J. Semancik, C.G. Andeen, J. Appl. Phys. **60**, 2665 (1986)
90. S. Schantz, L.M. Torell, J.R. Stevens, J. Chem. Phys. **94**, 6862 (1991)
91. M. Kakihana, S. Schantz, L.M. Torell, J. Chem. Phys. **92**, 6271 (1990)
92. S. Schantz, Solid State Ionics **28–30**, 1047 (1988)
93. A. Ferry, P. Jacobsson, J.D. van Heumen, J.R. Stevens, Polymer (Guildf). **37**, 737 (1996)
94. A. Ferry, P. Jacobsson, L.M. Torell, Electrochim. Acta **40**, 2369 (1995)
95. A.G. Bishop, D.R. MacFarlane, D. McNaughton, M. Forsyth, J. Phys. Chem. **100**, 2237 (1996)
96. Å. Wendsjö, J. Lindgren, C. Paluszkiewicz, Electrochim. Acta **37**, 1689 (1992)
97. S. Yoon, K. Ichikawa, W.J. MacKnight, S.L. Hsu, Macromolecules **28**, 4278 (1995)
98. P. Jacobsson, I. Albinsson, B.-E. Mellander, J.R. Stevens, Polymer (Guildf). **33**, 2778 (1992)
99. S. Schantz, J. Chem. Phys. **94**, 6296 (1991)
100. L.M. Torell, P. Jacobsson, G. Petersen, Polym. Adv. Technol. **4**, 152 (1993)
101. J. Manning, R. Frech, E. Hwang, Polymer (Guildf). **31**, 2245 (1990)
102. A. Bernson, J. Lindgren, Polymer (Guildf). **35**, 4848 (1994)
103. R. Frech, W. Huang, J. Solution Chem. **23**, 469 (1994)
104. D.R. MacFarlane, P. Meakin, A. Bishop, D. McNaughton, J.M. Rosalie, M. Forsyth, Electrochim. Acta **40**, 2333 (1995)
105. W. Huang, R. Frech, R.A. Wheeler, J. Phys. Chem. **98**, 100 (1994)
106. A. Ferry, G. Orädd, P. Jacobsson, Electrochim. Acta **43**, 1471 (1998)
107. A.G. Baboul, P.C. Redfern, A. Sutjianto, L.A. Curtiss, J. Am. Chem. Soc. **121**, 7220 (1999)
108. S.P. Gejji, C.H. Suresh, K. Babu, S.R. Gadre, J. Phys. Chem. A **103**, 7474 (1999)
109. Y. Chatani, S. Okamura, Polymer (Guildf). **28**, 1815 (1987)
110. P. Johansson, J. Tegenfeldt, J. Lindgren, Polymer (Guildf). **40**, 4399 (1999)
111. P. Johansson, S.P. Gejji, J. Tegenfeldt, J. Lindgren, Electrochim. Acta **43**, 1375 (1998)
112. A. Lundin, P. Jacobsson, Solid State Ionics **60**, 43 (1993)

113. W. Wieczorek, Z. Florjanczyk, J.R. Stevens, Electrochim. Acta **40**, 2251 (1995)
114. F. Capuano, F. Croce, B. Scrosati, J. Electrochem. Soc. **138**, 1918 (1991)
115. C.A. Vincent, Polym. Int. **33**, 343 (1994)
116. W. Wieczorek, D. Raducha, A. Zalewska, J.R. Stevens, J. Phys. Chem. B **102**, 8725 (1998)
117. A.S. Best, J. Adebahr, P. Jacobsson, D.R. MacFarlane, M. Forsyth, Macromolecules **34**, 4549 (2001)
118. M. Forsyth, D.R. MacFarlane, A. Best, J. Adebahr, P. Jacobsson, A.J. Hill, Solid State Ionics **147**, 203 (2002)
119. C. Karlsson, A.S. Best, J. Swenson, J. Kohlbrecher, L. Börjesson, Macromolecules **38**, 6666 (2005)
120. Y. Xiang, X. Li, Y. Cheng, X. Sun, Y. Yang, Mater. Today **36**, 139 (2020)
121. M. Spiro, J. Chem. Educ. **33**, 464 (1956)
122. J.W. Hittorf, A. Phys. Chem. **24** (1851)
123. C. Tubandt, E. Lorenz, Zeitschrift Für Phys. Chemie **87U**, 513 (1914)
124. P. Ravn Sørensen, T. Jacobsen, Electrochim. Acta **27**, 1671 (1982)
125. P.G. Bruce, C.A. Vincent, J. Electroanal. Chem. Interfac. Electrochem. **225**, 1 (1987)
126. A. Reiche, J. Tübke, R. Sandner, A. Werther, B. Sandner, G. Fleischer, Electrochim. Acta **43**, 1429 (1998)
127. Y. Ma, M. Doyle, T.F. Fuller, M.M. Doeff, L.C. De Jonghe, J. Newman, J. Electrochem. Soc. **142**, 1859 (1995)
128. M. Ciosek, M. Siekierski, W. Wieczorek, Electrochim. Acta **50**, 3922 (2005)
129. P.G. Bruce, *Solid State Electrochemistry* (Cambridge University Press, Cambridge, 1995)
130. E. Quartarone, P. Mustarelli, A. Magistris, Solid State Ionics **110**, 1 (1998)
131. E. Quartarone, P. Mustarelli, Chem. Soc. Rev. **40**, 2525 (2011)
132. Q. Lu, Y.-B. He, Q. Yu, B. Li, Y.V. Kaneti, Y. Yao, F. Kang, Q.-H. Yang, Adv. Mater. **29**, 1604460 (2017)
133. Y.C. Lin, K. Ito, H. Yokoyama, Polymer (Guildf). **136**, 121 (2018)
134. Z. Li, D. Guo, F. Li, G. Hou, X. Liu, C. Li, L. Cao, R. Wei, Z. Zhou, Z. Lai, Energy Storage Mater. **49**, 575 (2022)
135. J.-Y. Lee, T.-Y. Yu, P.-H. Chung, W.-Y. Lee, S.-C. Yeh, N.-L. Wu, R.-J. Jeng, A.C.S. Appl, Energy Mater. **4**, 2663 (2021)
136. H. Wang, L. Sheng, G. Yasin, L. Wang, H. Xu, X. He, Energy Storage Mater. **33**, 188 (2020)
137. A.M. Stephan, Eur. Polym. J. **42**, 21 (2006)
138. A.M. Christie, S.J. Lilley, E. Staunton, Y.G. Andreev, P.G. Bruce, Nature **433**, 50 (2005)
139. M. Marzantowicz, J.R. Dygas, F. Krok, A. Tomaszewska, G.Z. Ukowska, Z. Florjańczyk, E. Zygadło-Monikowska, Electrochim. Acta **55**, 5446 (2010)
140. G.T. Kim, G.B. Appetecchi, F. Alessandrini, S. Passerini, J. Power Sources **171**, 861 (2007)
141. E.H. Cha, D.R. Macfarlane, M. Forsyth, C.W. Lee, Electrochim. Acta **50**, 335 (2004)
142. B. Sandner, T. Steurich, K. Wiesner, H. Bischoff, Polym. Bull. **28**, 355 (1992)
143. L.-Z. Fan, Y.-S. Hu, A.J. Bhattacharyya, J. Maier, Adv. Funct. Mater. **17**, 2800 (2007)
144. E.M.A. Dannoun, S.B. Aziz, S.N. Abdullah, M.M. Nofal, K.H. Mahmoud, A.R. Murad, R.M. Abdullah, M.F.Z. Kadir, Polymers (Basel). **13**, 3613 (2021)
145. M.S. Grewal, M. Tanaka, H. Kawakami, Polym. Int. **68**, 684 (2019)
146. W.-S. Young, T.H. Epps, Macromolecules **45**, 4689 (2012)
147. E.D. Gomez, A. Panday, E.H. Feng, V. Chen, G.M. Stone, A.M. Minor, C. Kisielowski, K.H. Downing, O. Borodin, G.D. Smith, N.P. Balsara, Nano Lett. **9**, 1212 (2009)
148. I. Aldalur, M. Martinez-Ibañez, M. Piszcz, L.M. Rodriguez-Martinez, H. Zhang, M. Armand, J. Power Sources **383**, 144 (2018)
149. H.-D. Nguyen, G.-T. Kim, J. Shi, E. Paillard, P. Judeinstein, S. Lyonnard, D. Bresser, C. Iojoiu, Energy Environ. Sci. **11**, 3298 (2018)
150. H. Xu, A. Wang, X. Liu, D. Feng, S. Wang, J. Chen, Y. An, L. Zhang, Polymer (Guildf). **146**, 249 (2018)
151. D. Devaux, D. Glé, T.N.T. Phan, D. Gigmes, E. Giroud, M. Deschamps, R. Denoyel, R. Bouchet, Chem. Mater. **27**, 4682 (2015)
152. K.M. Diederichsen, E.J. McShane, B.D. McCloskey, ACS Energy Lett. **2**, 2563 (2017)
153. S. Guhathakurta, K. Min, Polymer (Guildf). **51**, 211 (2010)
154. R. Bouchet, S. Maria, R. Meziane, A. Aboulaich, L. Lienafa, J.-P. Bonnet, T.N.T. Phan, D. Bertin, D. Gigmes, D. Devaux, R. Denoyel, M. Armand, Nat. Mater. **12**, 452 (2013)
155. L. Porcarelli, M.A. Aboudzadeh, L. Rubatat, J.R. Nair, A.S. Shaplov, C. Gerbaldi, D. Mecerreyes, J. Power Sources **364**, 191 (2017)
156. P.F. Cao, Z. Wojnarowska, T. Hong, B. Carroll, B. Li, H. Feng, L. Parsons, W. Wang, B.S. Lokitz, S. Cheng, V. Bocharova, A.P. Sokolov, T. Saito, Polymer (Guildf). **124**, 117 (2017)
157. P.E. Stallworth, S.G. Greenbaum, F. Croce, S. Slane, M. Salomon, Electrochim. Acta **40**, 2137 (1995)
158. K. Zaghib, K. Striebel, A. Guerfi, J. Shim, M. Armand, M. Gauthier, Electrochim. Acta **50**, 263 (2004)
159. T. Michot, A. Nishimoto, M. Watanabe, Electrochim. Acta **45**, 1347 (2000)
160. G.T. Kim, G.B. Appetecchi, M. Carewska, M. Joost, A. Balducci, M. Winter, S. Passerini, J. Power Sources **195**, 6130 (2010)
161. P. Johansson, Electrochim. Acta **48**, 2291 (2003)
162. J. McBreen, H.S. Lee, X.Q. Yang, X. Sun, J. Power Sources **89**, 163 (2000)
163. H.S. Lee, X.Q. Yang, X. Sun, J. McBreen, J. Power Sources **97–98**, 566 (2001)
164. H.S. Lee, X.Q. Yang, J. McBreen, Y. Okamoto, L.S. Choi, Electrochim. Acta **40**, 2353 (1995)
165. H.S. Lee, X.Q. Yang, J. McBreen, L.S. Choi, Y. Okamoto, J. Electrochem. Soc. **143**, 3825 (1996)
166. A. Blazejczyk, W. Wieczorek, R. Kovarsky, D. Golodnitsky, E. Peled, L.G. Scanlon, G.B. Appetecchi, B. Scrosati, J. Electrochem. Soc. **151**, A1762 (2004)
167. A. Blazejczyk, M. Szczupak, W. Wieczorek, P. Cmoch, G.B. Appetecchi, B. Scrosati, R. Kovarsky, D. Golodnitsky, E. Peled, Chem. Mater. **17**, 1535 (2005)
168. M. Kalita, M. Bukat, M. Ciosek, M. Siekierski, S.H. Chung, T. Rodríguez, S.G. Greenbaum, R. Kovarsky, D. Golodnitsky, E. Peled, D. Zane, B. Scrosati, W. Wieczorek, Electrochim. Acta **50**, 3942 (2005)
169. A.F.D. Namor, R.G. Hutcherson, F.J.S. Velarde, M.L. Zapata-Ormachea, L.E.P. Salazar, I. Jammaz, N. Rawi, Pure Appl. Chem. **70**, 769 (1998)
170. H.S. Lee, X.Q. Yang, C.L. Xiang, J. McBreen, L.S. Choi, J. Electrochem. Soc. **145**, 2813 (1998)
171. X. Sun, Electrochem. Solid State Lett. **1**, 239 (1999)
172. F. Zhou, D.R. MacFarlane, M. Forsyth, Electrochim. Acta **48**, 1749 (2003)
173. M. Ciosek, M. Marcinek, G. Zukowska, W. Wieczorek, Electrochim. Acta **54**, 4487 (2009)
174. M. Marcinek, G.Z. Zukowska, W. Wieczorek, Electrochim. Acta **50**, 3934 (2005)
175. G. Zukowska, M. Szczechura, M. Marcinek, A. Zubrowska, A. Adamczyk-Woźniak, A. Sporzyński, W. Wieczorek, ECS Trans. **16**, 105 (2009)

176. C.-S. Peng, P.-W. Chu, ECS Meet bstr. **MA2022-01**, 126 (2022)
177. J. Wu, H. Li, Y. Liu, Y. Ye, Y. Yang, Electrochim. Acta **401**, 139485 (2022)
178. Z. Gadjourova, Y.G. Andreev, D.P. Tunstall, P.G. Bruce, Nature **412**, 520 (2001)
179. Z. Gadjourova, D. Martín y Marero, K.H. Andersen, Y.G. Andreev, P.G. Bruce, Chem. Mater. **13**, 1282 (2001)
180. C. Zhang, S. Gamble, D. Ainsworth, A.M.Z. Slawin, Y.G. Andreev, P.G. Bruce, Nat. Mater. **8**, 580 (2009)
181. Z. Stoeva, I. Martin-Litas, E. Staunton, Y.G. Andreev, P.G. Bruce, J. Am. Chem. Soc. **125**, 4619 (2003)
182. V. Seneviratne, R. Frech, J.E. Furneaux, Electrochim. Acta **48**, 2221 (2003)
183. C. Zhang, E. Staunton, Y.G. Andreev, P.G. Bruce, J. Am. Chem. Soc. **127**, 18305 (2005)
184. S.J. Lilley, Y.G. Andreev, P.G. Bruce, J. Am. Chem. Soc. **128**, 12036 (2006)
185. E. Staunton, Y.G. Andreev, P.G. Bruce, Faraday Discuss. **134**, 143 (2007)
186. C. Zhang, E. Staunton, Y.G. Andreev, P.G. Bruce, J. Mater. Chem. **17**, 3222 (2007)
187. S. Xue, D. Teeters, D.W. Crunkleton, S. Wang, Comput. Mater. Sci. **160**, 173 (2019)
188. W.A. Henderson, N.R. Brooks, W.W. Brennessel, V.G. Young, Chem. Mater. **15**, 4679 (2003)
189. V. Seneviratne, R. Frech, J.E. Furneaux, M. Khan, J. Phys. Chem. B **108**, 8124 (2004)
190. C. Zhang, Y.G. Andreev, P.G. Bruce, Angew. Chem. Int. Ed. **46**, 2848 (2007)
191. C. Zhang, S.J. Lilley, D. Ainsworth, E. Staunton, Y.G. Andreev, A.M.Z. Slawin, P.G. Bruce, Chem. Mater. **20**, 4039 (2008)
192. W.A. Henderson, N.R. Brooks, V.G. Young, Chem. Mater. **15**, 4685 (2003)
193. C.A. Angell, C. Liu, E. Sanchez, Nature **362**, 137 (1993)
194. M.G. McLin, C.A. Angell, Solid State Ionics **53–56**, 1027 (1992)
195. A. Ferry, L. Edman, M. Forsyth, D.R. MacFarlane, J. Sun, Electrochim. Acta **45**, 1237 (2000)
196. M. Forsyth, D. MacFarlane, A. Hill, Electrochim. Acta **45**, 1243 (2000)
197. M. Forsyth, S. Jiazeng, D. MacFarlane, Electrochim. Acta **45**, 1249 (2000)
198. C. Yi, W. Liu, L. Li, H. Dong, J. Liu, Funct. Mater. Lett. **12**, 1930006 (2019)
199. Y. Yamada, J. Wang, S. Ko, E. Watanabe, A. Yamada, Nat. Energy **4**, 269 (2019)
200. W.R. McKinnon, J.R. Dahn, J. Electrochem. Soc. **132**, 364 (1985)
201. S.-K. Jeong, M. Inaba, Y. Iriyama, T. Abe, Z. Ogumi, Electrochem. Solid State Lett. **6**, A13 (2003)
202. Y. Yamada, Y. Takazawa, K. Miyazaki, T. Abe, J. Phys. Chem. C **114**, 11680 (2010)
203. Y. Yamada, M. Yaegashi, T. Abe, A. Yamada, Chem. Commun. **49**, 11194 (2013)
204. Y. Yamada, K. Usui, C.H. Chiang, K. Kikuchi, K. Furukawa, A. Yamada, A.C.S. Appl, Mater. Interfaces **6**, 10892 (2014)
205. J. Wang, Y. Yamada, K. Sodeyama, C.H. Chiang, Y. Tateyama, A. Yamada, Nat. Commun. **7**, 12032 (2016)
206. M. Piszcz, M. Marczewski, G.Z. Żukowska, J. Wójcik, W. Wieczorek, M. Siekierski, Solid State Ionics **245–246**, 33 (2013)
207. J. Syzdek, M. Armand, M. Gizowska, M. Marcinek, E. Sasim, M. Szafran, W. Wieczorek, J. Power Sources **194**, 66 (2009)
208. J.S. Syzdek, M.B. Armand, P. Falkowski, M. Gizowska, M. Karłowicz, Ł Łukaszuk, M.Ł Marcinek, A. Zalewska, M. Szafran, C. Masquelier, J.M. Tarascon, W.G. Wieczorek, Z.G. Żukowska, Chem. Mater. **23**, 1785 (2011)