=== **REVIEWS** ===

Lithium-Conducting Polymer Electrolytes for Chemical Power Sources

V. S. Kolosnitsyn, G. P. Dukhanin, S. A. Dumler, and I. A. Novakov

*Institute of Organic Chemistry, Ufa Scientific Center, Russian Academy of Sciences,
Ufa, Bashkortostan, Russia*
Volgograd State Technical University, Volgograd, Russia

Abstract—Polymer electrolytes for lithium and lithium–ion chemical power sources are described.

INTRODUCTION

Lithium chemical power sources (CPSs) have high specific electrical characterisitcs and show promise for power supply to diverse autonomous objects [1–4]. The use of Li, which has a high negative potential and a low electrochemical equivalent (0.259 g A^{-1} h^{-1}), allowed an increase in the working voltage and specific energy of such power sources.

Success in development of lithium CPSs was stimulated by a suggestion to use melts of lithium-containing salts and solutions of lithium salts in aprotic dipolar organic solvents (ADSs) as electrolytes. However, power sources with a lithium-based anode and a molten electrolyte have not found wide use because of problems with structural materials, design, and service. At the same time, lithium power sources (and later lithium–ion batteries) with a nonaqueous (aprotic) electrolyte, despite certain drawbacks, became commercially available. The most widely used organic solvents in such electrolytes are propylene carbonate (PC), ethylene carbonate (EC), diethyl carbonate (DEC), dimethyl carbonate (DMC), or their mixtures; as lithium salts are used perchlorate (LiClO$_4$), hexafluorophosphate (LiPF$_6$), hexafluoroarsenate (LiAsF$_6$), and tetrafluoroborate (LiBF$_4$). The electrical conductivity of the nonaqueous electrolytes is within 10^{-2}–10^{-3} S cm^{-1}.

Comparative analysis of the characteristics of various electrochemical systems [5] demonstrates advantages of the new generation of batteries: lithium–ion batteries with liquid (Li–IB) and polymer solid or thickened electrolyte (PLi–IB). Such systems provide voltages of 2.7–3.7 V and have a specific energy of 150–200 W h^{-1} kg^{-1}, which is 2–2.5 times higher compared to the well-known nickel–cadmium and nickel–metal hydride batteries.

Experts engaged in development and production of lithium–ion batteries believe that, by 2010, virtually all the autonomous power sources used in military equipment will be based on the technology of a lithium–ion battery [5].

Studies aimed at development of new and improvement of existing working bodies for lithium power sources are being performed during the whole period since the development of the first lithium voltaic cell (more than three decades).

One of promising lines in improvement of lithium and lithium–ion CPSs is the use of polymer electrolytes (PEs), which allows improvement of their energy and service characteristics and simplification of the production process. Studies of PEs are being performed since 1970s, and today the electrochemistry of polymer electrolytes is one of the most actively developing fields of the modern electrochemistry [6]. Polymer electrolytes to be used in lithium CPSs should exhibit good physicomechanical properties, high ionic and low electronic conductivity, and wide range of electrochemical stability; they should be inert toward the electrode materials.

Polymer electrolytes are subdivided into two large groups with respect to the component composition. The first group includes PEs that contain no low-molecular-weight solvent; they contain a high-molecular-weight polymer, a lithium salt, and (in some cases) finely dispersed inorganic fillers. Polymer electrolytes of this type are termed polymer solid electrolytes (PSEs). The second group includes electrolytes containing, along with polymers, lithium salts, and fillers, also low-molecular-weight solvents. Electrolytes of

this group are further subdivided into microporous, gel, and plasticized polymer electrolytes [7].

Microporous PEs are microporous polymer films prepared from chemically resistant polymers (e.g., polyethylene or polypropylene) and impregnated with solutions of lithium salts in dipolar aprotic solvents. These electrolytes exhibit good mechanical properties and high ionic conductivity approaching that of liquid nonaqueous electrolytes (10^{-2}–10^{-3} S cm^{-1}).

Gel PEs (GPEs) are multicomponent systems consisting, at least, of a film-forming polymer, an aprotic dipolar solvent, and a lithium salt. The solution of the salt in ADS is distributed in a three-dimensional GPE network formed by macromolecules or their aggregates. These electrolyte systems have a relatively high ionic conductivity (up to 10^{-3}–10^{-4} S cm^{-1}) and, in some cases, also fairly good mechanical properties.

The solvent content in plasticized polymer electrolytes is considerably lower than in gel polyelectrolytes; their electrical conductivity, as a rule, is also appreciably lower.

An essential disadvantage of PEs containing a low-molecular-weight solvent (except microporous PEs) is the possible thermodynamic instability of their phase composition. Also, a common drawback of PEs of the second group is the possibility of solvent evaporation during storage and service of CPSs. Finally, the presence of a solvent is responsible for the drawbacks characteristic of liquid nonaqueous electrolytes: chemical activity toward lithium and the possibility of undesirable cointercalation of solvent molecules into the cathode matherial. All these processes may result in degradation of electrode materials and deterioration of the characteristics of CPSs based on such polymer electrolytes.

From the viewpoint of safety and convenience in production and service, PSEs in lithium CPSs are preferable. However, certain problems restrict today the use of PSEs. First, they have low ionic conductivity at common temperatures (10^{-5}–10^{-8} S cm^{-1}); second, not only lithium ions but also anions participate in the charge transfer, which may lead to concentration polarization; third, similarly to liquid electrolytes, PSEs can form a transition layer with a high resistance in contact with electrode (both cathode and anode) materials [7–9].

Therefore, development of lithium-conducting polymer electrolytes exhibiting high electrical conductivity in a wide temperature range, chemical and electrochemical stability, and good physicomechanical properties remain an urgent problem.

POLYMER SOLID ELECTROLYTES

Interactions in Polymer–Lithium Salt Systems

Organic polymers used for preparing PEs are dielectrics. Their low conductivity (10^{-12}–10^{-10} S cm^{-1}) is due, as a rule, to the presence of impurities. Therefore, fairly good polymer ionic conductors can be obtained by introducing ionogenic or ionophoric groups into the polymer molecule, or ionophores into the polymer system as a whole. Ionization of ionogens and ionophores is possible in the case if the polymer system exhibits sufficiently high dielectric permittivity and solvating power toward various ions. Such properties are exhibited by systems based on functional polymers, i.e., polymers whose molecules contain electron-donor or electron-acceptor groups. Interaction of macromolecules with low-molecular-weight ionophores (e.g., lithium salts) is possible owing to solvation of cations, anions, or both with functional groups of the polymers.

Anions are usually solvated by hydrogen bonding with relatively "acidic" hydrogen atoms, i.e., with hydrogen atoms directly bonded to electronegative atoms of the polymer molecule, e.g., with oxygen atoms in polyalcohols or hydrogen atoms in polyamides. However, the interchain interaction in such polymers is relatively strong, resulting in high cohesion energy. Therefore, such polymers are unfavorable media for diffusion of ions in the absence of protic solvents having high dielectric permittivity (water). Furthermore, the mobile hydrogen atom may be electroactive in a wide range of chemical potentials, which excludes the use of such polymers in lithium power sources. Anions can also be solvated by Lewis acids, e.g., by organoboron compounds R_3B, but stable macromolecules containing such fragments are unknown [10].

It should also be noted that one of the major problems in development of lithium-conducting polymer electrolytes is elimination of the undesirable contribution of the anionic conductivity [11, 12]. Because of binding of the cations with polar groups of the polymer molecule, the anion makes a significant contribution to the conductivity. The mobility of the anions usually decreases with an increase in their size. The undesirable anionic conductivity can also be eliminated by using polyelectrolytes, i.e., polymers in which the negative ion is chemically bound to macromolecules. The electrical conductivity of such systems usually does not exceed 10^{-5} S cm^{-1}.

The cations are solvated via interaction with lone electron pairs of heteroatoms in functional groups of

the polymer molecules [13]. The most typical functional groups are ether (–O–), sulfide (–S–), amino (–N<), phosphino (–P<), carbonyl (>C=O), and cyano (–C≡N) groups.

According to Pearson's concept of hard and soft acids and bases, the electron-donor properties of heavy heteroatoms (S, P) are realized most efficiently in the presence of soft acids, i.e., cations with polarizable d orbitals (e.g., Ag^+, Pb^{2+}) [14]. Cations of alkali and alkaline-earth metals strongly interact with oxygen and nitrogen atoms.

The possibility of polymer–salt complexation depends on the cohesion energy of the polymer and crystal lattice energy of the salt [15, 16]. Complexes with the above-mentioned types of macromolecules are formed only by salts with a low lattice energy. Such salts generally contain large anions with the delocalized charge.

Polyethers [in particular, poly(ethylene oxide), PEO] were the first macromolecular compounds considered as candidate materials for PSEs [17, 18]. In particular, Papke *et al.* [19] showed that with PEOs, indeed, the crystal lattice energy of the salt determines the possibility of the polymer–salt complexation. The complexation of PEO with lithium salts $LiClO_4$, $LiPF_6$, $LiBF_4$, and others was proved in [20–22]. Robitaille and Fauteux [23], based on the conductivity and X-ray diffraction data, confirmed the results obtained for the system $PEO–LiCF_3SO_3$ and constructed the phase diagrams for the systems PEO–X, where X = LiI, $LiAsF_6$, and $LiClO_4$. In the latter case, also, at least one crystalline complex is formed, $(PEO)_6–LiClO_4$. Poly(ethylene oxide) forms mixed crystals of the pure polymer and complex at temperatures below T_m, and above T_m the salt-containing melt (elastomer) is in an equilibrium with the complex. For the majority of crystalline polymers, the crystalline phase, as a rule, occupies only about 70–85% of the volume of the polymer body because of entanglement of the polymer chains. The remaining volume is occupied by the amorphous phase. Such phase equilibria govern the properties of such polymers as poly(ethylene succinate) $(–C_2H_4–O–CO–C_2H_4–COO–)_n$, polyaziridine $(–CH_2–CH_2–NH–)_n$, poly(ethylene adipate) $(–C_2H_4–O–CO–C_4H_8–COO–)_n$, and polypropiolactone $(–C_2H_4–COO–)_n$ [10].

The DSC and NMR studies made by Berthier *et al.* [24, 25] showed that the crystalline phase of the complex (three monomer units per mole of salt) starts to dissolve in PEO at temperatures above T_m of PEO. It is assumed that the crystalline phase of the complex has a helical structure with the cations located inside, and the ion motion occurs in the elastomer phase, with the crystalline complex acting only as a salt reservoir.

Armand [10] summarized data on interaction of PEO and poly(propylene oxide) (PPO) with the most commonly used alkali metal salts. It was noted that the complexing power of PEO considerably exceeds that of PPO, despite the fact that the electron-donor properties (*DN*) of both polymers are comparable. A decrease in the stability of polymer–salt complexes is due to steric hindrance caused by the methyl groups in PPO. In amorphous polymers above their glass transition points and in polymers incapable of crystallization because of structural disordering, the salts bound in a complex form continuous solutions up to saturation.

When studying ionic association of $PPO–LiClO_4$ complexes, Schantz [26] noted that the amount of the dissociated ions remained constant with variation of the polymer/salt ratio from 1000 to 30 [26]. With an increase in the salt concentration in PPO, the intensity of ion pair formation decreased. The major contribution to an increase in the PE conductivity at low $LiClO_4$ concentrations is made by an increase in the number of dissociating ions, rather than in their mobility. The IR and polarized Raman spectra of the $PPO–LiCF_3SO_3$ complexes suggest existence of three types of associates: two differently coordinated ion pairs and a ternary ion. Manning and Frech [27] state that the free ions which were believed previously to exist in these polymer–salt complexes are actually the cation–anion pairs in which the cation weakly interacts with the terminal CF_3 group of the anion.

It was found that polymers with the crystalline structure, tending to form crystalline complexes with dissolved lithium salts, do not ensure the electrical conductivity acceptable for PSEs. The conductivity of PSEs, including those based on PEO, can be increased by decreasing the crystallinity of the polymer, because the high ionic conductivity is mainly provided by the amorphous part of the polymer electrolyte.

Therefore, the majority of studies involve choosing amorphous polymers for PSEs, forming the network structure (cross-linking), and introducing additives that render the system amorphous.

Polymer Solid Electrolytes Based on PEO and Its Modifications

As a rule, solid inorganic electrolytes have a unipolar conductivity. It was initially expected that PSEs would also exhibit unipolar conductivity. Indeed, the

preliminary results were encouraging: For the PSE based on $LiCF_3SO_3$, the lithium transport number was ~0.8 [28]. However, it was found soon that the transport numbers of the positive ions t^+ for the majority of salts in PSEs are within 0.3–0.5.

The transport numbers in PSEs are usually determined by impedance spectroscopy [29, 30], Tubandt method [31], dc electrolysis [32], potentiometry [33], and NMR spectroscopy [34]. For the lithium salts with such anions as SCN^-, ClO_4^-, and BF_4^-, all these methods give similar values characteristic of these salts in liquid electrolytes. An apparent exception is the $CF_3SO_3^-$ ion for which independent measurements give $t^- \approx 0.3$–0.4 [33, 34]. Presumably, synthesis of polymer electrolytes with unipolar lithium conductivity will lead to a considerable progress in this field.

Bruce and Vincent [35] studied by the emf method the ion transport in amorphous complexes PEO–$LiClO_4$ of various compositions. In potentiostatic polarization, the steady-state current was attained in several hours and was determined by the mobility of both Li^+ and ClO_4^- ions, and at high salt concentrations, also by the mobility of the ion pairs [36]. According to [37], at a given temperature the conductivity depends on the lithium perchlorate concentration in a complex manner. At low concentrations, with an increase in the salt content, the specific molar conductivity σ rapidly decreases. Then, as the salt concentration is increased further, σ increases, reaches a maximum (whose position depends on temperature), and then decreases again. The shape of the dependences of σ on the temperature and lithium perchlorate concentration suggests the transfer of the electricity not only by the simple ions Li^+ and ClO_4^-, but also by ion clusters $Li(ClO_4)_2^-$ and $Li_2(ClO_4)^+$.

Studies by Brillouin and photon-correlation spectroscopy [38] showed that the cooperative motion of approximately 20 monomeric units of the polymer is required for the ionic transport. At $n > 4$, short-lived ion–polymer cross-links arise in the electrolyte, limiting the mobility of polymer segments. The density of the cross-links abruptly decreases with increasing temperature because of formation of ion pairs exerting a plasticizing effect of PSE.

Arumugam *et al.* [39] determined the diffusion coefficients of Li^+ and PF_6^- in the amorphous electrolyte PEO–$LiPF_6$ by ^7Li and ^{31}P NMR spectroscopy with pulse field gradient in a wide temperature range (25–100°C) at a salt concentration of up to 0.25 mol dm^{-3}. Their results suggest different mechanisms of transfer of the cation and anion at low and high concentrations of the salt. The diffusion coefficients of the cation appeared to be weakly sensitive to the salt concentration; the system showed a deviation from the Nernst–Einstein relationship. To interpret the results obtained, Arumugam *et al.* suggested hopping of the cation between ion clusters and diffusion of neutral ion pairs.

Blending of two or several polymers is widely used to decrease the crystallinity of polymer electrolytes. Li and Khan [40] studied an interesting type of polymer electrolytes with a conductivity of 10^{-5} S cm^{-1} at 25°C. The electrolytes were prepared by blending PEO with poly(2-vinylpyridine) (P2VP) or poly(4-vinylpyridine) (P4VP) with $LiClO_4$ in solution. In these composite electrolytes, $LiClO_4$ behaves as agent improving the compatibility of the polymers, as it was shown previously that PEO and P4VP are immiscible and PEO–P2VP (40/60 by weight) blends are only slightly miscible [41], as indicated by independence of T_m of PEO and T_g of P2VP from the blend composition. Ueda *et al.* [41] believe that increased miscibility in the PEO–polyvinylpyridine system is most probably due to the fact that the lithium ion interacts simultaneously with the PEO oxygen atoms and nitrogen atom of the pyridyl unit. The probable structure of the complexes formed by this type of ion–dipole interactions is shown below:
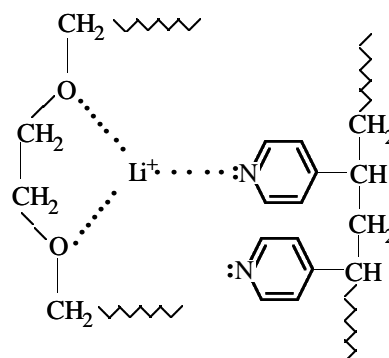

It was shown that the ion–dipole interactions improve the miscibility of polystyrene ionomers with poly(alkylene oxide) systems [42] and of polyamide-6 with lithium or sodium salts of sulfonated polystyrene [43, 44]; $LiCF_3SO_3$ improves the miscibility of poly(methyl methacrylate) and poly(propylene glycol) [45]. The increased miscibility is explained by simultaneous interaction of Li^+ with the carbonyl oxygen atoms of poly(methyl methacrylate) and ether oxygen atoms of poly(propylene glycol). Furthermore, it was shown that the blends have a phase-segregated structure with $LiCF_3SO_3$ acting as an emulsifier stabilizing the two-phase microstructure [46].
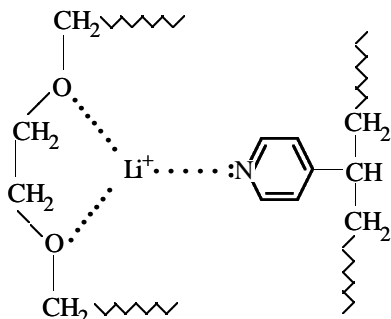
Mani *et al.* [46] explained the conductivity and

thermal transitions assuming the existence of three different types of ion–dipole complexes:
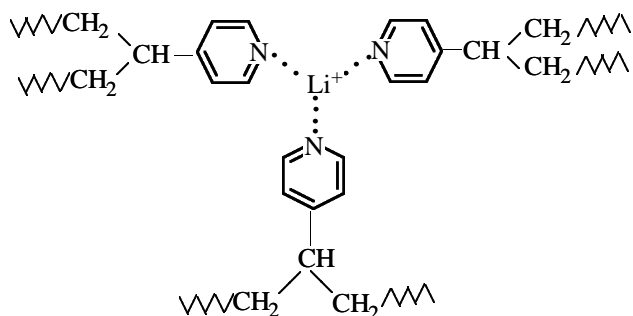
Complex of type 1
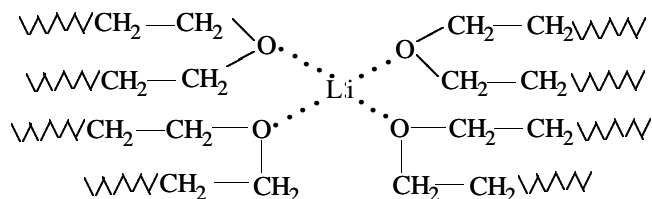
Complex of type 2

Complex of type 3

Complexes of type 1 are present in the pure PEO phase, and complexes of type 3, in the pure P2VP or P4VP phase. Complexes of type 2 stabilize the two-phase microstructure and are present at the phase boundary. Mani *et al.* suggested that the ions incorporated in complexes of types 1 and 2 are mobile and hence participate in the ionic transport. Complexes of type 3 form a rigid phase with a low segmental mobility at room temperature. Therefore, the ions in these phases are mostly immobile and do not make a significant contribution to the ionic conductivity. Preferential formation of complexes of types 1 and 2 increases the amount of charge carriers, increasing the ionic conductivity. However, the larger the amount of complexes of type 1, the weaker the segmental motion and the higher T_g [47]. As the segmental motion becomes less intense, the mobility of charge carriers and hence the ionic conductivity decrease. Wintersgill *et al.* showed that the amplitude of segmental motion plays

an important role in the ion transport in polymer–salt complexes [48].

Zhukovskii *et al.* [49] blended two polymers to prepare an electrolyte based on PEO and amorphous poly(vinyl acetate) (PVA). The PEO crystallinity decreased with increasing PVA content and fully disappeared at a PVA content of about 30 wt %. The highest conductivity at room temperature was 10^{-5} S cm^{-1} at 10–20% PVA content.

Carre and Hamaid [50] succeeded in suppressing PE crystallization by adding to PEO an elastomer (butadiene–acrylonitrile copolymer) and a macromonomer derived from styrene. The polymer electrolyte consisting of a blend of a poly[bis(methoxyethoxyethoxidophosphazene)] complex salt (I) and PEO (II), doped with LiCF$_3$SO$_3$ or LiClO$_4$, was cast from a solution of I + II in acetonitrile and vacuum-dried at 100°C [51]. At a I : II ratio of 1 : 1, the specific conductivity of the electrolyte was 2×10^{-4} (at 20°C) and 5×10^{-2} S cm^{-1} (at 100°C).

Sehlenoff *et al.* [52] suggested a PE based on poly-(*p*-phenylenevinylene) (PPV). Films were prepared from a mixture of aqueous solutions of the polymers, a PPV precursor (water-soluble sulfonium salt) and a water-soluble polymer such as PEO, methyl cellulose, or hydroxypropyl cellulose, taken in 1 : 1 ratio. To prepare PPV, the salt precursor was subjected to heat treatment. The best results were obtained with PPV–PEO blends doped with LiClO$_4$. Such blends are resistant to thermal degradation (up to 225°C) and have good mechanical properties.

Bannister *et al.* [53] reported on the conducting properties of PEO alloys with a polymer containing sulfonate or perfluorocarboxylate groups. The conductivity obtained was relatively low ($\sigma = 10^{-5}$ S cm^{-1} at 100°C), probably because the initial monomeric salts either were insoluble or dissociated only slightly in the polyether phase.

In [54], the polymer matrix was PEO in which each monomeric unit of the backbone contained a pendant –(CH$_2$–CH$_2$–O)$_x$–R chain ($1 < x < 20$, R is alkyl). The backbone and pendant chains in the polymer were linked via ether groups. The molecular weight (MW) of the backbone was 10^4–5×10^6, and that of the pendant chain, 50–2000. Such a PSE has a high conductivity at 20°C and can be used in lithium batteries.

PEs derived from PEO can be modified by introducing lithium salts of various fluorinated monobasic acids. The complex of PEO with LiCF$_3$SO$_3$ shows the highest conductivity among the complexes studied

($\sigma = 4 \times 10^{-4}$ S cm^{-1} at 100°C). With an increase in the size of the anion in these salts, the conductivity decreases, which is attributable to changes in the interaction and mobility of the ions. With a mixture of LiCF$_3$SO$_3$ and NaI, the electrical conductivity of a PE based on PEO substantially increases, and the micro-viscosity decreases [55]. Presumably, this effect is associated with a considerable increase in the content of the amorphous elastomer phase and to nonuniform distribution of different cations and anions in different phases.

Zapol'skikh *et al.* [56] studied the properties of PSEs based on poly[poly(ethylene glycol) dimethacrylate] (PPEGDM) and lithium salts of fluorinated sulfonic acids CF$_3$SO$_3$Li and CF$_3$CF$_2$CF$_2$SO$_3$Li. They found that the anion does not participate actively in the salt–polymer intermolecular interaction. The structure of the anion affects the solubility and degree of dissociation of the salt in cross-linked PPEGDM and exerts no direct influence on the flexibility of the polymer chains and mobility of the cations. As the anion size increases, the salt solubility decreases, but the electrical conductivity of the PSE increases.

To enhance the ionic conductivity of polymer electrolytes and improve the service characteristics of power sources based on them, many researchers [57–62] introduced into PSEs organic and inorganic additives decreasing the degree of crystallinity of the formulations. Chervakov *et al.* [62] synthesized and tested as additives certain nitrogen-containing compounds. Organosilicon derivatives of 4,4'-bipyridine appeared to be among the best additives; they increased the PE conductivity by a factor of 2.

Relatively high conductivity and good mechanical properties are exhibited by PSEs of the composition (PEO)$_8$LiClO$_4$ filled with finely divided (<5 μm) β-Al$_2$O$_3$ by mixing with a solution of PEO and LiClO$_4$ in acetonitrile [57]. Addition of Al$_2$O$_3$ [58] and LiAlO$_2$ ceramic microspheres 1 μm in diameter [59] (to 10–30% content) positively affects the mechanical properties and conductivity of PSEs. The conductivity increases by an order of magnitude on adding to PEO-based PEs such fillers as β-Al$_2$O$_3$, Li$_2$O–B$_2$O$_3$–SiO$_2$ ionic glasses, and ion-exchange resins in the lithium form [60, 61]. Assuming that the relationship between the preexponential term in the conductivity equation and the activation energy obeys the Meyer–Neldel rule in the entire range of the filler concentrations, Wieczorek and Florjanczyk [60, 61] concluded that the ionically conducting fillers do not participate in the charge transport through the solid

electrolyte; their only role is that they make the composite more amorphous.

An increase in the PE conductivity on mixing with Al$_2$O$_3$ powder was reported in numerous papers. Such PEs were studied by impedance spectroscopy, X-ray diffraction, and NMR. It was shown that the conductivity of the PEO–NaI polymer electrolyte increases on mixing with Al$_2$O$_3$, exceeding 10^{-5} S cm^{-1} at room temperature [63].

One more method for preventing crystallization of amorphous polymers is cross-linking, e.g., cross-linking of PEO induced by irradiation with γ-rays or an electron beam [64]. The PEs thus obtained have increased lithium ion conductivity at low temperatures. The mechanisms of radiation-induced degradation and cross-linking of PEO in the solid state and in aqueous solution were studied by ESR [65]. A decrease in the crystallinity of cross-linked polymer materials and enhancement of their mechanical properties and conductivity at 20°C show that γ-irradiation is a simple and efficient procedure for preparing highly conducting and mechanically stable PEs. However, Kronfli *et al.* [66] have not confirmed the effect exerted by γ-irradiation of PE samples based on PEO and lithium salts (LiClO$_4$, LiCF$_3$SO$_3$).

Cross-linking of PEO containing the terminal groups CO–CH=CH–C$_6$H$_4$R (R = NO$_2$, Cl, OCH$_3$), CO–CH=CH–CH=CH–C$_6$H$_5$, CO–C(CN)=CH–C$_6$H$_5$, and CO–C(CN)=CH–CH=CH–C$_6$H$_5$ was described in [67]. The cross-linking occurs under irradiation with accelerated electrons or UV light. A thin-film PE sample (in a mixture with lithium salts) with 90% degree of cross-linking was obtained; its ionic conductivity was 1.7×10^{-4} S cm^{-1} at 20°C.

A polymer solid electrolyte with good mechanical properties and fairly high electrical conductivity, 5×10^{-5} S cm^{-1} at 25°C, was prepared from lithium perchlorate and cross-linked PPEGDM with a low cross-linking density [68]. The behavior of the boundary between the lithium electrode and PSE based on PPEGDM and lithium perchlorate was studied by impedance Fourier spectroscopy [69, 70]. It was shown that the behavior of a passivating film on the lithium electrode at anodic and cathodic polarization is unsymmetrical. A dc polarization decreases the resistance of the electrode|PSE boundaries, probably owing to enrichment of the passivating film with charge carriers.

Methods for chemical cross-linking of the polymer matrix were described in [71–73]. For example, a film PE with satisfactory conductivity at 30°C [71] and a

strong and elastic PE with $\sigma = 6 \times 10^{-5}$ S cm^{-1} at 25°C [72] were prepared by mixing of a product of copolymerization of polyglycerol with ethylene oxide, or of a mixture of ethylene and propylene oxides, with a polyfunctional cross-linking agent (polyisocyanate) at 50–200°C and $P > 10$ atm. Procedures for preparing PEs based on lithium salts and poly(ethylene glycols) cross-linked with siloxane tetraisocyanate were described in [73].

Hu and Wright [74] reported on cross-linking of PEO-based resins with vinyl monomers. Lithium perchlorate was added to PEO-400 maleate isophthalate resins prior to cross-linking with styrene (I), vinylpyrrolidone (II), or vinylpyridine (III). At the ratio [PEO]/[Li$^+$] = 50, the conductivity of the resulting PEs increased in the order III < II < I, inversely correlating with the strength of Li$^+$ binding, which increases in going to more polar comonomers.

Wieczorek et al. [75] prepared composite electrolytes from amorphous PEO copolymer cross-linked with oxymethylene groups (OMPEO), with additions of poly(N, N-dimethylacrylamide) (NNPAAM); these electrolytes showed a room-temperature conductivity of 4×10^{-4}–10^{-5} S cm^{-1}. There is no hydrogen bonding in such systems, which allowed the interactions of both polymers with the Li$^+$ ions to be studied in a wide range of temperatures and NNPAAM concentrations. Three types of complexes were revealed in the OMPEO–NNPAAM–LiClO$_4$ system: polyether–Li$^+$–polyether (type 1), polyether–Li$^+$–NNPAAM (type 2), and NNPAAM–Li$^+$–NNPAAM (type 3). Wieczorek et al. suggest that, above T_g, the ion motion is associated with the segmental motions of polymeric chains. Below T_g, the ion motion is a result of activated hoppings and is associated with the segmental motion of chains to a minor extent.

In parallel with the attempts to reduce the crystallinity of known PSE matrices, some researchers chose another approach: preparation of polymers with intrinsic amorphous structure by copolymerization of different monomers, one of which, as a rule, was oxirane [76]. In particular, amorphous single-phase solid electrolyte with enhanced ionic conductivity, no crystallinity, and good elasticity at 20°C was prepared by copolymerization of ethylene oxide and other oxides of the type –CH$_2$–CH(R)–O–, where R is alkyl, alkenyl, or alkynyl group containing 1 to 12 carbon atoms, or –CH$_2$–O–R'–R, where R' is a polyether –(CH$_2$–CH$_2$–O–)$_p$ (p is an integer from the range 0–10) or a cyclic ether containing more than three carbon atoms in the ring [77]. The oxides are chosen from the group of tetrahydrofuran, dioxolane, and

their derivatives. Short cross-links in the electrolyte are provided by additions of silicon, cadmium, boron, titanium, zinc, magnesium, or tin compounds. The polymer electrolyte contained 1.5 to 25 wt % LiClO$_4$ or LiCF$_3$SO$_3$. A PE with LiClO$_4$ was prepared from an amorphous copolymer of ethylene and propylene oxides and alkyl glycidyl ether (98% amorphous phase). Its maximal conductivity at 25°C was 7.5×10^{-5} S cm^{-1} at a lithium to oxygen ratio of 0.05 [78].

It was suggested in [79, 80] to use as a base of a polymer electrolyte for a lithium battery a cross-linked copolymer of ethylene and propylene oxides. In a combination with a lithium salt, such a PE ensures the specific conductivity of the order of 10^{-5} S cm^{-1} at 25°C. The product of the copolymerization of the vinyl ether R(O–CH$_2$CH$_2$)$_n$–O–CH=CH$_2$ (R = Me or Et, $n = 1$–16) with the divinyl ether CH$_2$=CH–(O–CH$_2$CH$_2$)$_n$–CH=CH$_2$ ($n = 1$–16) is a cross-linked polyether with a glass transition point of about 60–80°C; this polymer was used as a matrix for preparing solid PE.

A procedure for preparing PE by mechanical mixing of acrylic poly(alkylene oxide) and a lithium salt with polyurethane (PU) or polyurethane–urea in a solvent at room temperature, followed by a heat treatment of the resulting mixture, was suggested in [81]. The resulting solid electrolyte had a conductivity of 1.5×10^{-5} S cm^{-1} and satisfactory mechanical properties. On adding LiClO$_4$ to PU, the ionic conductivity at 20°C increased to $\sigma = 4 \times 10^{-4}$ S cm^{-1} at PU : LiClO$_4$ = 8 : 1 [82]. At a high LiClO$_4$ content, the conductivity decreased because of growing viscosity. The difference between the conductivities of the PEs based on PU and PEO is especially significant below 80°C, since, as the temperature is decreased, the conductivity of PEO drastically (by a factor of about 10) decreases because of structural rearrangement. Experiments with lithium electrodes showed that the transport numbers of lithium cations at 50–100°C were 0.5–0.8. To prevent deterioration of the PE in prolonged storage, it was suggested to use as a polymer matrix a urethane-like polymer with the hydrogen atoms substituted by alkali or alkaline-earth metal atoms [83].

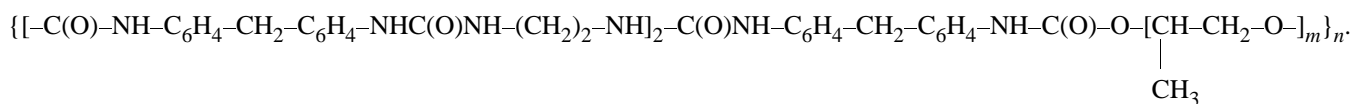A polymer electrolyte having the structure of a modified polyurethane network was prepared from poly(dimethylsiloxane) with grafted PEO, cross-linked with an aliphatic diisocyanate and containing 10 wt % LiClO$_4$. Its ionic conductivity was 10^{-5} S cm^{-1} at 30°C. This electrolyte was used in solid-state lithium batteries. The voltammetric data showed that, after the completion of the formation of the polyurethane net-

work, the unchanged cross-linking agent can prevent the diffusion of lithium ions at the electrode–electrolyte phase boundary. The limiting currents were determined from the cathodic branches of the voltammogram. The internal resistance of the RuO_2/Li battery with the PE, 5 kΩ, was determined from the discharge curves taken at 60–80°C. After two discharge cycles with 95 and 73% degree of discharge, the adhesion of the PE film on RuO_2 and on Li remained unchanged [84].

The morphology and physical properties of the electrolytes from linear segmented polyurethanes based on PEG and alkali metal salts are described in [85]. Systems based on siloxane polymers can be prepared by mixing in a common solvent lithium salts and organopolysiloxane containing more than two COOH groups [86]. The conductivity of such PE at 25°C is 5.6×10^{-5} S cm^{-1}.

Another way to retain PE in the amorphous state is formation of segmented block copolymers in which the chain order is distorted and hence the crystallization is hindered. Watanabe *et al.* [87, 88] studied a series of materials in which this principle is followed, especially the system with segmented polyether–urethane–urea as primary crystal. This substance has an (A–B)$_n$ structure, where A is a rigid polyurethane–urea segment (~30 wt %) and B is a flexible polyether segment:

$$\{[-C(O)-NH-C_6H_4-CH_2-C_6H_4-NHC(O)NH-(CH_2)_2-NH]_2-C(O)NH-C_6H_4-CH_2-C_6H_4-NH-C(O)-O-[CH-CH_2-O-]_m\}_n.$$
$$\overset{|}{CH_3}$$

The polyurethane–urea segments tend to aggregate by hydrogen bonding with the formation of a two-phase microstructure, which imparts to the electrolyte excellent mechanical properties. Salts such as $LiClO_4$ selectively dissolve in the polyether. The relationships between the morphology, dynamic and mechanical properties, and ionic conductivity of these materials are given in [88, 89].

Liu *et al.* [90] suggested a related matrix polymer, polyurethane–urea (PUU) derived from 4,4'-methyl-enebis(phenyl isocyanate), ethylene diamine, and poly(ethylene glycol). The molecular weight of the flexible (polyether) segment was 1000, the weight fraction of the rigid (polyurethane–urea) segment, 35, and the melting point of the polymer, 180°C. A film prepared from the complex of a lithium salt with polyurethane–urea had the ionic conductivity $\sigma = 10^{-5}$ S cm^{-1} at 33°C; its mechanical strength was sufficiently high. To extend the assortment of polymer matrices, oligo(ethyleneoxy)polyphosphazene (OPP) containing alkyl groups was prepared in [91]. The procedure involved transformation of hexachlorotriphosphonitrile into dichlorophosphonitrile followed by its reaction with appropriate alcoholates. Up to 5 wt % $LiClO_4$ is introduced into OPP in the course of the synthesis, which ensures sufficiently high lithium ion conductivity of the PE.

Nagaoka *et al.* [92] prepared polymers with a very low glass transition point by polycondensation of dimethyldichlorosilane with poly(ethylene glycol):

$$[-Si(CH_3)_2-O-(CH_2-CH_2-O-)_n]_m.$$

The high flexibility of the backbone and the absence of crystallinity (because of irregular chain structure) provide relatively high conductivity of such polymers: 10^{-4}–10^{-5} S cm^{-1} (considerably higher than that of MEEP, see below).

Zapol'skikh *et al.* [93] studied the PSEs based on poly(ethylene glycols) of various molecular weights, cross-linked with methyl- and phenyltrichlorosilanes. The polymers were transparent elastic heat-resistant materials. The highest room-temperature conductivity, 5×10^{-5} S cm^{-1}, was shown by the PSE prepared by cross-linking of PEG-300 with methyltrichlorosilane. However, the use of such systems is restricted by high susceptibility of siloxanes to hydrolysis.

Polymer Solid Electrolytes Based on Other Polymer Matrices

Numerous attempts to improve PSEs based on the traditional poly(ethylene oxide) matrix failed, which stimulated search for new polymer materials with low crystallinity and low glass transition point. Such properties are exhibited, e.g., by comb-shaped branched polymers.

Flexible comb-shaped branched systems can be prepared from polymers whose backbone has a low

glass transition point [94]. With the aim to prepare such PEs, Allcock *et al.* [95–97] studied systems based on phosphazene and siloxane polymers. One of the best polymers for PEs was prepared by replacement of chlorine atoms in poly(dichlorophosphazene) with alkoxy groups under the action of sodium 2(2-methoxyethoxy)ethylate in the presence of tetra-*n*-butylammonium bromide to obtain the compound

$$O-(CH_2CH_2O)_2CH_3$$
$$|$$
$$(-N=P-)_m$$
$$|$$
$$O-(CH_2CH_2O)_2CH_3.$$
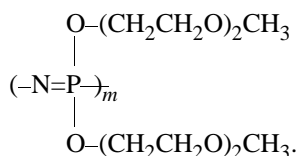
This polymer, poly[bis(methoxyethoxyethoxy)-phosphazene] (MEEP), forms single-phase amorphous electrolytes with salts of various uni-, bi-, and tri-valent metals [95]. The complexes of some lithium salts with this inorganic polymer are PEs with a high conductivity. For example, the room-temperature conductivity of MEEP–$(LiBF_4)_{0.25}$ is 2×10^{-5} S cm^{-1}. However, the mechanical properties of these electrolytes are unsatisfactory, and they cannot be cast as free films to be used in solid-state lithium CPSs. Several approaches are used to enhance the mechanical stability of MEEP-based electrolytes [98]. One of them is blending of MEEP with PEO, PPO, poly-vinylpyrrolidone, or poly(tetraethylene glycol diacrylate). The resulting composite electrolytes can be cast as free films. Their conductivity is somewhat lower than that of MEEP–$(LiX)_n$ but considerably higher than that of PEO–$(LiX)_n$. The dependences of the ionic conductivity of solid-phase polymer complexes of the oligo(ethylene oxide)–polyphosphazene graft copolymer on the temperature and salt concentration were studied by Hara [99]. The highest conductivity ($\sigma_{max} = 10^{-4}$ S cm^{-1}) of the complexes was observed at 25°C and 15 wt % content of $LiClO_4$. For the com-

plexes of $LiClO_4$ (7.5 wt % salt content) with poly-phosphazene modified by grafting of oligooxyethylene with the degree of oligomerization of 7, σ was as high as 3.5×10^{-4} S cm^{-1}. For the systems of polycyclotri-phosphazene of a complex structure with $LiClO_4$, $\sigma = 1.2 \times 10^{-4}$ S cm^{-1} (at 90°C); with increasing temperature, the conductivity maximum shifted toward higher salt concentrations [100].

It was shown in [101] that liquid comb-shaped branched polymers of the structure

$$CH_3$$
$$|$$
$$(-Si-O-)_x$$
$$|$$
$$O-(CH_2CH_2O)_nCH_3$$
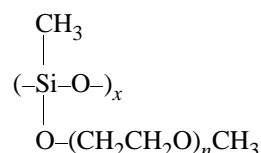
can be additionally cross-linked by heating to 150°C (to obtain rubber-like films). The length of the pendant chain in this case affects the conductivity insignificantly. For the PE containing $LiClO_4$ as an ionic additive, the conductivity was 10^{-4} S cm^{-1} at 25°C. Liquid curable organosiloxanooxyalkylene copolymer formulations with acrylate functional groups, containing $LiCF_3SO_3$ and azobis(isobutyronitrile), were patented. After curing at 85–90°C for 30 min, 1-mm-thick elastic films with a conductivity of 1.6×10^{-5} S cm^{-1} were obtained.

Yamamoto *et al.* prepared and studied polymer solid electrolytes based on polyvinyl alcohol (PVAl, MW 25 000, degree of saponification 88%) and heat-resistant polyarylene(1,3-imidazolidine-2,4,5-trione-1,3-diyl) (polyparabanic acid, PPA) [102]. These polymers dissolve large amounts of alkali metal salts such as $LiCF_3SO_3$, $LiBF_4$, $LiClO_4$, and $NaBF_4$ (1–1.5 g g^{-1} polymer) to form homogeneous films. Dissolution of lithium salts renders the polymers amorphous.

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$$, \quad x : y = 1 : 1.$$

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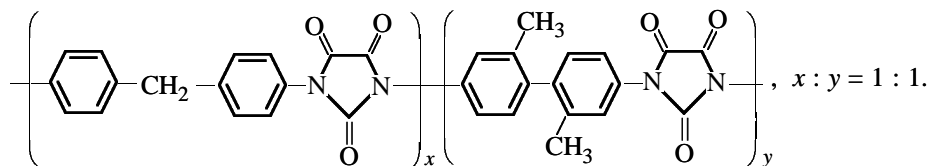
A DSC study of the pure polymers and polymer–salt compounds showed that T_g and T_m decreased on introducing salts into the polymer matrix. This contradicts the usually observed trend that formation of polymer electrolytes from commonly used polymers causes T_g and T_m to increase. Yamamoto *et al.* attri-

bute a decrease in T_g and T_m to decreased degree of crysrtallinity and, correspondingly, to facilitated micromotions of the chain. It was suggested that a decrease in T_g facilitates motion of ions in polymer solid electrolytes. These results indicate that low T_g is important for migration of ions in a polymer electrolyte.

At the same time, ions can also migrate even in a polymer matrix containing relatively rigid domains. A polymer electrolyte can consist of amorphous domains with a high concentration of a lithium salt and domains with a relatively rigid structure and lower salt concentration; the ions mainly migrate through amorphous domains. Yamamoto *et al.* also examined the possibility of using as polymer electrolyte water-soluble and highly heat-resistant polysulfone–ether–imide (PSEI, $[\nu] = 0.5$ g dl^{-1}):
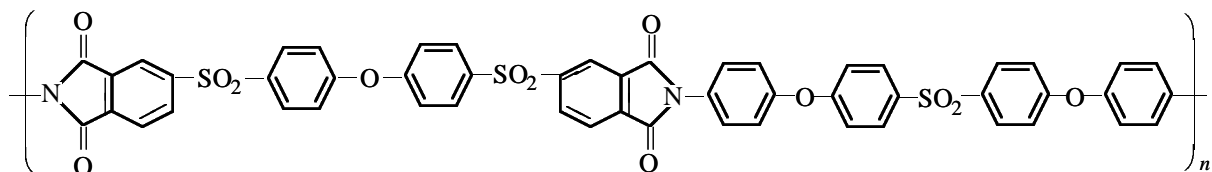
In contrast to PPA, this polymer gave only heterogeneous and brittle films on introducing LiCF$_3$SO$_3$ (0.16–0.5 g g^{-1} PSEI), despite the presence of a large amount of electron-donor atoms theoretically capable of solvating Li$^+$ cations.

Zapol'skikh *et al.* [103] studied the properties of PSEs based on poly(piperylene sulfone) and lithium perchlorate. They found that the room-temperature electrical conductivity of the PSE was 10^{-6} S cm^{-1} and explained this relatively high value by the presence of residual solvent, which could not be fully removed upon preparation of the films from a solution of the polymer and salt in dimethylformamide. An IR study showed that the lithium ion was coordinated with three oxygen atoms of sulfone groups and nitrogen atom of dimethylformamide. This results in displacement of the perchlorate ion from the inner coordination sphere of the lithium ion and thus in higher degree of electrolytic dissociation of the salt in the polymer matrix.

The goal of Smirnov *et al.* [104] was to develop new highly conducting PEs free of aprotic solvent. The formulation for preparing a PE consisted of an amorphous rigid-chain polymer (polyheteroarylene) and a lithium salt (LiClO$_4$ or LiBF$_4$). The polymer solid electrolytes exhibited high elasticity, mechanical strength, and acceptable adhesion to the electrode materials. Their conductivity at 20–60°C reached about 10^{-3} S cm^{-1}. The polarization at the PSE|Li phase boundary was 30–60 mV, and it gradually decreased in the course of charging–discharge, which was due to mutual adjustment of the components of the Li–PSE system. The photomicrographs of the surface of the lithium foil before and after the cycling revealed no significant changes.

Studies of the structure and mechanisms of the ion transfer in PE showed that the required set of transport properties can be attained in PSEs based on noncrystallizing polymer matrices, acrylonitrile–butadiene copolymers. Lirova *et al.* [105] used a 40 : 60 acrylonitrile–butadiene copolymer (SKN-40 rubber) containing highly polar CN groups capable of coordination interaction with the metal salts. The electrolyte films 40–120 μm thick were prepared by a modified casting procedure, with introduction of LiClO$_4$, LiCF$_3$SO$_3$, or LiAsF$_6$. The interaction of the lithium ions with the CN groups was studied by IR spectroscopy. By analogy with the well-studied interaction of Li$^+$ with acetonitrile, it was found that the solvation of the cations in SKN-40 is due to formation of coordination bonds with the cyano groups: $-C\equiv N^{\delta-}\cdots Li^+$. Lirova *et al.* [105] conclude that the solvation of the cation with the polar groups of the polymer is the factor ensuring solubility of the salt both in the low-molecular-weight solvent and in the chemically related polymer, and formation of a macromolecular ionic solution ensures high ionic conductivity of the electrolytes.

As a continuation of these studies, Dusheiko [106] prepared films from copolymers of acrylonitrile with styrene and vinyl acetate as PSEs. The solid electrolyte films prepared with these polymer matrices showed a conductivity of 10^{-5}–10^{-6} S cm^{-1} and high physicomechanical properties. Bushkova *et al.* systematically studied the ion solvation in PSEs in wide temperature and concentration ranges. As polymer matrices they used amorphous acrylonitrile copolymers (SKN-40, SKN-26, SKN-50) and polyacrylonitrile, into which LiClO$_4$, LiAsF$_6$, and LiCF$_3$SO$_3$ were introduced. The measurements of the temperature and concentration dependences of the PSE conductivity suggested that, in the range of maximally high salt concentrations, a specific mechanism of ion transport is realized, involving higher ionic associates.

In some cases, the conductivity of such electrolytes reached about 10^{-3} S cm^{-1}. However, stabilization of the highly conducting structure in the concentrated electrolytes was not yet attained.

Amorphous polymer electrolytes can be obtained from a copolymer of acrylonitrile with sulfoalkyl methacrylate [109]. The conductivity of various salt species of PE varies in the order Li salts > Na salts > K salts and increases as the oxygen to lithium ratio is increased from 20 to 100. The new PEs based on copolymers with polyvinyl alcohol, PVA, and poly-acrylamide exhibit high heat resistance at fairly high conductivity [110].

Novakov *et al.* [9] tested as polymer matrices aliphatic polycarbonates: poly(ethylene carbonate) (PEC) and poly(propylene carbonate) (PPC), with lithium perchlorate introduced in various molar ratios. The electrical conductivity of the best formulations varied from 10^{-6}–10^{-5} at 293 K to 10^{-3} S cm^{-1} at 393 K. *Ab initio* quantum-chemical calculations of the PEC–LiClO$_4$ and PPC–LiClO$_4$ system showed that the lithium ion preferentially coordinates with the carbonyl oxygen atom, in agreement with the IR data.

Dusheiko *et al.* [111] used as PEs copolymers of acrylonitrile with butyl methacrylate (1 : 1), vinylpyridine (1 : 1), and vinyl fluoride (2.3 : 1). The copolymers were amorphous white nonhygroscopic powders. From their solutions, elastic transparent films 30–60 μm thick, doped with lithium perchlorate, were prepared. The highest conductivity, with preservation of the required physicomechanical properties, was attained at a LiClO$_4$ content of 15–20 wt %.

PLASTICIZED POLYMER ELECTROLYTES

Attempts to develop PSEs based on polymer–lithium salt systems, exhibiting acceptable electrochemical characteristics (in particular, room-temperature conductivity), were yet unsuccessful. Despite the optimism expressed in [104, 108, 112, 113], the results obtained with true PSEs are mainly inferior to those obtained with plasticized PEs. Therefore, much efforts were focused in the recent years on the development of plasticized or gel-polymer electrolytes (GPEs) containing, along with a polymer and a lithium salt, also plasticizers (solvents) and other components. The requirements to the plasticized PEs are mainly the same as those to PSEs: high electrical conductivity, satisfactory physicomechanical properties, chemical stability toward electrode materials, and wide range of electrochemical stability. However, in development of plasticized PEs, it is necessary to take into account also other factors: compatibility of the polymer matrix with the organic solvent, necessary for retention of the solvent in GPE; phase stability and efficiency in a wide temperature range. Otherwise, the GPE film can lose the solvent and the mechanical strength.

The above properties are largely determined by the kind of the polymer, composition of the plasticized PE, and temperature. Complex physicochemical processes involving the components and governing the characteristics of plasticized PEs occur in the system. The mechanisms of these processes are not fully understood. Presumably, donor–acceptor, ionic, and van der Waals interactions occur in the system [114].

The problem of enhancing the conductivity of PEO-based polymer electrolytes was solved in [115–119] by introducing crown ethers. Measurements of the electrical and electrochemical properties of PE films consisting of PEO and LiCF$_3$SO$_3$, LiBF$_4$, or LiClO$_4$ and containing 12-crown-4 (12C4) or free of it showed that, with each salt, the conductivity at a given temperature depends on the crown ether concentration and reaches a maximum at [12C4] : [Li] = 0.003 [116].

Eyring [117] studied the kinetics of complexation of alkali metal cations with macrocyclic ligands: 12-crown-4, 18-crown-6, and 15-crown-5. The crown ether groups (16-crown-5) were also introduced into polyphosphazenes (PPs) as pendant groups [120, 121]. The temperature dependence of the conductivity of such PEs containing LiClO$_4$ or NaClO$_4$ was studied. The $\log \sigma$–T^{-1} dependence was linearized using the VTF equation. The highest conductivity was attained in the system PP–NaClO$_4$, which was due to higher degree of ionization of the salt bound by the macro-cyclic moiety of the polyphosphazene.

Introduction of 12-crown-4 both into a solid PE consisting of PEO and LiBF$_4$ and into the cathodic formulation enhances the ionic conductivity [119]. The electrolyte has a very low leakage current. Addition of the crown ether improves the cell performance, decreases the resistance to charge transport, increases the current, and makes the cell operation more reversible (with CoO$_2$ and TiS$_2$ cathodes). Along with crown ethers, a suitable additive is crypt-and, a bicyclic compound also forming a complex with lithium ions [122].

Yarmolenko *et al.* [123] prepared and studied a series of new polymeric electrolytes based on LiClO$_4$ and PEO with additions of finely divided β-LiAlO$_2$,

γ-LiAlO$_2$, or Al$_2$O$_3$ powder and of 2,4-dioxo-16-crown-5. Measurements by impedance spectroscopy showed that the room-temperature conductivity of the samples was as high as 10^{-4}–10^{-5} S cm^{-1}; the compatibility with the cathodes based on thermally cross-linked polyacrylonitrile (TCPAN) and lithium anode was good. Introduction of 2,4-dioxo-16-crown-5 into PEO-based PSE improved its parameters owing to complexation of the lithium salt with the crown ether. In a later work [124], Yarmolenko *et al.* studied a series of new PSEs based on LiClO$_4$ and PEO with additions of 15-crown-5, benzo-15-crown-5, and 2,4-dioxo-16-crown-5. A series of the samples obtained exhibited high (10^{-4}–10^{-3} S cm^{-1}) room-temperature conductivity, good compatibility with the lithium anode, and stability in prolonged storage. Yarmolenko *et al.* found that introduction of 15-crown-5 and 2,4-dioxo-16-crown-5 into PEO-based PSE enhances its conductivity by two orders of magnitude, whereas introduction of benzo-15-crown-5 exerts no effect on the conductivity of this electrolyte.

Additions of 15-crown-5 and benzo-15-crown-5 to polymer electrolytes based on polyacrylonitrile, lithium perchlorate, and propylene carbonate allowed preparation of PEs with the conductivity at 20°C as high as 10^{-3} S cm^{-1} [118].

To enhance the electrical conductivity of films based on acrylonitrile copolymers, Clericuzio and Parket [125] added a mixture of propylene carbonate and dimethoxyethane as plasticizer; their content in the copolymer did not exceed 10 wt %. The conductivity of the PEs obtained was within 10^{-6}–10^{-4} S cm^{-1}.

Addition of low-molecular-weight plasticizers such as ethylene and propylene carbonate to electrolytes based on PEO [126, 127], polyacrylonitrile (PAN), poly(tetraethylene glycol diacrylate), or polyvinylpyrrolidone [128], and also to hybrid films based on poly(methyl methacrylate), polystyrene, poly(vinyl chloride) (PVC), PVA, PAN, and poly(vinylidene fluoride) in amounts of up to 30 mol % increased the electrical conductivity to 10^{-5}–10^{-3} S cm^{-1} [129]. The stable voltage of a Li|PE|MnO$_2$ voltaic cell, which operated for more than 70 h without electrolyte degradation, shows that hybrid films are suitable as PEs for solid-state batteries. The possibility of plasticizing PEO-based compounds by adding poly(propylene glycols) of various molecular weights was examined in [130, 131]. Such plasticization enhances the conductivity owing to an increase in the content of the amorphous phase in the electrolyte, with a simultaneous increase in the salt concentration in this phase.

The properties of gel polymer electrolytes based on PVC and solutions of lithium salts in sulfolane were studied in [132, 133]. An electrolyte solution in a polymer matrix acts as an intra- and interstructural plasticizer. The distribution of an electrolyte solution in a polymer matrix is determined by the kind and concentration of the electrolyte salts. In some cases, structural nonuniformity of GPEs results in dendrite formation in the course of prolonged dc polarization [134].

To obtain an amorphous polymer with PVC as a PE matrix, Chervakov *et al.* [135] performed a chemical modification by chlorination. As a result, the chlorine content increased from 56.8 (initial PVC) to 65%. The other electrolyte components were a salt and a plasticizer (aprotic solvent).

Polishchuk *et al.* [112] studied the system Li|Li$^+$|PE|FeS$_2$. The polymer matrix for the electrolyte was modified PVC. The modification of the polymer electrolyte was performed by additional chlorination, which afforded a more amorphous material. The conductivity of the polymer electrolytes prepared by this procedure was as high as 10^{-3} S cm^{-1}; it depended on the kind of the low-molecular-weight plasticizer and lithium salt.

The problem of development of a GPE based on PVC, which is insoluble in EC and PC, was solved by using tetrahydrofuran as solvent, in which all the components (PVC, EC, PC, LiClO$_4$) are soluble. Films with a conductivity of 1.2×10^{-3} S cm^{-1} at 20°C were prepared by casting [136].

A procedure for preparing new plasticized and microporous PEs based on poly(vinylidene fluoride) and chlorinated poly(vinyl chloride), with a room-temperature conductivity of 10^{-4}–10^{-3} S cm^{-1} and electrochemical stability in the range from 0.5 to 4.5 V (vs. lithium electrode), was suggested by Chervakov *et al.* [137]. A characteristic feature of the procedure developed is the possibility of preparing a polymer matrix with the required pore structure morphology and specific interaction with solutions of lithium salts in aprotic solvents. This is attained by a proper choice of a plasticizing system and a process for forming PE. It was shown that the nature and composition of the plasticizing system for PE essentially influence the formation of passivating films on metallic lithium and graphite anode and govern the specific characteristics of the cathode materials, stability in cycling, and self-discharge of the electrochemical systems. A process for preparing PEs for the systems Li|PE|LiCoO$_2$ and Li–MnO$_2$ involves preparation of a microporous polymer material and its subsequent

activation with a solution of a lithium salt in an aprotic solvent.

Kelly and Owen [138–140] enhanced the low-temperature conductivity of the systems PEO–$LiClO_4$ and PEO–$LiCF_3SO_3$ by adding low-molecular-weight polyethers $CH_3(OCH_2CH_2)_nOCH_3$. The materials obtained behaved similarly to solutions of the salts in poly(ethylene glycol) dimethyl ether ($\sigma = 10^{-4}$ S cm^{-1} at 40°C); however, the mechanical properties of the products appeared to be unsatisfactory.

An X-ray diffraction study showed that the unit cell of the PEO crystal remained monoclinic on adding the elastomer and macromonomer. The diffraction patterns and conductivities remained unchanged during a period of 15 months. The conductivity was also stabilized by partial replacement of PEO by oligo(ethylene oxide) with terminal styrene groups, with the weight ratio of ethylene oxide units to Li$^+$ kept unchanged [141]. The best results ($\sigma = 2 \times 10^{-4}$ S cm^{-1}) were obtained with $LiCF_3SO_3$ on adding 20 to 50% low-molecular-weight oligo(ethylene oxide) with MW 550.

Xia et al. [142] studied how the conductivity of solid polyelectrolyte complexes of alkali metal salts NaSCN, $NaCF_3SO_3$, and $LiCF_3SO_3$ with polymers derived from methoxypoly(ethylene glycol) methacrylate $CH_2=C(CH_3)COO(CH_2-CH_2O)_nCH_3$ [$n = 8$ (PMG-8) and $n = 22$ (PMG-22)] depend on the temperature and salt concentration. The systems based on copolymers of PMG-22 with polystyrene, like the systems plasticized with propylene carbonate, showed considerably higher conductivity than the systems based on the homopolymers. A highly conducting formulation based on a blend of alkylacrylate (alkyl C_1–C_8) and/or alkoxyacrylate (alkoxy C_2–C_5) polymer with 5–100% (relative to the weight of the acrylate polymer) of $LiClO_4$ or a lithium salt of a polymeric acid (polystyrenesulfonic, polyethylenesulfonic) was described in [143] as a thin-film electrolyte. The plasticizer and solvent was an organic solvent with a high dielectric permittivity.

Polymers derived from phosphazene with various alkyl ether and alkoxy pendant groups were prepared. The room-temperature ionic conductivity of the electrolytes consisting of such polymers and $LiCF_3SO_3$ was 10^{-4}–10^{-3} S cm^{-1} [144]. Villarreu [145] studied the behavior of polymer electrolytes formed by a blend of PEO and perfluorinated polyphosphazene and filled with γ-$LiAlO_2$ or propylene carbonate. It was found that the filler appreciably increases the ionic conductivity of the polyelectrolyte, whereas propylene carbonate decreases it; these effects were attributed to structural changes in the formulation.

Kicheev et al. [146] suggested aromatic polymers as the polymeric components, in view of the high thermal, chemical, and electrochemical stability of these polymers. As plasticizer they used a 1 M solution of $LiClO_4$ in a mixture of propylene carbonate and dimethoxyethane. The best of the polyelectrolytes studied showed the conductivity of 2.25×10^{-2} S cm^{-1} (298 K). An XPES study of the lithium anode showed that the polyelectrolyte was chemically inert.

Siling et al. [147] suggested a highly conducting gel-polymer electrolyte for lithium power sources, based on poly(phenylene oxide) prepared by a special procedure. The gel-polymer electrolytes were prepared by impregnation of the polymer with a solution of $LiClO_4$ in a mixed solvent. The electrical conductivity of the GPE was $(1.25$–$7) \times 10^{-2}$ S cm^{-1} at room temperature and $(4.1$–$7) \times 10^{-3}$ S cm^{-1} at 30°C; it was chiefly determined by the conditions of the synthesis of the polymeric component.

No oxide film is formed on lithium in the course of operation of Li–MnO_2 and Li–LiV_3O_8 cells with the GPE developed. No dendrites are formed either.

Yarmolenko and Efimov [148] found that oligo-(urethane–methacrylates) derived from polytetrahydrofuran of molecular weight 1400–1600 (SKU–PFL) and poly(ethylene glycol) monomethacrylate) (PPMBE) of molecular weight 370 can be used for preparing gel-polymer electrolytes for lithium batteries by introduction of liquid organic electrolytes (e.g., 1 M $LiClO_4$ in a 1 : 1 mixture of propylene carbonate and dimethoxyethane) into the oligomer, followed by film forming and photochemical or thermal curing. The conductivity of the film electrolytes is increased by formation of a branched network copolymer with a methacrylic comonomer in combination with addition of organic solvents for alkali metal salts; these solvents also act as plasticizers. Gel-polymer electrolytes based on SKU–PFL + PPMBE (1 : 1 by weight) and 1 M solution of $LiPF_6$ in EC + dimethyl carbonate (volume ratio 1 : 1) showed a conductivity of 2.5×10^{-3} S cm^{-1} (at 20 wt % content of the polymer in the system). The resulting thin-film electrolyte was a structured gel rather than a monolithic film. Therefore, a special procedure was developed to enhance the mechanical stability of PE. It involved introduction of the electrolyte formulation into a porous polypropylene separator, followed by photocuring. The highest conductivity (2.8×10^{-4} S cm^{-1}) was attained with the GPE containing 20 wt % SKU–PFL + PPMBE (1 : 1) and 80 wt % organic electrolyte (1 M $LiClO_4$ in γ-butyrolactone), applied to a fibrous polypropylene separator (99% porosity).

Gel-polymer electrolytes can also be prepared on the basis of anion- and cation-exchange polyelectrolytes [149–151]. Such electrolytes exhibit fairly high electrical conductivity (10^{-4}–10^{-3} S cm^{-1}) and selectivity with respect to the transported ion.

Papers concerning development of solid and plasticized polymer electrolytes show that it is very promising to search for nontraditional ways to improve the electrochemical and service properties of PEs. Among such ways are synthesis and use of new lithium salts with hyperlarge anions and chemical modification of electrolytes of lithium power sources with the aim to optimize the current transport in liquid and solid polymer media [5, 137, 152].

In particular, Chervakov *et al.* [137] develop procedures for preparing new lithium salts of N,N'-disubstituted alkyliminosulfinic acid amides. These resinous substances are readily soluble in aprotic solvents and are electrochemically stable in the range 1.1–4.6 V. By optimizing the structure of the anion, Chervakov *et al.* prepared lithium salts acting in PE not only as conducting additives but also as plasticizers. The following ionic salts with large anions were involved recently in PE studies: lithium tris(trifluoromethanesulfonyl)methide $LiC(CF_3SO_2)_3$, lithium bis-(trifluoromethanesulfonyl)imide $LiN(CF_3SO_2)_2$, and lithium bis(perfluoroethanesulfonyl)imide $LiN \cdot (C_2F_5SO_2)_2$ [5].

CONCLUSION

Although a large body of data have been accumulated on lithium-containing polymer composites, search for new formulations of polymer electrolytes for lithium and lithium–ion batteries is being continued. The interest in basic and applied research in the field of development of new polymer electrolytes and high-capacity CPSs based on them undoubtedly grows.

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