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Polymeric electrolytes for lithium chemical power sources

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Abstract. **The review deals with the properties of solid and polymeric electrolytes incorporating (co)polymers or mixtures of polymers and copolymers doped with inorganic lithium salts. Such electrolytes are used for lithium chemical power sources. Attention is concentrated on the methods for the modification of the structure and composition of these systems by means of amorphous and network (co)polymers, additives promoting conversion into an amorphous form, crown-ethers, plasticisers, and ceramic powders, which increase the ionic conductivity of polymeric electrolytes. The methods for the preparation of thin films of polymeric electrolytes by plasma polymerisation and also procedures for the modification of the electrodes of lithium chemical power sources with polymeric electrolytes are considered.**

Data on the ionic conductivities of the systems described are presented. The bibliography includes 129 references.

I. Introduction

Considerable efforts by specialists in the development and manufacture of chemical power sources (CPS) are nowadays directed to the creation of superminiaturised autonomous power sources. Studies in the last 10 years have shown that this problem can be solved with the aid of film-type polymeric electrolytes (PE). High specific characteristics are then attained (for example, a power capacity up to 200 W h kg^{-1} subject to a high degree of discharge) and satisfactory storage properties. The use of PE for the creation of rechargeable accumulators with a lithium anode is of special interest. The principal advantages of such accumulators are virtually total safety in use, the possibility of preparing CPS of any shape, the absence of liquid and gaseous components, a high resistance to mechanical influences, and a capacity for operation at high temperatures. Lithium accumulators with PE are employed most effectively in electric automobiles, in military and space technology, in microelectronics, in communication devices, and, especially, in combination with solar batteries.

According to the estimates of a number of investigators, lithium CPS with a polymeric electrolyte can replace in the future sulfuric acid-sodium batteries, accumulators based on systems of the Li/metal sulfide type, and even, partially, nickel–cadmium batteries.[1] Apart from their use in CPS, PE can be employed in sensor devices, condensers, and other solid state electrochemical devices.[2]

The principal task in the creation of solid PE involves nowadays the search for new compositions with a high ionic conductivity for ions of different species over a wide temperature range. The stability of the PE in air, their low cost, and the ease of their technological application are also very important. It is noteworthy that the possibility of constructing thin 0.5–100 μm films from electrolytes of the class considered and their elasticity constitute their major advantages compared with ceramic electrolytes. Furthermore, in terms of their transport properties, PE are only slightly inferior to liquid electrolytes.

Depending on the nature of the ionogenic centre, PE can be divided into two groups: (1) polymeric complexes — complexes of functional polymers with metal salts; (2) composite PE — compositions comprising film-forming polymers with low-molecular-mass solvents and electrolytic salts.

The polymeric complexes may be synthesised from polyesters, polynitriles, polyamides, polysulfones, and other functional polymers. By varying the structure of the polymer matrix and the composition of the complex, it is possible to obtain compounds with conductivities σ up to 10^{-2} S cm^{-1}. However, the variation of the properties under the conditions of constant current polarisation constitutes a significant disadvantage of this type of PE.

Composite PE may be obtained from a wide variety of polymers, solvents, and ionogenic salts. This makes it possible to regulate their properties over a wide range. The conductivity of the composite electrolytes is extremely sensitive to their composition and methods of preparation. After prolonged storage and also after polarisation with a direct current, an irreversible change in their structure takes place in many instances and leads to a significant decrease in conductivity. In order to obtain solid electrolytes, it is essential to have polymers with a high flexibility of the chain, a low cohesion

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energy density, etc. The necessary and sufficient conditions for the employment of various polymers and matrices in polymeric electrolytes for CPS have been most fully considered in the review of Bruce and Vincent.[3]

In the present review, attention is concentrated on questions of the modification of solid polymeric electrolytes in order to increase their conductivity, of the influence of the purity of the PE components on the ionic conductivity and the electrical parameters of the CPS, and also of the chemical interaction in the lithium anode–polymeric electrolyte system.

II. The mechanism of ionic conduction in solid polymeric electrolytes

In composite PE, the driving force leading to the dissolution of the salt in the polymer arises from the oxygen, nitrogen, or sulfur atoms forming part of the composition of the polymer molecule and surrounding the lithium cations. The coordination groups in PE are the oxyalkanes $-CH_2-CH_2-O-$, azoalkanes $-CH_2-CH_2-NH-$, thioalkanes $-CH_2-CH_2-S-$, and the esters $-CH_2-CH_2-OCO-$. The following types of polymers are used for the preparation of the PE: linear homopolymers — poly(ethylene oxide) (PEO), poly(propylene oxide) (PPO), and polyethyleneimine (PEI), nonordered polymers–PEO/PPO; network polymers (with cross-links); cellular-branched copolymer blocks.

The organic polymers used for the preparation of the PE are usually insulators themselves. Their insignificant conductivity (of the order of $10^{-12}-10^{-10}$ S cm^{-1}) is due to the presence of impurities and is due to the diffusion of ions through the free volume of their macromolecules. Therefore fairly satisfactory ionic conductors can be obtained by dispersing various salts in the polymers at the molecular level. Among metal ions, those of lithium are the smallest and have the lowest activation energy and for this reason lithium salts are frequently employed to prepare electrically conducting compositions for different purposes. With increase in the size of the cation, there is an increase in the degree of binding of the salts to the macromolecules. An increase in the complexity of the structure of the cations lowers the degree of solvation of the low-molecular-mass ions by the macromolecules. The donor capacity (DN) of the solvents also influences the complex formation process. For example, in acetonitrile ($DN = 14.3$), the degree of association of polyesters with low-molecular-mass salts is higher than in methanol ($DN = 19.0$) solutions.[4–6]

The mechanism of the conduction in polymeric electrolytes, first proposed by Armand et al.,[7] presupposes ionic conduction in continuous conducting regions of the helical structure of the PEO and also the fact that it is effective predominantly in the amorphous phase of the PEO–salt system. Under these conditions, the ion migrates between the polymer chains by virtue of the segmental motions of the polymer matrix. It may be that such movement in the polymer is an important factor which determines the order of magnitude of the ionic conductivity in the solid state.

Bruce and Vincent[8] investigated ionic transport in polymeric electrolytes — amorphous PEO–$LiClO_4$ complexes — by an e.m.f. method for different compositions of the complexes. In this case, the steady-state current during polarisation by a permanent field was attained after several hours and was determined by the mobility of both Li^+ and ClO_4^- ions, while at a high salt concentration ion pairs are also mobile.[9] According to the data quoted by Gray,[10] at a fixed temperature the dependence of the conductivity on the perchlorate concentration is a complex function. At low concentrations, the conductivity σ diminishes rapidly with increase in the salt content. It then increases to a maximum, the position of which depends on the temperature, after which it again falls. The form of the observed dependences of σ on temperature and perchlorate concentration is caused, according to the authors, by charge transfer involving the Li^+ and ClO_4^- ions, the mobilities of which are influenced by the incomplete dissociation of the salt and by the formation of the cluster ions $Li(ClO_4)_2^-$ and $Li_2(ClO_4)^+$.

It has been shown by Brillouin and photon-correlation spectroscopy[11] that the cooperative movement of ~20 monomer units of the polymer is needed for ion transport. For $n > 4$, short-lived ion–polymer cross-links, restricting the mobility of the polymer segments, arise in the electrolyte. The density of the cross-links diminishes sharply with increase in temperature as a consequence of the formation of ion pairs, which exert a plasticising effect on the electrolyte.

In the study of the ionic association of the PPO–$LiClO_4$ complexes, the constancy of the number of dissociated ions under conditions when the monomer : salt ratio varies from 1000 to 30 was noted.[12] With increase in the salt concentration in PPO, the rate of formation of ion pairs also rises. The main contribution to the increase in the conductivity of the PE at low $LiClO_4$ concentrations comes from the increase in the number of dissociated ions and not from their mobility. The IR and polarised Raman spectra of the PPO–$LiCF_3SO_3$ complexes indicate the existence of three types of associated species: two differently coordinated ion pairs and a triple ion. It is claimed[13] that the free ions which had been believed previously to exist in these polymer–salt complexes are in fact cation–anion pairs in which the cation interacts weakly with the terminal CF_3 group of the anion.

The data of Arumugam et al.[14] on the diffusion coefficients of Li^+ and PF_6^- in the amorphous PEO–$LiPF_6$ electrolyte obtained using ^7Li and ^{31}P NMR with a pulsed field gradient over a wide range of temperatures (25–100 °C) and salt concentrations (up to 0.25 M) indicate different mechanisms of the transport of the cation and anion at a high salt concentration. A reduced sensitivity of the diffusion of the cation to the salt concentration and a deviation from the Nernst–Einstein relation have been observed. Cation jumps between ionic clusters and the diffusion of neutral ion pairs have been proposed as mechanisms to account for the results.

III. Modification of the polymeric electrolytes used in lithium chemical power sources

The main obstacle in the creation of low-temperature solid-state batteries with a polymeric electrolyte is the marked impairment of its ionic conductivity during storage caused by the crystallisation of the PE and a sharp increase in the size of its particles.[15] One of the ways of solving this problem is to base the electrolytes on complex polymeric compounds or to use these to modify the traditionally employed PE.

A survey of the experimental studies in recent years demonstrated that complexes of PEO with lithium salts are mainly employed as the solid PE, but their practical use in the manufacture of CPS is difficult, firstly, as a consequence of the tendency of PEO to crystallise, secondly, as a consequence of the hygroscopicity of the films based on it, and, thirdly, due to the small transport numbers of the cations.

Analysis of the literature data makes it possible to differentiate the following principal modification methods which increase the ionic conductivity of the polymeric electrolytes: the use of amorphous polymers and additives inducing conversion into an amorphous structure; the formation of a network system (cross-links); the introduction of crown-ethers, plasticisers, and ceramic powders. The application of such methods makes it possible to employ the PE in lithium CPS at normal temperatures.

The efforts of investigators engaged in the development of the PE have been directed mainly to the stabilisation of the state of the polymers containing amorphous sections or their preparation in the amorphous state. This is associated with the fact that the majority of polymeric electrolytes containing lithium salts have the maximum ionic conductivity when they exist in the amorphous state, which is the reason for the level of working

temperatures being approximately 100 °C. The possibility of creating electrolytes in a stable amorphous form, i.e. the preparation of polymers with a secondary structure having optimum electrochemical and mechanical properties, has therefore been discussed in recent years.[18,19] In particular, an amorphous single-state solid electrolyte with an improved ionic conductivity, the absence of crystallinity, and a satisfactory elasticity at 20 °C has been obtained by copolymerising ethylene oxide and other oxides of the type $-CH_2-CH(R)-O-$, where R = alkyl, alkenyl or alkynyl, containing between 1 and 12 carbon atoms, or $-CH_2-O-R'-R$, where R' is a polyether $-(CH_2-CH_2-O-)_p$ (p is an integer in the range from 0 to 10), or a cyclic ether containing more than three carbon atoms in the ring.[20] The oxides are selected from the group comprising tetrahydrofuran, dioxolane, and their derivatives. Short cross-links in the electrolyte are ensured by adding silicon, cadmium, boron, titanium, zinc, magnesium, or tin compounds. The polymeric electrolyte contains between 1.5 and 25 mass% of $LiClO_4$ or $LiCF_3SO_3$.

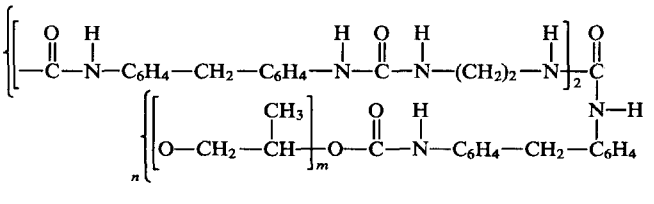
A PE with $LiClO_4$ has been obtained from an amorphous copolymer of ethylene and propylene oxides and allyl glycidyl ether (the content of the amorphous phase was 98%). Its maximum conductivity proved to be 75×10^{-5} S cm^{-1} at 25 °C for an electrolyte composition with a lithium : oxygen ratio of 0.05.[21]

In another study,[22] the polymer matrix was PEO, each monomer unit of the main chain of which contained the $-(CH_2-CH_2O)_x-R$ side chain, where $1 < x < 20$ and R is an alkyl group. The bond between the main and side chains in the polymer is formed via an ether group. The molecular mass (M) of the main polymer chain was $10^4-5 \times 10^6$, while that of the side chain was 50–2000. Such a solid PE has a high conductivity at 20 °C and may be used in lithium accumulators.

It proved possible to increase the conductivity of the PEO–$LiClO_4$ and PEO–$LiCF_3SO_3$ systems at low temperatures by adding low-molecular-mass polyethers $CH_3(OCH_2.CH_2)_nOCH_3$.[23–25] The materials obtained behave similarly to a solution of salts in the polymer of the dimethyl ether of ethylene glycol ($\sigma = 10^{-4}$ S cm^{-1} at 40 °C), but their mechanical properties turned out to be unsatisfactory.

The PE based on PEO may be modified by introducing various lithium salts of fluorinated monobasic salts. The complex of PEO with $LiCF_3SO_3$ has the highest conductivity among the complexes investigated ($\sigma \approx 4 \times 10^{-4}$ S cm^{-1} at 100 °C). An increase in the size of the anion in these salts leads to a decrease in σ. This has been attributed to a change in the interactions and mobilities of the ions. In the case of the $LiCF_3SO_3$ and NaI salts, there is a significant increase in the conductivity of the PEO-based PE and a decrease in the microviscosity.[26] It has been suggested that the observed effect is associated with the strong influence of the fraction of the amorphous 'elastomeric' phase and also with the inhomogeneity of the distribution of various cations and anions in different phases.

The PE can also be maintained in the amorphous state by creating segmented block copolymers in which the regularity of the chain is disturbed and hence crystallisation is hindered. A series of materials have been investigated[27,28] in which this principle holds, especially the system employed as the primary polymeric crystal, namely segmented polyether-polyurethane-urea, which has the structure $(A-B)_n$, where A is the solid segmented polyurethane-urea (~30 mass%) and B is a soft polyether segment.

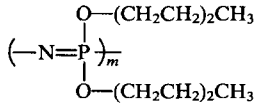


The polyurethane-urea segments tend to aggregate as a result of the formation of hydrogen bonds and of a two-phase microstructure, ensuring thereby that the electrolyte has excellent mechanical properties. Salts such as $LiClO_4$ dissolve selectively in the polyether. The relation between the morphologies, the dynamic-mechanical properties, and the ionic conductivities of the materials has been described.[28,29]

A similar matrix polymer — polyurethane-urea (PUU) — has been described.[30] 4,4-Dimethylbis(phenylene isocyanate)ethylenediamine and poly(ethylene glycol) ($M = 1000$) were used as the starting materials for its synthesis. The molecular mass of the soft (polyether) segment of the polymer is 1000, the mass fraction of the hard segment (polyurethane-urea) is 35, and the melting point of the polymer is 180 °C. A film formed from a complex of an alkali metal salt with PUU has a high ionic conductivity ($\sigma = 1 \times 10^{-5}$ S cm^{-1}) at 33 °C and a fairly high mechanical strength.

A method has been proposed for the preparation of the PE by the mechanical mixing in a solvent at room temperature of an acrylic poly(alkylene oxide) and a lithium salt with polyurethane (PU) or polyurethane-urea and subsequent heat treatment of the mixture.[31] The resulting solid electrolyte has $\sigma = 1.5 \times 10^{-5}$ S cm^{-1} and satisfactory mechanical properties. When the salt $LiClO_4$ is introduced into polyurethane, the ionic conductivity increases by three orders of magnitude: $\sigma_{max} = 10^{-4}$ S cm^{-1} at 20 °C is attained in PU : $LiClO_4$ = 8 : 1 mixtures.[32] In the presence of high contents of $LiClO_4$, the conductivity falls owing to the increase in viscosity. The difference between the conductivities of the PE based on PEO and PU is especially significant at temperatures below 80 °C, since a decrease in temperature entails a sharp (by a factor of ~10) decrease in the conductivity of PEO due to a structural rearrangement. Experiments in which lithium electrodes were employed established that the transport numbers of the lithium cations at 50–100 °C are 0.5–0.8. In order to prevent the impairment of the characteristics of batteries having PE as a result of prolonged storage, it has been suggested that a polymer having a urethane-like structure, in which the hydrogen atoms have been replaced by alkali or alkaline earth metal atoms, be used as the electrolyte.[33]

More flexible comb-branched systems may be obtained from polymers the main chain of which has a low glass point. These probably result in the formation of electrolytes with a maximum conductivity.[34] In order to synthesise such PE, a study has been made[35–37] of systems based on phosphazene and siloxane polymers. One of the most successful PE has been synthesised by substituting the chlorine atoms in poly(dichlorophosphazene) by alkyl groups as a result of treatment with the sodium salt of 2-(2-methoxyethoxy)ethanol in the presence of tetra-n-butylammonium bromide, which results in the formation of a compound having the formula

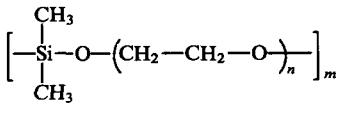


This polymer gives rise to single-phase amorphous electrolytes with different univalent, divalent, and trivalent salts.[35] The dependence of the ionic conductivity of the solid-phase polymeric complexes of an oligo(ethylene oxide) graft copolymer with polyphosphazene on temperature and concentration has been investigated.[38] The maximum value of σ ($\sigma_{max} = 10^{-4}$ S cm^{-1}) was observed for complexes of the copolymers with $LiClO_4$ at 25 °C and for a salt content of 15%. For the complexes of $LiClO_4$ (salt content 7.5%) with polyphosphazene modified by the grafting of oligo-oxyethylene with a degree of oligomerisation of 7, $\sigma = 3.5 \times 10^{-4}$ S cm^{-1}. For structurally involved complexes of a polycyclotriphosphazene with $LiClO_4$, the conductivity was $\sigma = 1.2 \times 10^{-4}$ S cm^{-1} (at 90 °C), the

maximum in σ shifting towards a higher salt concentration with increase in temperature.[39]

The main advances in the field of ionic polymeric conductors based on linear phosphazenes and polyacrylates containing PEO with different degrees of polarisation as substituents in the side chains have been considered in reviews.[40,41] It was shown that the complexes of the above polymers with the salts $LiCF_3SO_3$ and $AgCF_3SO_3$ exhibit an anomalously high conductivity with respect to the metal cations (up to 10^{-3} S cm^{-1}). These results agree well with the experimentally determined diffusion coefficients of the cations. A polymeric electrolyte, consisting of a mixture of the complex salt of poly[bis(methoxyethoxyethoxide)-phosphazole] (I) and PEO (II) and doped with $LiCF_3SO_3$ or $LiClO_4$ was cast from a I + II solution in acetonitrile and dried in vacuo at 100 °C.[42] For the ratio I : II = 1 : 1, the specific conductance of the electrolyte was 2×10^{-4} S cm^{-1} at 20 °C and 5×10^{-2} S cm^{-1} at 100 °C. A method of synthesis of oligoethyleneoxypolyphosphazene (OPP), containing allyl groups, has been proposed.[43] The method includes a stage in which hexachlorotriphosphonitrile is converted into dichlorophosphonitrile and the latter interacts with the corresponding alkoxides. During the synthesis, up to 5 mass% of $LiClO_4$ is introduced into the OPP, which ensures a fairly high conductivity of the PE with respect to lithium ions.

Polymers with a very low glass point have been obtained by the polycondensation of dichlorodimethylsilane with poly-(ethylene glycol).[44]



The high flexibility of the main chain and the absence of crystallinity (as a consequence of the irregularity of the chain) ensure a high conductivity of such polymers — much higher than the conductivity of poly[bis(methoxyethoxyethoxide)phosphazene].[35] The conductivity is comparable to that of the comb-branched siloxanes.[45] However, the practical employment of such systems is held back by the high sensitivity of siloxanes to hydrolysis.

PE based on poly-*p*-phenylenevinylene (PPV) have also been proposed for the manufacture of accumulator batteries.[46] The films consist of a mixture of aqueous solutions of polymeric precursors of PPV (a water-soluble sulfonium salt) and a water-soluble polymer such as PEO, methylcellulose, or hydroxypropylcellulose in proportions of 1 : 1. PPV is obtained from the precursor salt form by heat treatment of it. The best results were obtained for mixtures of PPV and PEO doped with $LiClO_4$. Such mixtures are resistant to thermal degradation (up to 225 °C) and possess satisfactory mechanical properties.

Polymeric electrolytes with an amorphous structure are formed from a copolymer of acrylonitrile and sulfoalkyl methacrylate.[47] The conductivity of different salt forms of the PE then varies in the sequence lithium salt > sodium salts > potassium salts and increases with increasing oxygen : lithium ratio in the range 20 – 100. The new PE based on the copolymers with poly(vinyl alcohol), PVA, and polyacrylamide have a high thermal stability combined with a fairly high conductivity.[48]

One of the methods for retarding the transition of the polymer from the amorphous to the crystalline state involves the cross-linking of the polymer matrix, for example the cross-linking of PEO by exposure to γ-radiation or an electron beam.[49] In this case, one obtains PE with an improved conductivity with respect to lithium ions at a reduced temperature. The mechanisms of the radiolytic degradation and cross-linking of PEO in the solid state and in aqueous solutions have been investigated by the EPR method.[50] The decrease in crystallinity, the improvement in mechanical properties, and the increase in conductivity at 20 °C of the cross-linked polymeric materials indicate that γ-irradiation is a simple and effective method for the preparation of highly conducting and mechanically stable PE. However, the effect of the γ-irradiation of PE specimens based on PEO and lithium salts ($LiClO_4$ and $LiCF_3SO_3$) at 78 °C has not been confirmed.[51]

The cross-linking of a polymer composition consisting of PEO units with terminal C(O) – CH=CH – C_6H_4R (R = NO_2, Cl, OCH_3), C(O) – CH=CH – CH=CH – C_6H_5, C(O) – C(NC)= CH – C_6H_5, and C(O) – C(NC)=CH – CH=CH – C_6H_5 groups has been described.[52] The cross-linking takes place under the influence of accelerated electrons or UV irradiation. A thin-film PE (in a mixture with lithium salts) with a degree of cross-linking of 90% and an ionic conductivity of 1.7×10^{-4} S cm^{-1} at 20 °C was obtained.

Chemical methods for the cross-linking of the polymer matrix have been described in a series of studies. For example, film PE with satisfactory conductivity at 30 °C[53] as well as a strong and elastic PE with $\sigma = 6 \times 10^{-5}$ S cm^{-1} at 25 °C[54] have been obtained by mixing the product of the copolymerisation of polyglycerol with ethylene oxide or a mixture of ethylene and propylene oxides with a polyfunctional cross-linking agent (polyisocyanate) at 50 – 200 °C and a pressure of >10 kg cm^{-2}. The methods of preparation of PE based on lithium salts and poly(ethylene glycols) cross-linked by siloxane tetraisocyanate have been described.[55]

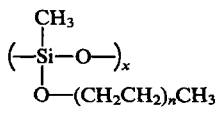
It has been suggested that a cross-linked copolymer of ethylene oxide and propylene oxide be used as the base of a polymeric electrolyte for a lithium accumulator.[56] In combination with a lithium salt, such a PE ensures a specific conductance of the lithium ions of the order of 10^{-5} S cm^{-1} at 25 °C. The product of the copolymerisation of the vinyl ether R – (O – CH_2 – CH_2)$_n$ – O – CH=CH_2 (R = Me or Et, n = 1 – 6) with the divinyl ether [CH_2=CH – (O – CH_2 – CH_2)$_n$ – O – CH=CH_2] (n = 1 – 6) is a cross-linked polyether with a glass point of 60 – 80 °C, which has been used as the matrix for the preparation of a solid PE.[57] The cross-linking of PEO-based resins by vinyl polymers has been described.[58] Before cross-linking, the (PEO-400)-maleate-isophthalate resins by styrene (St), vinylpyrrolidinone (VP), or vinylpyridine (VPD), $LiClO_4$ was added to the resins. For the ratio [PEO]/[Li^+] = 50, the conductivity of the PE obtained increases in the sequence VPD < VP < St. This sequence is correlated with the increase in the strength of binding of Li^+ on passing to more polar comonomers.

A polymeric electrolyte with stable characteristics,[59] capable of being used for a long time without a decrease in capacity, has been obtained from a polyether with cross-links of the urethane type. It contained the (O – CO – NR) (R = an inert group or an element in Group I of the Periodic System other than hydrogen) repeating unit. The electrolyte also contained an inorganic salt and an inert additive.

A polymeric electrolyte — a modified polyurethane network obtained from polydimethylsiloxane containing grafted PEO, cross-linked by an aliphatic diisocyanate, and incorporating 10% of $LiClO_4$ — has an ionic conductivity of 10^{-5} S cm^{-1} at 30 °C. It was used in solid-state electrochemical lithium batteries. Analysis of voltammetric data showed that, after the completion of the synthesis of the polyurethane network, the unreacted cross-linking agent may interfere with the diffusion of lithium ions at the electrode – electrolyte interface. The limiting currents were determined from the cathodic branches of the voltammogram. The internal resistance of the RuO_2/Li accumulator with a PE was determined from its discharge curves recorded at 60 and 80 °C. It proved to be 5 kΩ. After two discharge cycles with degrees of discharge of 95% and 73%, the adhesion of the PE film to RuO_2 and Li remained unchanged.

The morphology and physical properties of the electrolytes prepared from linear segmented polyurethanes based on PEG and alkali metal salts have been described in fair detail.[61] Systems based on siloxane polymers may be obtained by mixing in a common solvent lithium salts with an organopolysiloxane containing more than two COOH groups in the molecule.[62]

The conductivity of such a PE at 25 °C is 5.6×10^{-5} S cm^{-1}. Liquid comb-branched polymers of the type



may be additionally cross-linked by heating to 150 °C (in order to form rubber-like films).[45] The length of the side chain exerts only a slight influence in this case on the conductivities of the electrolytes. For a PE of this kind, containing $LiClO_4$ as the ionogenic additive, $\sigma = 1 \times 10^{-4}$ S cm^{-1} at 25 °C.

A number of authors patented liquid solidifying organosiloxane-oxyalkylene copolymers with acrylate functional groups into which $LiCF_3SO_3$ and azobisisobutyronitrile (AIBN) had been introduced. After solidifying at 85–90 °C for 30 min, elastic films 1 mm thick and with $\sigma = 1.6 \times 10^{-5}$ S cm^{-1} were obtained.

It is noteworthy that the assignment of a particular polymeric electrolyte in terms of the method of modification to the first or second group is arbitrary, since the appearance of cross-links between the macromolecules is a means of fixing the amorphous state.

One of the promising ways of modifying PE involves the introduction of crown-ether additives, which greatly increase the ionic conductivity.[64] Studies on the electrical and electrochemical properties of PE films consisting of PEO and the salts $LiCF_3SO_3$, $LiBF_4$, or $LiClO_4$, both containing and not containing 12-crown-4 (12Cr4), showed[65] that at a constant temperature σ for each salt depends on the concentration of the crown-ether, which is a maximum for the concentration ratio [12Cr4]:[Li] = 0.003.

The kinetics of the complex formation reactions between alkali metal cations and macrocyclic ligands — 12-crown-4, 18-crown-6, and 15-crown-5 — have been investigated.[66] Crown ethers of the 16-crown-5 group were also introduced into polyphosphazenes (PP) as side groups.[67,68] The temperature dependences of the conductivities of such PE, containing $LiClO_4$ or $NaClO_4$, have been investigated. The lg $\sigma - 1/T$ relation was linearised with the aid of the Vogel–Tammann–Fulcher relation. The highest value of σ was attained for PP–$NaClO_4$, which is associated with the higher degree of ionisation of the salt bound to the macromolecular part of the polyphosphazene. The introduction of 12-crown-4-ether both into the solid PE consisting of PEO and $LiBF_4$ and into a cathodic composition consisting of Li_xCoO_2, PEO, and $LiBF_4$ improves the ionic conductivity of the PE.[69] The electrolyte has a very low leakage current. The addition of a crown-ether improves the operation of the cell, lowers the dissociation peak and the resistance to charge transfer, and increases the current capacity and reversibility of the cell (this has been observed in the case of CoO_2 and TiS_2 cathodes).

Apart from crown-ethers, a bicyclic compound (cryptand), which also forms a complex with lithium ions, may be used as an additive.[70]

The addition of low-molecular-mass plasticisers such as ethylene and propylene carbonates to electrolytes based on PEO,[71,72] polyacrylonitrile (PAN) poly(tetraethylene glycol diacrylate), or polyvinylpyrrolidinone and also into hybrid films based on PMMA, polystyrene, PVC, PVA, PAN, and poly(vinylidene fluoride) in amounts up to 30 mol.% increased σ to 10^{-5}–10^{-3} S cm^{-1}.[74] The suitability of the hybrid films as PE in solid-state batteries is indicated by the stable potential of the Li/specimen/MnO_2 galvanic cell operating for more than 70 h without the decomposition of the electrolyte. The possibility of plasticising the PEO-based compositions by introducing poly(ethylene glycols) with different molecular masses has been investigated.[75,76] Such plasticisation increases σ by increasing the content of the amorphous phase in the electrolyte and simultaneously increasing the salt concentration in this phase.

The study of the conductivites of solid polyelectrolytic complexes of the alkali metal salts NaSCN, $NaCF_3SO_3$, and $LiCF_3SO_3$ with polymers based on methoxypoly(ethylene glycol methacrylate) $CH_2{=}C(CH_3)COO(CH_2CH_2O)_nCH_3$ [$n = 8$ (PMG-8) and $n = 22$ (PMG-22)] as a function of temperature and salt concentration showed[77] that the systems based on the copolymers of PMG-22 with polystyrene as well as systems plasticised by poly(propylene carbonates) have much higher values of σ than systems based on the homopolymers. Compositions based on a mixture of an alkyl acrylate (alkyl C_{1-8}) and/or alkoxyacrylate (alkoxy C_{2-5}) polymer with 5%–100% (relative to the mass of the acrylate polymer) of $LiClO_4$ or the lithium salt of a polymeric acid (polystyrenesulfonic acid, polyethenesulfonic acid) with a high conductivity, used as a thin-film electrolyte, have been described.[78] The organic solvent, with a high relative permittivity, serves as both the plasticiser and the solvent.

An interesting phenomenon — a sharp increase in the conductivity of the PE on mixing it with Al_2O_3 powder — has been observed by the authors of a series of investigations. Such PE were investigated by impedance spectroscopy, X-ray diffraction, and NMR. It was shown[79] that the conductivity of the polymeric PEO–NaI electrolyte increases on mixing with Al_2O_3, reaching a value in excess of 10^{-5} S cm^{-1} at room temperature.

An increase in conductivity and satisfactory mechanical properties are also manifested by the PE having the composition $(PEO)_8LiClO_4$ into which powdered β-Al_2O_3 with a small grain size (< 5 μm) have been introduced by mixing with a solution of PEO and $LiClO_4$ in acetonitrile.[80] The addition of Al_2O_3 [81] and of ceramic $LiAlO_2$ microspheres 1 μm in diameter[82] (up to a concentration of 10%–30%) has a positive effect on the mechanical properties and conductivities of solid PE. An increase in the conductivity by an order of magnitude is attained by introducing β-Al_2O_3, Li_2O–B_2O_3–SiO_2 ionic glasses, and ion-exchange resins in the lithium-form as fillers into PEO-based.[83,84] Since the ratio of the pre-exponential factor for the conduction and the activation energy satisfies the Mayer–Neldel rule for the entire range of filler concentrations, the authors concluded that the ion-conducting fillers do not participate in charge transfer through the solid electrolyte and that their presence leads merely to the composites being more amorphous.

IV. The influence of the purity of the components of the polymeric electrolyte on its electrochemical characteristics

It was noted above that the composition for the preparation of the PE consists as a rule of a polymeric binder, an ionogenic alkali metal salt, and the solvent. PEO is the polymer most often employed in PE and has been most thoroughly investigated, but it is extremely hygroscopic like many other polymers employed in the PE; the lithium salts are also hygroscopic. The stability of the properties of the PE films is largely determined by the purity of the components and their moisture content. Therefore all manipulations involving the PE component are as a rule carried out under a dry or inert atmosphere.

A high-molecular-mass highly pure PEO is obtained by anionic polymerisation. The mechanism of the absorption of water by polymers, including poly(ethylene oxide), and the influence of the polymer structure on this process have been described.[85] It was shown that the absorption of water depends greatly on the composition of the aqueous solution: it diminishes with increase in the salt concentration, and to a greater extent the higher the ionic charge. The interactions of PEO with water have been investigated by differential scanning calorimetry (DSC) and NMR spectroscopy.[86] The plasticised PEO was characterised by the ratio of the number of moles of D_2O to the number of moles of monomer units (R). The DSC results showed that an increase in R to 0.6 leads to a monotonic decrease in the melting point of

the PEO from 56 to 35.9 °C. For $R > 0.135$, another low-temperature fusion isotherm appears, which has been attributed to the decomposition of the eutectic mixture. It was observed that an increase in R leads, on the one hand, to a decrease in the melting point from 22.7 to 11.9 °C and, on the other, to a linear increase in the enthalpy of fusion. The absence of a low-temperature endotherm for lower R has been attributed to the small size of the pores through which D_2O diffuses. Analysis of the NMR line shape indicates the presence of a doublet for $R = 0.07$ and 0.096, which has been explained by the low rate of exchange (on the time scale of the NMR experiment) between the bound and free water.

Studies showed that the method of preparation of the PEO has actually no influence on the properties of the PEO–lithium salt polymeric electrolyte.[87] On the other hand, the purity of the solvent employed for the preparation of the composition (acetonitrile) is strongly reflected in the properties of the polymeric complexes formed. In 'dry' solvents, complexes with high melting points and high degrees of crystallinity are formed, whereas in 'moist' solvents the complexes produced have low melting points. Complexes with low melting points are suitable as electrolytes for use at 120 °C and above.

The dehydration of the PE films is necessary, since an insulating coating comprising lithium hydroxide is formed on the lithium anode when the latter comes into contact with moisture. In order to protect the lithium electrode against oxidation, Japanese investigators[88] introduced tin salts into the liquid electrolyte. Tin ions are substituted by metallic lithium and a thin coating of metallic tin, suppressing the formation of lithium hydroxide, is formed on the surface of the negative electrode.

The study of the influence of hydration and dehydration processes on the conductivity of films of a PEO-based solid electrolyte showed that the hydration of the PE having the initial composition $(PEO)_8NiBr_2$ results in the formation of at least two types of bound water:[89] weakly bound water, which is removed at temperatures of approximately 80 °C, and strongly bound water which can be removed only at 130–140 °C. It is suggested that the strongly bound water is present as the complex $(PEO)_8NiBr_2 \cdot 6H_2O$. The ionic conductivity depends greatly on the degree of hydration of the electrolyte, increasing by ~8–10 orders of magnitude during the moisture absorption process. A method for the preparation of anhydrous films comprising polymers (PEO, PPO) and salts (mercury and sodium perchlorates) from their hydrated forms has been described.[90]

Thus the electrochemical properties of polymeric electrolyte films can be easily reproduced, provided that the water content in the components and the solvent is strictly controlled and also when films in a dry, inert form are employed.

V. Preparation of thin films of polymeric electrolytes by plasma polymerisation

One of the most important problems in the development of solid polymeric electrolytes is that of the preparation of thin films with a high mechanical strength. Japanese investigators developed a technology for the preparation of thin polymeric films with ionic conductivity for lithium accumulators by plasma polymerisation.[91] Hybrid layers of the polymeric product, exhibiting ionic conductivity, are obtained in three consecutive stages: (1) plasma polymerisation (PM) of the monomer in a vacuum with a residual inert gas, (2) spraying of a lithium salt solution over the polymer layer (0.5 μm), and (3) plasma polymerisation of a fresh portion of the monomer. The characteristics of the solid PE which depend on the plasma parameters have been established.[91] A relative increase in the energy of the glow discharge leads to an increase in the number of cross-links in poly[tris(2-methoxyethoxyvinyl)-silane] and to a decrease in its conductivity. Ultrathin films (~1 μm) of a homogeneous PE have been obtained by the plasma polymerisation of methyl acrylate (MA) and tris(2-methoxy-ethoxyvinyl)silane (TMVS).[92] According to IR spectroscopic data, the structure of the polymer obtained is close to that of the MA–TMVS copolymer. A layer of LiI was sprayed on to the polymer layer and then a further polymer layer was deposited. The three-layer composite was maintained for 24 h in vacuo (10^{-3} Torr). On interaction with LiI, the ester group $COOCH_3$ is then converted into the carboxylate group. The conductivity of such PE at 20 °C is 10^{-8} S cm^{-1}, which is less than the value for the TMVS–$LiClO_4$ complex (10^{-6} S cm^{-1}).

A technology for the preparation of ultrathin solid-state lithium accumulators involving the use of a plasma-polymerised solid polymeric electrolyte has been described.[93] A layer of TiS_2 (~12 μm) was deposited on a borosilicate glass support by the vacuum spraying of $TiCl_4 + H_2S$ vapour; a layer of a solid PE (~1.5 μm) was then deposited on it by the plasma polymerisation of the 1:10 TMVS–Ar mixture in vacuo. A 3% methanol solution of $LiClO_4$ was sprayed onto the polymer film at 60 °C and then a further layer of the polymer and a layer of the lithium salt (~1.5 μm) were deposited. After being kept in vacuo at 80 °C, the resulting solid PE had a conductivity of 10^{-4}–10^{-3} S cm^{-1} at 20 °C. The accumulators operated at a current density of 100 mA m^{-2}.

The properties of such a thin three-layer PE film with a high conductivity, laid on a glass plate with gold deposited from a high-frequency plasma in a stream of gold and TMVS vapour, have been investigated.[94] It was noted that there are no alkene groups in the polymer film and the distribution of the ClO_4^- ions with respect to thickness is nearly homogeneous, which corresponds to a homogeneous distribution of lithium ions. Pin holes were not detected in the film by electron microscopy. For the films containing 7% of $LiClO_4$, the conductivities are respectively 4.4×10^{-5}, 4.5×10^{-6}, and 3×10^{-7} S cm^{-1} at 100, 50, and 10 °C.

Apart from the plasma-generated TMVS polymers, a solid polymeric electrolyte for chemical lithium batteries has been obtained from polyoctamethylcyclotetrasiloxane and $LiClO_4$ by plasma polymerisation under glow discharge conditions. The conductivity of such films, reaching 10^{-6} S cm^{-1}, is determined by the $LiClO_4$ content.[95] A solid-state lithium accumulator with a thin-film (10–15 μm) cathode comprising TiS_2 and a PE film obtained by the plasma polymerisation of octamethylcyclotetra-siloxane with subsequent grafting of the poly(propylene oxide)–$LiClO_4$ complex has also been described.[96,97] The structure of this plasma-generated polymer is similar to that of polydimethyl-siloxane. The ionic conductivity of the hybrid PE reaches 2.6×10^{-6} S cm^{-1} at 60 °C. For a current density of 8 μA cm^{-2} and room temperature, the discharge plateau for the first discharge of the accumulator corresponded to the 85% utilisation of the cathodic material. The chargeability of the accumulator was satisfactory, but its internal resistance was fairly high.

A CPS with an increased operating lifetime, capacity, and number of charge-discharge cycles has been patented.[98] In this CPS, the solid PE consists of a plasma-polymerised layer of an organic compound containing an alkali metal ion and an element with a higher electronegativity.

VI. Electrochemical stability of solid polymeric electrolytes

When polymeric electrolytes are employed in lithium accumulators, complex problems associated with the electrochemical stability of the electrolytes arise. However, the number of publications devoted to this problem is small.

Thus Armand noted[99] that the electrochemical stability of polyethers is comparable to that of aprotic solvents such as tetrahydrofuran and propylene carbonate. The kinetics of the electrochemical process occurring in the lithium cell and involving the PEO–$LiClO_4$ solid electrolyte are as a rule controlled by the diffusion of ions.[100] The study of the PE films based on phosphazenes with $LiCF_3SO_3$ showed that the limits of the electrochemical stability are determined by the

reduction of the lithium salt.[101] Molecular complexes of lithium salts with poly[bis(methoxyethoxyethoxide)phosphazene] (MEEP) and its analogues with a high ionic conductivity, but are unstable.[102,103] In order to increase the stability of the polymeric structure, the MEEP was cross-linked by poly(ethylene glycol) ($M = 1000$), since the cross-linked macromolecules are very stable. This made it possible to employ their complexes with $LiCF_3SO_3$ as ionic conductors up to 140 °C. Stable polymeric electrolytes for lithium CPS, in which the dimensions are satisfactorily maintained during operation and the conductivity is 6.7×10^{-5} S cm^{-1} at 25 °C, have been obtained from MEEP and PEO–[$LiN(CF_3SO_3)_2$].[104] Cyclic voltammograms indicate the stability of the PE at potentials up to 4.5 V relative to the Li^+/Li electrode. Their use in the Li/TiS_2 lithium cell ensures 200 charge-discharge cycles.

Preliminary data on their cyclic nature and stability have been obtained for PE based on Li/poly[*N*-3,6-dioxaheptylpyrrole] to which [poly(ethylene oxide)-styrene macromonomer]$_{20}$–$LiClO_4$ had been added.[105] The possibility of using such PE at room temperatures was demonstrated.

Films based on the complex $(PEO)_9LiCF_3SO_3$ were investigated in the temperature range 100–170 °C using voltammetry at a low scanning rate.[16] The reversible reduction of the electrolytes was observed over a wide range of external conditions and subject to the stipulation that a certain threshold potential was not exceeded. It was shown that the stability of the reduction of the PE is limited by the discharge of Li^+ and the stability of the oxidation is limited by the discharge of $CF_3SO_3^-$. At temperatures of about 140 °C, the region of the oxidative-reductive stability of the film exceeds 3.3 V. In the range 140–160 °C, the stability region diminishes by 1 V as a result of the oxidation of $CF_3SO_3^-$. The authors[16] note that, by virtue of their high electrochemical stability and effective mechanical properties, the PE films investigated may find an application in solid-state batteries.

In order to devise batteries of a similar type capable of working with satisfactory operating characteristics for a long time, it is necessary to suppress the crystallisation process in the PE, which is achieved by adding an elastomer (a butadiene–acrylonitrile copolymer) and a macromonomer based on styrene and PEO.[106] It has been shown by X-ray diffraction that, when the elastomer and the macromonomer are added, the PEO crystal cell remains monoclinic. In the course of 15 months, the diffraction patterns and the conductivities remained unaltered. The stabilisation of the conductivity was also achieved by the partial replacement of the PEO by oligo(ethylene oxide) (OEO) with terminal styrene groups keeping the ethylene oxide unit/Li^+ ratio unaltered.[107] Best results ($\sigma = 2 \times 10^{-4}$ S cm^{-1}) were obtained by employing $LiCF_3SO_3$ and by introducing from 20% to 50% of a low-molecular-mass oligo(ethylene oxide) with $M = 550$.

VII. Chemical interaction at the lithium anode – polymeric electrolyte interface

The electrochemical reactions at the electrode/polymeric electrolyte interface have been considered in a review.[108] It was shown that although an analogy with the reactions in a liquid electrolyte is in fact observed, the former reactions are more complex. Under open-circuit conditions, the formation and growth of a passivating film are observed at the lithium/polymeric electrolyte interface. The growth kinetics depend on the nature and composition of the electrolyte, which agrees well with data on the phase diagram of the PEO–electrolyte system.[109] It was established that the behaviour of the passivating film on polarisation of the lithium electrode cannot be described in terms of a simple model comprising a solid electrolytic or polymeric surface film, and a model comprising an ion-conducting film of a modified polymeric electrolyte with a high resistance was therefore proposed. The stability of the vacuum-sputtered lithium electrode in an ultrathin film electrochemical cell of the type Ni/PE/Li with PEO, PPO, and the oxyethylene–oxymethylene copolymer as the polymeric electrolyte was therefore investigated by impedance spectroscopy at room temperature.[110] The most intense reactions at the interface are observed in the case of PPO. This is due to the rapid reaction between lithium and the amorphous copolymer, which was demonstrated with the aid of cyclic voltammetry. Owing to the phenomenon of passivation, the Faraday efficiency depends to a large extent on the rate of scanning of the potential. Its decrease from 20 to 5 mV s^{-1} decreases the degree of reduction of lithium from 85% to 30%.[111]

The resistance at the lithium/PE interface was investigated in thin secondary CPS with a solid PE (PEO–$LiClO_4$).[112] It was shown that the discharge characteristics of the CPS are impaired during storage, which is apparently associated with the increase in the internal resistance of the polymeric electrolyte.

In order to improve the mutual adhesion and to reduce the ohmic resistance at the negative electrode/PE interface, it was suggested that an intermediate layer of the halide of the metal constituting the anode (Li, Na, K, Ag) be formed on the electrode surface. Such a layer exhibits cationic conductivity and plays the role of the solid electrolyte.[113] Small transitional resistances are established between this layer, on the one hand, and the metallic anode and the PE on the other.

Overall, the study of the processes at the lithium/PEO interface leads to the conclusion that the characteristics of the lithium accumulators with PE are limited not so much by the intrinsic ionic conductivity of the polymeric electrolyte as by the charge transfer to the interface.

VIII. Modification of the electrodes in lithium chemical power sources with a polymeric electrolyte

In selecting the PE for use in solid-state batteries, it is necessary to take into account not only their ionic conductivity and transport numbers but also their compatibility with the anodic and cathodic materials.

In assembling the primary cells based on PEO and lithium salts, metallic lithium or its alloy with aluminium are employed as the anode and MnO_2 [114] TiS_2, MoO_2, or V_6O_{13} [115,116] as the cathode. The composite cathode contains as a rule a metal oxide, carbon black, and a polymeric electrolyte. For example, the active mass of the positive electrode contained 45 vol.% of V_6O_{13}, 5 vol.% of acetylenic carbon black, and 50 vol.% of the PEO–$LiClO_4$ composition[32,116] or 75 mass% TiS_2, 10 mass% of graphite powder, and 15 mass% of PEO + NaI.[117]

The improvement of parameters of the cells such as the current density and the specific capacity is achieved by improving the technique for the preparation of the composite cathode.[118] In the first discharge cycle, 100% and 50% utilisations of the active material of the cathode are attained at current densities of 0.27 and 0.8 mA cm^{-2} respectively. The increase in the size of the cells from 1 to 100 cm does not impair their properties. A sol-gel technology for the preparation of positive electrodes has been described.[119]

Japanese investigators[120] proposed five compositions of the negative active substance: an alkali metal, an alkali metal alloy, an electrically conducting polymer, a complex of an alkali metal and an electrically conducting polymer, and a layered interstitial compound. The characteristics of thin-film rechargeable accumulators operating at 20 °C and employing solid polymerisation redox electrodes have been investigated.[121] The anodes were prepared from various substances: the product of the polymerisation of salt synthesised by the interaction of 2,5-dimercapto-1,3,4-thiadiazole with LiOH; carbon black; a mixture of poly(ethylene oxide) with a lithium salt. Such accumulators withstood 100 charge-discharge cycles without a significant impairment of the parameters.

The Bridgestone Corporation and Seiko Electronic Components Ltd (Japan) have jointly developed a series of rechargeable polymeric lithium power sources[122] having a capacity three times as great as that of the existing lithium accumulators and a 2–3 times greater potential compared with the nickel–cadmium batteries. In the new lithium accumulators, a Li–Al alloys, ensuring a high capacity, is employed as the negative electrode, and a conducting polymer is used as the positive electrode. The nominal potential of the accumulators is 3 V and the capacity is 2 mA h.

The development of lithium accumulators is hindered by the poor rechargeability of the negative electrode associated with the formation of lithium dendrites at a current density > 0.5 mA cm^{-2}.[123] It has therefore been suggested that a negative electrode consisting of interstitial lithium compounds be employed. It has been proposed that Wood's alloys (Pb–Sn–Cd–Bi), having low melting points and ensuring a high diffusion coefficient of lithium, be used as the material of such electrodes.

The reversibility of the lithium electrode, operating in conjunction with polymeric electrolytes $(PEO)_x \cdot LiCF_3SO_3$, where x is in the range $4 < x < 16$, has been investigated[124] by potentiometric and polarographic methods in the temperature range 100–170 °C. Satisfactory results were obtained.

A tendency has arisen in recent years to employ polymeric electrodes in chemical batteries with polymeric electrolytes. Thus an accumulator with a PE has been described.[125] Its negative electrode was made of an alkali metal (Li, Na, K) and a conducting polymer or a composite of a conducting polymer and an alkali metal, while the cathodic mass consisted of a composite of a conducting polymer and a polymeric electrolyte. The composite cathode for solid-state lithium accumulators may also consist of polypyrrole (PP),[126] into which between 0% and 50% of PEO of polybithiophene (PBT)[127] has been added. It was shown that the capacity of the PBT electrode in contact with the solid PE is lower than that of the substance in contact with a liquid electrolyte (propylene carbonate–$LiClO_4$), but increases with increase in temperature from 50 to 70 °C.

The possibility of creating thin-film polymer batteries with a high energy capacity from a complex of PEO and $LiClO_4$ has been described.[128] The use of TiS_2 or V_6O_{13} as the cathodes and of metallic lithium as the anode makes it possible to create batteries which ensure a current density of 0.5–1.0 mA cm^{-2} at 80–100 °C and can undergo up to 250 charge-discharge cycles.[129] The Faraday efficiency is 80%–90% and the specific energy capacity is not less than 100 Wh kg^{-1}. The replacement of $LiClO_4$ by $LiCF_3SO_3$ in the polymer complex impairs the characteristics of the cell (the efficiency is $< 15\%$) and requires an increase in the working temperature to 130 °C. The authors suggest that the new PE based on PEO make it possible to create CPS operating at room temperature and likely to be useful in transport systems.

The data presented indicate the undoubted growth of interest in the theoretical and practical studies on the creation of new solid polymeric electrolytes and the construction on their basis of CPS with a high energy capacity.

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