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Polymer electrolytes for metal-ion batteries

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The results of studies on polymer electrolytes for metal-ion batteries are analyzed and generalized. Progress in this field of research is driven by the need for solid-state batteries characterized by safety and stable operation. At present, a number of polymer electrolytes with a conductivity of at least 10^{-4} S cm^{-1} at 25 °C were synthesized. Main types of polymer electrolytes are described, *viz*., polymer/salt electrolytes, composite polymer electrolytes containing inorganic particles and anion acceptors, and polymer electrolytes based on cation-exchange membranes. Ion transport mechanisms and various methods for increasing the ionic conductivity in these systems are discussed. Prospects of application of polymer electrolytes in lithium- and sodium-ion batteries are outlined.
The bibliography includes 349 references.

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1. Introduction

The idea of creating lithium-ion batteries dates back to 1970. At present, five decades later, these reliable power sources supply power to numerous portable devices including cell phones, notebooks and digital cameras. Lithium-ion batteries are superior to other ones in specific capacity and power density and therefore occupy a leading position in the market of power supplies for portable electronic devices. However, recently, there has been demand for devices that require batteries with much higher power density, *e.g*., cordless tools and electric vehicles. Prospects for replacing traditionally used fossil energy sources with renewable ones (solar batteries, wind turbines, *etc*.)[1–3] require the development of high-capacity energy storage systems.[4–6]

However, the wider the use of lithium-ion batteries the more serious the problem of their replacement. The reason is low natural abundance and high dispersion of lithium in Earth's crust,[7–10] which account for high cost of Li-ion batteries. Although they occupy an unshakable position in the field of batteries for portable devices, there has been intensive research into alternative sources of energy to meet the requirements of more powerful devices. One of the most abundant elements in Earth's crust is sodium,[11] whose natural abundance is three orders of magnitude higher than that of lithium.[12] This feature, together with similarity between physical properties and a small electrode potential difference (−3.04 V for Li *vs* −2.71 V for Na) allow Na-ion batteries to be considered as a promising alternative to Li-ion ones.

High capacity and power density belong to the key requirements for batteries. These characteristics are first of all determined by the electrode materials.[7] Preference is given to electrode materials having lower mass. The difference between the atomic masses of lithium and sodium is responsible for their small contribution to the total mass of

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the electrode materials and has little effect on the characteristics of the entire battery.

The most important difference between lithium and sodium consists in their ionic radii. That of sodium (1.06 Å) is nearly 40% larger than that of lithium (0.76 Å), which significantly influences the transport properties of corresponding materials.[13] On the one hand, Na^+ along with Ag^+ and Cu^+ is in the top three highest-mobility ions due to the lower polarizability and formation of weaker bonds. On the other hand, bulkier sodium ions are more difficult to incorporate into the structure of electrode materials during battery charging–discharging and change the specific volume of electrode materials to a greater extent upon intercalation, which causes a power reduction and makes the battery operation less stable.[14]

Modern lithium- and sodium-ion batteries succeed to the batteries with metallic negative electrode (anode).[15] Their operation involves intercalation–deintercalation (as in conventional metal–ion batteries) of metal ions at the positive electrode (cathode) and dissolution–deposition of metal ions at the anode. In metal–air batteries, metallic anode is involved in electrochemical reaction with the atmosphere through a ceramic composite membrane.[16] Metal–sulfur batteries have a sulfur-based cathode and metallic anode.[17, 18]

A conventional modern metal-ion battery includes an electrolyte and two electrodes supported on inert current collectors. The electrodes are made of materials capable of reversibly intercalating–deintercalating alkali metal ions[19, 20] while the electrolyte is usually a liquid or gel through which metal cations are transferred.[14, 21] Charging a battery connected to an external power supply causes extraction of cations from the cathode material followed by their motion towards the anode to intercalate into the anode material. Intercalation and deintercalation of cations from the electrode material occurs through insertion or extraction of cations and electrons. Electron transfer proceeds *via* an external circuit, while cations are transferred between electrodes through the electrolyte.

The electrolyte belongs to the key components responsible for the power, operating temperature range, cyclability and safety of the electrochemical device.[22–24] The most important characteristic of an electrolyte is high ionic conductivity that underlies rapid ion transport between electrodes during the operation of a battery.[25, 26] When improving the electrolyte, one of the priority tasks is to increase the ionic conductivity.[27–29] Other important parameters are as follows. The operational stability of a battery is governed by the inertness of the electrolyte to other materials used to fabricate the electrochemical cell, first of all, the cathode and anode materials. A wide electrochemical stability window specifies the absence of changes in the electrolyte material induced by redox reactions during cycling. One more parameter is the self-discharge through leakage currents, which requires that the electronic conductivity be as low as possible. Eventually, the electrolyte should provide stable operation of the battery in a wide temperature range from −50 to 65 °C. For instance, it is freezing of electrolytes that significantly slows down ion transport during the operation and is thus responsible for an abrupt decrease in power and battery fault at low temperatures.

From the standpoint of physical state, there are liquid and solid electrolytes as well as those containing both phases. Usually, modern Li-ion and Na-ion batteries utilize liquid electrolytes, *i.e.*, solutions of lithium or sodium salts with bulky monovalent anions in various aprotic solvents.[30–32] Most often, mixtures of two or more solvents are used.[33, 34] Batteries with liquid electrolytes require porous separators that are placed between anode and cathode to hold the electrodes at a certain distance. Separators should be electrochemically stable in a wide potential range, chemically inert to all components of the electrochemical cell, and mechanically and thermally stable.[35, 36] The most widely used separators include polyethylene, polypropylene, polystyrene and their combinations.[37] A great advantage of liquid electrolytes is high ionic conductivity (σ). For instance, that of 1 M $LiClO_4$ and $NaClO_4$ solutions in an EC–DMC mixture (EC is ethylene carbonate and DMC is dimethyl carbonate) is 5.7×10^{-3} and 6.9×10^{-3} S cm^{-1}, respectively.[38] The drawbacks of liquid electrolytes first of all include unsafe cycling, hygroscopicity, simultaneous transfer of anions and cations and a decrease in capacity and power due to the formation of a so-called solid electrolyte interphase (SEI) representing a layer of ion-conducting products of electrolyte reduction.[39] Therefore, the search for alternative to liquid electrolytes is relevant. Liquid electrolytes can be replaced by solid inorganic or polymer electrolytes.

Solid inorganic electrolytes for batteries are materials based on lithium or sodium compounds containing mobile alkali metal cations, *e.g.*, sulfides $M_{10}XP_2S_{12}$ ($M = Li^+$, Na^+; X = Si, Ge, Sn), NASICON-type phosphates [$(Li_{1+x}Al_xGe_{2-x}(PO_4)_3$, $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$, $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$], Li-ion superionic conductors ($Li_{2+2x}Zn_{1-x}GeO_4$), $Li_7La_3Zr_2O_{12}$ with a garnet structure, *etc.*[24, 40–43] Their main advantages include safety, the possibility of operating in a wide temperature range and no dendrite growth. Solid electrolytes do not require separators, which should provide an increase in the energy density in the battery. However, most inorganic solid electrolytes are characterized by insufficiently high ionic conductivity at room temperature ($\sim 10^{-7}$–10^{-4} S cm^{-1}) and poor contact with the electrode materials.[44] Also, nonporous ceramic plates with good mechanical properties are usually too thick, which increases the resistance.

The most promising systems are polymer electrolytes[19, 20] that offer the same advantages as solid electrolytes. Besides, the ductility properties of polymers allow one to fabricate thin films with high mechanical strength, which provides great advantages in conductivity and in the design of batteries. Polymer electrolytes can be classified with respect to (i) the presence or absence of liquid phase (solid-state and gel polymer electrolytes), (ii) the phase composition (homogeneous and composite systems) and (iii) to the number of types of charge carriers (with parallel transport of counterions or with selective transfer of cations).[45–47]

A number of recent reviews on polymer electrolytes for lithium- and sodium-ion batteries are available.[14, 25, 28, 40, 45, 48, 49] Each of them is concerned with a particular problem, *e.g.*, studies on a series of electrolytes with Na-ion conductivity with particular attention paid to the temperature dependences of conductivity.[14] The authors of one more review[48] considered various methods for the synthesis and the properties of solid electrolytes with single-ion (cationic) conductivity. Main methods of synthesis and the electrochemical characteristics of single-ion conducting gel polymer electrolytes for lithium-ion batteries have been summarized.[45] There is a review on composite polymer

electrolytes.[28] In the text below we will consider various types of polymer electrolytes used in present-day metal-ion batteries. Data on the key characteristics of these classes of electrolytes, *viz*., the ionic conductivity, selectivity of cation transfer and range of operating temperatures are summarized, and the possibility of their application in metal-ion batteries are outlined. The emphasis is placed on the mechanisms of ion transfer in polymer electrolytes.

The list of notations and abbreviations used in the review is as follows:

D — diffusion coefficient,
DEC — diethyl carbonate,
DMA — *N*,*N*-dimethylacetamide,
DMC — dimethyl carbonate,
DME — dimethoxyethane,
DMF — *N*,*N*-dimethylformamide,
DMSO —dimethyl sulfoxide,
E_a — activation energy of ion transfer,
EC — ethylene carbonate,
HFP — hexafluoropropylene,
k_B — Boltzmann constant,
MFSI — bis(fluorosulfonyl)imide salts,
MTf — trifluoromethanesulfonic acid salts,
MTFSI — bis(trifluoromethanesulfonyl)imide salts,
n — concentration,
PAN — polyacrylonitrile,
PC — propylene carbonate,
PEC — poly(ethylene carbonate),
PEO — poly(ethylene oxide),
PHFP — poly(hexafluoropropylene),
PMMA — poly(methyl methacrylate),
PPC — poly(propylene carbonate),
PVA — polyvinyl alcohol,
PVDF — polyvinylidene difluoride,
R — universal gas constant,
SEI — solid electrolyte interphase,
SSEBS — sulfonated poly[styrene-*b*-(ethylene-*co*-butylene)-*b*-styrene] triblock copolymer,
THF — tetrahydrofuran,
t — transference number,
T — temperature,
T_g — glass transition temperature,
q — ion charge,
μ — ion mobility,
σ — ionic conductivity.

2. Ion transport: general principles

A key property of an electrolyte, which provides ion transfer between electrodes during the operation of a battery, is the ionic conductivity. It depends on the concentration and mobility of charge carriers and is described by the Kohlrausch equation

$$\sigma = \sum n_i q_i \mu_i \quad (1)$$

and by the Nernst–Einstein equation [50]

$$\sigma = \frac{nq^2 D}{k_B T} \quad (2)$$

where n is the concentration, q is the charge, μ is the ion mobility, D is the ion diffusion coefficient, k_B is the Boltzmann constant and T is absolute temperature.

Most polymers contain crystalline and amorphous phases where cation transport proceeds by different mechanisms. The largest contribution to the ionic conductivity in polymer electrolytes comes from cation transport in amorphous phase by the solvation–desolvation mechanism involving the interaction with electronegative atoms of the macromolecule and segmental mobility of polymer chains. In crystalline phase, ions hop between adjacent positions analogously to the motion of ions in ionic crystals. Depending on the ion transport mechanism, the temperature dependence of ionic conductivity in polymers is described by the Arrhenius equation, the Vogel–Tammann–Fulcher equation or by their combinations.[28,51] The Vogel–Tammann–Fulcher equation has the form

$$\sigma = \sigma_0 T^{-0.5} \exp\left(-\frac{B}{T - T_0}\right) \quad (3)$$

where σ_0 is the pre-exponent related to the concentration of charge carriers, B is the pseudoactivation energy of ionic conductivity, and T_0 is a constant temperature, which is most often 10–50 °C lower than the glass transition temperature (T_g) of the polymer.[40,46]

Equation (3) accounts for the temperature dependence of viscosity and for the dielectric and magnetic relaxation times of the polymer. It describes the motion of cations in amorphous phase, which is determined by the segmental mobility of polymer chains or by the mobility of solvent molecules,[42] thus being applicable to solid polymer electrolytes in the temperature range from T_g to $T_g + 100$ °C.[40]

At temperatures above $T_g + 100$ °C, the contribution of the motion of the polymer matrix to the ionic conductivity decreases appreciably. The reason is the higher mobility of polymer chains, which leads to shortening of the distance between coordination sites that can be occupied by cations, which accelerates cation transfer. In this case, the ionic conductivity is described by the Arrhenius equation

$$\sigma = \sigma_0 \exp\left(-\frac{E_a}{RT}\right) \quad (4)$$

where σ_0 and A are the pre-exponents, E_a is the activation energy of ion transfer, and R is the universal gas constant.

For a wider temperature range, the Frenkel equation [25,46,52] is used:

$$\sigma T = A \exp\left(-\frac{E_a}{RT}\right) \quad (5)$$

These equations are also valid for cation-exchange membranes in the temperature range where no phase transitions occur.[53–55]

Typical temperature dependences of the ionic conductivity in polymer electrolytes, which follows different mechanisms, are plotted in the coordinates of the Arrhenius equation in Fig. 1. Linear dependence of the conductivity of a gel polymer electrolyte (Nafion membranes, curve *1*) is typical of plasticized membrane materials provided that no phase transitions occur.[55,56] The temperature dependence of the conductivity in an electrolyte based on poly[(ε-caprolactone)-*co*-poly(trimethylene carbonate)] (curve *2*) has an arc-like shape and is described by Eqn (3). It is typical of amorphous electrolytes whose ionic conductivity has a contribution from the segmental mobility of polymer chains at temperatures above T_g. The temperature dependence of the conductivity of an electrolyte based on poly(ethylene

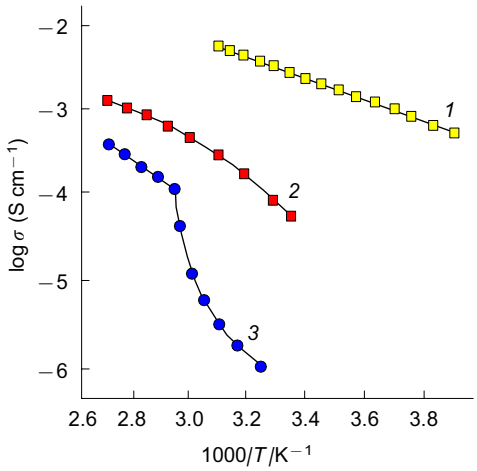


Figure 1. Temperature dependences of ionic conductivity of polymer electrolytes: Nafion-Li membrane solvated by propylene carbonate–ethylene carbonate–tetrahydrofuran mixture (*1*), poly(ε-caprolactone)$_{80}$–poly(trimethylene carbonate)$_{20}$/LiTFSI (*2*) and PEO/LiTf (*3*). Notations of anions: TFSI stands for $(CF_3SO_2)_2N^-$ and Tf stands for $CF_3SO_3^-$. The plots were drawn using the data obtained by the authors of Ref. 56 (private communication) and the data taken from Refs 57 and 58.

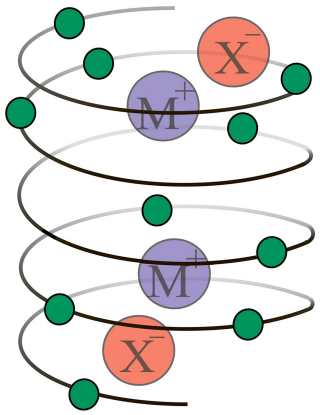


Figure 2. Structure model for PEO/salt polymer electrolyte.[62,64] M^+ is the metal cation and X^- is the salt anion. Solid green circles denote oxygen atoms.

oxide) (PEO) (curve *3*) exhibits a kink corresponding to the melting point of the polymer matrix.[57–59]

High ionic conductivity requires that the ion concentration and mobility be high. The charge carrier concentration is determined by the chemical composition of the material. The charge carrier mobility in polymer electrolytes can be varied in a wide range by varying the polymer matrix. A properly chosen matrix should favour an increase in ionic conductivity and minimize the contribution of anion transfer to this property.

3. Polymer/salt electrolytes

Solid polymer/salt electrolytes represent the first class of polymer electrolytes that has found application in Li-ion batteries.[60] These are salt solutions in polymer matrices. By convention, the composition of polymer/salt electrolytes is characterized by the ratio of the number of polar groups in the polymer (*e.g.*, oxygen atoms in the polymer chain of PEO) to the number of salt cations (M^+).

3.1. Structural features

Among polymer/salt electrolytes, those based on PEO have been best studied. High concentration of oxygen atoms in PEO allows ionic salts to dissolve easily; this gives partially crystallized systems. The degree of crystallinity of a certain PEO/salt system can vary over a wide range up to complete amorphization.[61–63] Usually, the crystalline phase has a stoichiometric chemical composition in contrast to the amorphous phase.

In most crystalline phases, polymer macromolecules form helices with cavities occupied by alkali metal cations. Most often, these cations are surrounded by oxygen atoms from PEO molecules and by anions (Fig. 2).[62,64]

As an example, consider the crystal structure of the polymer electrolyte $(PEO)_3$/LiTf. Poly(ethylene oxide) macromolecules form helices extended parallel to the crystallographic axis *b*. Each Li^+ ion is coordinated by five oxygen atoms [three O atoms from the PEO ether moieties and two O atoms from two $CF_3SO_3^-$ (Tf^-) ions]. Each Tf^- anion bridges two adjacent Li^+ cations to form zigzag chains parallel to the PEO chains.[58] Inter-chain interactions are much weaker than intrachain ones. The atomic and electronic structures of $(PEO)_3$/LiTf obtained from density functional calculations agree with the published experimental data and confirm the ionic nature of the conductivity in $(PEO)_3$/LiTf.[65]

The electrolyte $(PEO)_3/NaClO_4$ has a similar structure except that the Na^+ cation is coordinated by six oxygen atoms (four O atoms from the PEO ether moieties and one O atom from each of the two ClO_4^- groups).[58]

Materials based on low-molecular-mass PEO and having the composition $(PEO)_6/LiXF_6$ (X = As, P, Sb) are isostructural. Two PEO macromolecules entangle, thus forming tunnels occupied by Li^+ cations coordinated by five ether oxygen atoms. Bulky anions are outside the tunnels and not involved in the coordination of cations.[61,66]

Note that these electrolytes often contain both crystalline and amorphous phases and that the degree of crystallinity of the electrolytes usually increases with increasing concentration of the ionic salt. Amorphous domains of polymer electrolytes were studied by various methods including IR and NMR spectroscopies.[14,19,21,36,63,64] An IR study of $(PEO)_3$/LiTf revealed retention of short-range order in molten amorphous electrolyte with the same structural fragments as those of the crystalline material.[64] Using high-resolution solid-state ^{13}C NMR spectroscopy,[63] it was established that the electrolyte $(PEO)_n$/LiTf (n = 3, 6, 12 and 30) contains crystalline and amorphous solvate $(PEO)_3$/LiTf at all values of the parameter n. Samples with lower concentration of the salt ($n > 3$) also contained amorphous PEO while samples with $n > 6$ contained both amorphous and crystalline polymer.

At high concentrations of salts, these alkali metal ion solutions in polymers contain not only free ions or ions solvated by macromolecules, but also ionic associates including contact or solvent-separated ion pairs M^+X^-, triatomic groups M_2X^+ or MX_2^- and higher-order associates $[M^+X^-]_n$.[67–71] Ionic association is due to low dielectric constants of the macromolecular solvents and the degree of association increases with increasing salt concentration and temperature.[72]

3.2. Ion transport in polymer/salt electrolytes

The ionic conductivity in polymer electrolytes is mainly governed by the transport processes in elastomers and considerably decreases in the crystalline phase. The temperature dependence of conductivity in these systems usually differs from that typical of solid electrolytes. Near the glass transition temperature, the conductivity abruptly increases and obeys Eqn (3). Ion transfer in amorphous polymer electrolytes or in their amorphous domains is governed by the segmental mobility of macromolecules and by the relaxation of the polymer.[50, 73–75] According to the theory of free volume, activation of segmental mobility requires the formation of a cavity whose size exceeds a certain critical value; however, a too large cavity is also not favourable. The cavity volume distribution and the local environment of each segment of the polymer chain change continuously due to thermal motion of molecules. The motion of cations in an electric field is accompanied by their solvation–desolvation by polar groups of the polymer.[76] A cation transfer model with inclusion of correlation between the ionic conductivity of electrolytes and the polymer viscosity[77] assumes that cation hopping is correlated with rotation of polymer chain segments, which leads to changes in the coordination of the cation. A schematic view of the cation transport in amorphous PEO is presented in Fig. 3. Ion hopping from one site to another is correlated with local structural rearrangements, which leads to optimization of the environment of the cation when it arrives at a new site. Since the glass transition is hindered, the conductivity at temperatures in the vicinity of the transition temperature measured during cooling is much higher than that measured during heating the sample. Endothermic effects corresponding to transition of the polymer to the elactic state are often not observed on subsequent heating.[76]

Above the glass transition temperature, the largest contribution to the ionic conductivity comes from cation transport in amorphous domains of the polymer,[78, 79] while cation transport in the crystalline phase contributes much lesser.[61, 80, 81]

Since electrolytes contain differently charged ions, cations and anions are transferred simultaneously. The fraction of the total electric current carried by cations is characterized by the transference number (t_+), which can vary from 0 to 1. Usually, anions contribute largely to the overall ion transfer, so low t_+ values are one of the main drawbacks of solid polymer/salt electrolytes. Often, one has $t_+ < 0.5$ because of weaker bonding of anions to the polymer matrix. This causes concentration polarization at electrodes followed by a voltage drop and reduction of battery performance. The t_+ values can be increased as follows:

— using composite materials,

— by covalently bonding anions to the polymer matrix,[48] and

— by introducing anion acceptors.

Widely used anion acceptors include calixarenes,[82] boron-containing anions[83, 84] and other compounds. For instance, the polymer electrolyte $Li(PEO)_{20}I(calixarene)_{0.3}$ is characterized by $t_+(Li^+) = 0.59$ at 50 °C [*cf.* 0.39 for $Li(PEO)_{20}I$].[85] Although this modification strategy is very simple, its major drawback is agglomeration and low selectivity of cation transfer,[86, 87] which often leads to a decrease in ionic conductivity. Therefore, the anion acceptor approach is not of great practical interest. In the text below, we present a detailed consideration of composite polymer electrolytes and polymer electrolytes based on cation-exchange membranes.

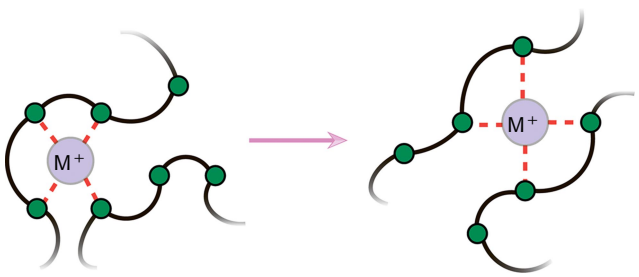


Figure 3. A schematic view of cation transport in a polymer, governed by segmental mobility of macromolecules.[55] Solid green circles denote electronegative atoms capable of coordinating the cation.

3.3. Interaction of polymers with ionic salts

Dissolution of a salt in a polymer is possible if the process is accompanied by a decrease in the Gibbs energy. Changes in the entropy of the system are due to (i) breakdown of ordered salt lattice (increase in entropy) on the one hand and (ii) ordering of polar groups of the polymer in the local environment of ions (decrease in entropy) on the other hand. For the systems in question, the entropy of dissolution usually takes positive values, although it can also be negative.[71] The enthalpy of dissolution of a salt in a polymer matrix is determined by the following:[58, 60, 71]

— salt lattice energy;

— cohesive energy of polymer molecules;

— energy of solvation of salt ions (first of all, cations); and

— energy of electrostatic interaction between dissolved ions.

The key factors include the energy expenditure for breakdown of the salt lattice and the enthalpy of solvation of ions by polar groups of the polymer. The former quantity is always positive, and its compensation and dissolution of the salt in the polymer matrix requires that cations be solvated.[88] It follows that the polymer molecule should contain electronegative atoms (oxygen, nitrogen, sulfur, *etc.*) capable of coordinating lithium or sodium ions.[89, 90] That is why electrolytes are often synthesized using polyoxides, polyimines, various polycarbonates, polysiloxanes, polynitriles, *etc.* as matrices.[25, 91–98] Efficient dissolution of salts requires that the concentration of electronegative atoms and distances between them be short. An example of a polymer providing a sufficiently high energy of solvation is PEO $-(-CH_2-CH_2-O-)_{\overline{n}}$. Polyethers of the composition $-(-CH_2-O-)_{\overline{n}}$ or $-(-CH_2-CH_2-CH_2-O-)_{\overline{n}}$ are much poorer solvents for ionic salts and cannot supply a sufficiently high concentration of charge carriers.[71]

Pearson's theory[99] treats the Li^+ and Na^+ ions as hard acids that form chemical bonds mainly with hard bases, *viz.*, atomic groups containing nitrogen and oxygen atoms.[71] In this case the binding energy is primarily determined by the electrostatic interaction; therefore, the energy of solvation should decrease as follows when considering the formation of solvates of alkali metal cations:[100] O > NR > NH > S.

An ionic salt used in polymer electrolytes should have a rather low lattice energy. The anion should be sufficiently stable and, unlike the cation, have low mobility in the polymer matrix.[101] Taking account of this requirement,

preference is usually given to salts with bulky monovalent anion, *e.g.*, hexafluorophosphates MPF_6, hexafluoroarsenates $MAsF_6$, perchlorates $MClO_4$, bis(fluorosulfonyl)imides $M(FSO_2)_2N$ (MFSI), bis(trifluoromethanesulfonyl)imides $M(CF_3SO_2)_2N$ (MTFSI), trifluoromethanesulfonates MCF_3SO_3 (MTf), bis(oxalato)borates $MB(C_2O_4)_2$ (MBOB), lithium 2-trifluoromethyl-4,5-dicyanoimidazolide $LiC_3N_2(CN)_2CF_3$ (LiTDI), trifluoromethanesulfonyl-(n-nonafluorobutanesulfonyl)imides $M[(CF_3SO_2)(n\text{-}C_4F_9SO_2)N]$ (MTNFSI), *etc.*[22, 25, 76, 102 – 108] Emphasize that salts containing bulky anions also favour a decrease in the degree of crystallinity of the polymer.[76]

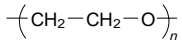
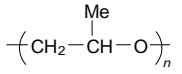
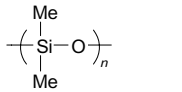
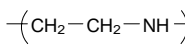
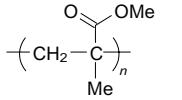
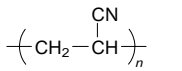
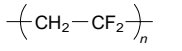
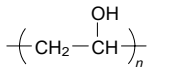
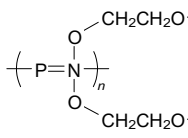
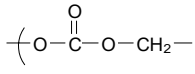
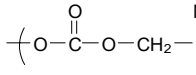
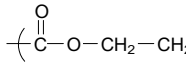
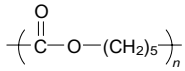
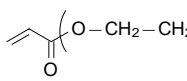
Various polymer matrices for the preparation of electrolytes are available. Selected parameters of certain matrices are listed in Table 1. They depend on the molecular mass and sample prehistory. Note that different authors reported somewhat different numerical values.

The polymer matrices in question can be divided into the following large groups:

— polymers containing heteroatoms in the main chain;
— carbochain polymers bearing polar side groups;
— polymers containing heteroatoms in the main chain and polar side fragments; and
— polymeric ionic liquids.

The first-mentioned group of polymers most often includes polyethers, polyimines, polythioethers and polysiloxanes. A salient feature of the systems in hand is strong intramolecular polydentate coordination of cations by the flexible polymer chain. Dissolution of an ionic salt causes the degree of crystallinity and the glass transition temperature to increase owing to local ordering of the polymer in the vicinity of the cation and a decrease in the segmental mobility due to the formation of additional bonds.[96, 117] The maximum conductivity is achieved at relatively low salt concentrations (at $O : Li \approx 16 : 1$ ratio for PEO).[96] Among major drawbacks, there are low transference numbers of cations (for PEO, most often one has $t_+ < 0.5$) and a low conductivity at room temperature (usually, less than 10^{-5} S cm^{-1} for PEO).[25, 118] Acceptable (for battery applications) ionic conductivity ($\geqslant 10^{-4}$ S cm^{-1}) in PEO-based electrolytes is often achieved at temperatures above the melting point of crystallites, namely, at 60 – 80 °C.[119] For instance, the ionic conductivity of the system PEO/LiFSI is

Table 1. Chemical compositions, glass transition temperatures and melting points (T_m) of polymers used to prepare solid electrolytes.

Polymer	Chemical formula	T_g/°C	T_m/°C	Ref.
Poly(ethylene oxide) (PEO)		−60	64	109
Poly(propylene oxide)		−60	Amorphous	109
Polydimethylsiloxane		−127	−40	109
Polyethyleneimine		−28	40 – 47	110
Poly(methyl methacrylate) (PMMA)		105	Amorphous	111
Polyacrylonitrile (PAN)		109 – 129	335 – 362	112
Polyvinylidene difluoride (PVDF)		from −40 to −30	155 – 192	113
Polyvinyl alcohol (PVA)		33 – 48	~230	114
Poly[bis(methoxyethoxyethoxy)phosphazene]		−83	Amorphous	109
Poly(ethylene carbonate) (PEC)		13	Amorphous	115
Poly(propylene carbonate) (PPC)		34	Amorphous	115
Poly(trimethylene carbonate) (PTMC)		−15	Amorphous	98
Poly(ε-caprolactone)		−65	56	116
Poly(ethylene glycol) diacrylate		−73	Amorphous	90

about 10^{-5} S cm^{-1} at 30 °C and reaches a value of 7.4×10^{-4} S cm^{-1} at 70 °C and very low transference number of lithium ($t_{Li+}=0.13$).[120] A polymer electrolyte prepared from PEO and a structurally similar salt lithium (fluorosulfonyl)(pentafluoroethylsulfonyl)imide (LiFPFSI) was characterized by a similar ionic conductivity, *viz.*, $\sigma=6.2\times10^{-4}$ S cm^{-1} at 80 °C ($t_{Li+}=0.29$).[94] The ionic conductivity of $NaClO_4$ in PEO is at most 7.7×10^{-7} S cm^{-1} at room temperature.[121] In spite of low ionic conductivity, PEO and its derivatives still belong to the most widely used matrices for solid polymer electrolytes since they are readily available and can dissolve salts.[76]

Carbochain polymers bearing polar side substituents (PAN, PMMA, PVA, polymethacrylonitrile, polyacrylamide, *etc.*) offer the advantage of forming solutions with higher concentrations of salts compared to polyethers ($\geqslant$50 mol.% for lithium).[96] In this case, both intra- and intermolecular coordination of cations by the polymer seem to be the most likely.[96] Random coordination by the polymer favours the formation of ionic aggregates since there is no chelate effect. The glass transition temperatures of the polymers in question are much higher than room temperature; however, they can be considerably decreased upon dissolution of an inorganic salt.[96] Such systems are characterized by mainly cationic conductivity that increases with increasing concentration of the dissolved salt since the amount of charge carriers increases while the degree of crystallinity of the polymer decreases. The conductivity in highly concentrated electrolytes can be as high as $10^{-4}-10^{-3}$ S cm^{-1} at room temperature.[96,122–127]

One more group, *viz.*, polymers containing heteroatoms in the backbone and polar side substituents, includes polycarbonates, which are intensively studied at present. Polycarbonates contain oxygen atoms in the backbone and are thus more flexible and have lower glass transition temperatures than carbochain polymers. It is mainly the C=O groups that are responsible for the solvating ability of polycarbonates since a long distance between oxygen atoms in the backbone precludes the formation of polydentate loops surrounding the cation.[96,128] As a result, bonding of the cation to the polymer matrix is weaker than that in the PEO-based electrolytes and therefore the transference numbers of cations increase to $\sim$0.5–0.8 for electrolytes prepared from polycarbonates and salts with bulky anions (LiFSI, LiTFSI, NaFSI).[129–131] For instance, the transference number of Li^+ in PEC/LiTFSI at 80 °C varies in the range $0.5 < t_{Li+} \leqslant 0.63$ depending on the salt concentration,[132] while for PTMC/LiTFSI one has $t_{Li+}=0.8$ at 60 °C.[124]

The concentration of the salt has strong effect on the ionic conductivity of polymer electrolytes.[98,115,131] At high concentrations of the dissolved salts, the conductivity reaches $10^{-5}-10^{-4}$ S cm^{-1} at room temperature.[115,131,133] Data on the influence of salt concentration on the glass transition temperature are contradictory. Dissolution of LiTFSI in most polycarbonates causes the glass transition temperature to decrease with increasing salt concentration.[115,128,131,132] However, the reverse was observed for the electrolytes PTMC/NaTFSI and PTMC/$NaClO_4$.[98] The authors of a study[134] of two electrolytes, PEC/LiTFSI and PPC/LiTFSI, dried in different regimes concluded that the decrease in the glass transition temperature of the polycarbonates upon dissolution of lithium salts and the high conductivity of the electrolytes based on polycarbonates ($\sim10^{-4}$ S cm^{-1}) can be due to partial degradation of the polymer resulting in the formation of EC or to the presence of residual solvent; these compounds can act as plasticizers.

High hopes were put on polymeric ionic liquids since they exhibit unique properties and have a potential for targeted synthesis of nanostructured materials with extended domains that are formed upon aggregation of fragments of ionic liquids.[135–138] When such domains undergo percolation, the ionic mobility is independent of local segmental mobility and fast transfer of charge carriers can proceed analogously to their transfer in the 'polymer-in-salt' systems, but at lower lithium concentrations.[74] Examples of electrolytes with lithium conductivity are provided by polycationic polymeric liquids based on imidazolium or piperidinium and the $TFSI^-$ anion and dissolved salt LiTFSI.[139,140] Systems with various polycations have been considered.[137,140,141] The ionic conductivity in the electrolytes based on ionic liquids can be as high as nearly 10^{-5} S cm^{-1} at room temperature. The transference numbers of Li^+ or Nai^+ cations are usually not very high (usually, at most 0.5)[137,142] without modification.

The ionic conductivity of polymer electrolytes is to a great extent determined by the fraction of the amorphous phase of the polymer, the salt concentration, and by the strength of bonding between the cation and the polymer matrix and anion. In this connection, the following methods are used to increase the ionic conductivity in polymer electrolytes and to improve the mechanical properties of the polymers:[74,76,111,143]

— formation of branched structure or introduction of bulky side substituents; the most widely used systems include graft copolymers with short PEO oligomers grafted onto side substituents,[76,144,145] such as poly(methoxy polyethylene glycol monomethacrylate),[144] poly(ethylene glycol) monomethyl ether methacrylate grafted onto poly(styrene-*co*-4-vinylanisole),[145] polyphosphazenes,[117,146] or polycarbonate derivatives bearing various hydrocarbon or ether substituents;[115]

— synthesis of linear block copolymers, *e.g.*, poly(ethylene oxide-*b*-propylene oxide-*b*-ethylene oxide),[147] poly(isoprene-*b*-styrene-*b*-ethylene oxide),[148] poly(styrene-*b*-ethylene oxide-*b*-styrene),[149,150] poly(ethylene oxide-*co*-ethylene carbonate),[151,152] poly(acrylonitrile-*co*-butadiene),[96] poly(vinylidene difluoride-*co*-hexafluoropropylene) [P(VDF-HFP)]; copolymers are most often synthesized from oligomers of compounds listed in Table 1 and other monomers;[25,40,153]

— chemical cross-linking of polymer chains to form a 3D network structure; often, cross-linked polymers contain fragments of ethylene oxide,[154–156] alkylsiloxanes,[20] alkyl methacrylates and diacrylates;[90,157–159]

— blending two or more polymers (copolymers) to obtain, *e.g.*, $LiClO_4$ solutions in blends of poly(vinyl chloride) with poly(butyl methacrylate)[160] or PEC with PTMC;[161,162] however, polymer blends are characterized by low conductivity and usually require low-molecular-mass liquid plasticizer additives;[160,163]

— synthesis of composites by doping with inorganic particles;[28,164–168] and

— introduction of low-molecular-mass liquid plasticizers; systems thus prepared are called gel polymer electrolytes.[169–171]

Summing up the material presented in this Section, mention should be made that solid polymer/salt electrolytes are the first and best studied class of polymer electrolytes. They offer an undoubted advantage of being free from

liquid organic components and, as a consequence, have improved stability. From the standpoint of ionic conductivity and selectivity of cation transfer, highly concentrated electrolytes based on polycarbonates and carbochain polymers with polar side substituents seem to be the most promising. However, in spite of considerable progress in the development of polymer/salt electrolytes, the selectivity of cation transfer in them seems to be the key issue. The anion mobility can be reduced considerably, but not in full.

3.4. Gel polymer/salt electrolytes

Plasticization of solid polymer electrolytes by liquid low-molecular-mass solvents (plasticizers) is the most efficient method of increasing their ionic conductivity. Electrolytes thus prepared combine the mechanical properties of polymers and the ability to provide fast cation diffusion typical of liquids.[14, 172, 173]

In addition to meeting general requirements for the properties, such as inertness to all components of the electrochemical cell and thermal stability, plasticizers should be characterized by high dielectric constant, which favours dissociation of salts,[174] and low viscosity to facilitate ion transfer.[175] The most widely used plasticizers are aprotic solvents. Solvents containing active protons can enter undesired reactions with lithium or sodium salts and are characterized by narrow electrochemical stability windows (2.0–4.0 V *vs* Li/Li^+ electrode),[176] whereas the working potentials of anode and cathode are most often in the ranges of 0.0–0.2 and 3.0–4.5 V (*vs* Li/Li^+ electrode), respectively.[177–180] To provide a wide electrochemical stability window, aprotic solvents having carbonyl (C=O), nitrile (C≡N), sulfonyl groups (S=O) or ether (O) linkages are used, since these systems are able to dissolve necessary amounts of salts.[176] Among them, various cyclic and linear organic carbonates (components of liquid electrolytes), ethers and sulfoxides are most widely used. Selected physical properties of solvents for Li-ion and Na-ion batteries are listed in Table 2.

Optimum characteristics can be achieved using mixed solvents since low-viscosity compounds are usually characterized by low dielectric constants (see Table 2). The most widely used mixed solvents include EC–DME, EC–DMC–DEC, EC–PC, EC–THF with various component ratios.[176, 188, 189]

Structurally, gel polymer electrolytes represent 3D networks of macromolecules or their aggregates containing a salt solution in polar aprotic solvent.[40, 190–192] Examples of the polymer matrices for gel polymer/salt electrolytes are PAN, P(VDF-HFP), PMMA and poly(vinyl chloride).[191–194] Usually, gel polymer electrolytes are prepared by impregnating a pre-formed polymer film with an alkali metal salt solution[192, 195] and usually contain a large amount of liquid components. The lithium and sodium conductivity of this type of electrolytes reaches more than 10^{-3} S cm^{-1}, which is comparable with the ionic conductivity of commercially available liquid electrolytes.[169, 170] For instance, the ionic conductivity of a gel polymer electrolyte based on poly(acrylonitrile-*co*-methyl methacrylate) and 1 M $LiPF_6$ solution in EC–DMC–DEC mixture (swelling ~150 mass %) was 2.1×10^{-3} S cm^{-1} at room temperature.[196] Similar ionic conductivity values were achieved using a conventional polymer matrix based on the copolymer P(VDF-HFP) plasticized by 1 M $LiPF_6$ solution in EC–DEC mixture (2×10^{-3} S cm^{-1} at room temperature).[193] The effect of cation on the ionic conductivity of polymer electrolytes based on P(VDF-HFP) and 1 M $MClO_4$ solutions (M = Li, Na) in EC–DMC—DEC mixture was studied.[197] It was found that the sodium-containing electrolyte provides a higher room-temperature ionic conductivity compared to the lithium-containing one (0.60×10^{-3} *vs* 0.51×10^{-3} S cm^{-1}, respectively; swelling ~110 mass %, $t_{Na+} = 0.30$). The addition of 1 M LiTFSI solution in a mixture of *N*-methyl-*N*-butylpyrrolidonium and poly(ethylene glycol) dimethyl ether to a composite based on PAN/PMMA electrospun membrane with a 3D network structure (swelling 480 mass %) caused the ionic conductivity to increase to 3.6×10^{-3} S cm^{-1}.[194] In addition, gel polymer electrolytes are characterized by relatively high transference numbers of cations, which can be as high as 0.6–0.9 for electrolytes based on oxygen-free polymer matrices (*e.g.*, PAN and PMMA) and solutions of lithium salts in organic carbonates.[198, 199]

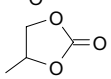
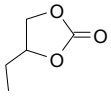
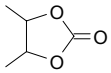
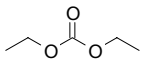
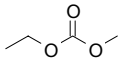
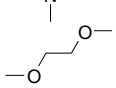
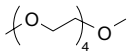
Electrolytes containing liquid phase are also divided into gel polymer and plasticized ones.[46] The latter contain much lower amounts of aprotic solvent than the former and usually have a noticeably lower conductivity.[40, 190, 191] A salient feature of plasticized electrolytes is that they are solids, whereas gel polymer electrolytes are essentially two-phase systems.[192] Plasticized polymer electrolytes are most often prepared by solution casting (from acetonitrile solutions) with the addition of plasticizer to the initial solution.[137, 200] Examples of plasticized electrolytes include PEO/LiTf/50 mass % EC–PC ($\sigma = 1.8 \times 10^{-6}$ S cm^{-1} at 25 °C), PEO/LiTFSI/18 mass % poly(ethylene glycol) dimethyl ether ($\sigma = 8.3 \times 10^{-6}$ S cm^{-1} at 25 °C, $t_{Li+} = 0.48$)[201] or PEO/LiTFSI/30 mass % tetraglyme ($\sigma \approx 10^{-5}$ S cm^{-1} at 25 °C).[137]

It is difficult to distinguish between gel and plasticized electrolytes, and the authors of many recent studies simplify the situation by treating polymer electrolytes containing liquid phase as gel polymer (or plasticized) electrolytes irrespective of the amount of the liquid component[80] and considering them as belonging to a common class.[168, 192]

The addition of solvents leads to weakening of intermolecular bonds between polymer chains, a decrease in the degree of crystallinity of the polymer, an increase in the free volume,[80, 192] reduction of the glass transition temperature[174] and thus to an increase in segmental mobility of polymer chains, as was confirmed by NMR data.[192] Besides, solvents solvate cations and weaken the ion–ion interaction.[61] Charge transfer in gel polymer electrolytes occurs mainly in the plasticizer phase containing the dissolved salt, while the polymer acts as flexible supporting matrix.[191] However, if the polymer is also a good solvent for the cation, ion transport can proceed in both phases.[192] Thanks to the factors mentioned above, the ionic conductivity of gel polymer electrolytes is higher than that of solid polymer electrolytes.

Recently, there has been intensive research into application of ionic liquids for plasticization of polymer electrolytes for metal-ion batteries.[138, 171, 202, 203] Both polymers mentioned above[204] and polymeric ionic liquids[141, 142, 172, 205, 206] can be used as matrices for the preparation of plasticized electrolytes. Ionic liquids are very promising since they are characterized by low toxicity and flammability, a wide electrochemical stability window, high chemical and thermal stability[40, 135–138, 143, 207–209] and good solvating ability, which makes possible efficient dissolution of many organic and inorganic compounds.[210]

Table 2. Dielectric constants (ε), dynamic viscosities (η), dipole moments (μ), melting points (T_m) and boiling points (T_b) of solvents used in Li-ion and Na-ion batteries.[175, 176, 181–187]

Solvent	Structure	ε (25 °C)	η (25 °C) /cP	μ /D	T_m /°C	T_b /°C
Ethylene carbonate (EC)		89.8	1.9 (40°)	4.6	36	248
Propylene carbonate (PC)		64.9	2.5	4.8	−50	242
1,2-Butylene carbonate		53.0	3.1	5.1	−53	241
2,3-Butylene carbonate		57	2.8	–	34	243
Dimethyl carbonate (DMC)		3.1	0.6	0.8	5	91
Diethyl carbonate (DEC)		2.8	0.8	1.0	−74	126
Ethyl methyl carbonate		3.0	0.7	0.9	−53	110
Dimethyl sulfoxide (DMSO)		45	2.0	4.0	18	189
Acetonitrile		38	0.4	3.5	−44	82
N,*N*-Dimethylformamide (DMF)		36.7	0.9	3.8	−61	153
N,*N*-Dimethylacetamide (DMA)		39	2.0	3.8	−20	165
Dimethoxyethane (DME)		7.2	0.4	1.1	−71	85
Tetrahydrofuran (THF)		7.5	0.5	1.6	108	66
γ-Butyrolactone		43	1.7	4.2	−44	204
Tetraethylene glycol dimethyl ether (tetraglyme)		7.8	3.3	2.4	−30	275

A drawback of most ionic liquids is high viscosity, which limits fast ion transport.[40] The lowest-viscosity ionic liquids are based on pyrrolidinium and imidazolium.[211, 212] One more drawback is a considerable decrease in the transference number of cations ($\leqslant 0.2$) upon plasticization of polymer/salt electrolytes.[27] The problem can be solved using polymer electrolytes plasticized by ionic liquids based on zwitter-ions.[213] This can increase the transference number of cations to 0.7; however, high viscosity and melting points of this type ionic liquids result in decreasing ionic conductivity of the polymer electrolytes based on them.[40]

Gel polymer electrolytes are chemically and electrochemically stable. Their ionic conductivity is higher than that of solid electrolytes while the mechanical properties are better than those of liquid electrolytes.[80, 209, 214] The introduction of a low-molecular-mass plasticizer allows one to attempt to shift the range of operating temperatures towards negative temperatures by increasing the ion mobility.[215] It is gel polymer electrolytes that are used in the so-called lithium-polymer batteries (main energy sources for portable devices).[216] However, the addition of liquid phase can induce gas generation at 50–60 °C (for plasticization by organic carbonates and ethers), which makes the batteries less safe, reduces the mechanical strength of the electrolytes and eventually increases the probability of dendrite growth.[40, 48, 49, 80, 82] This probability can be minimized by, *e.g.*, supporting the gel electrolyte on porous membranes [142, 193, 196] or by doping with inorganic particles to give composite polymer electrolytes. Yet another drawback of gel polymer/salt electrolytes is a low transference number of cation. The best method for solving this problem is to synthesize polymer electrolytes based on cation-exchange membranes.

4. Polymer electrolytes based on cation-exchange membranes

Materials based on cation-exchange membranes form a promising class of polymer electrolytes where anions are covalently bound to the polymer matrix. These electrolytes

exhibit only cationic conductivity and are characterized by t_+ values close to unity. They are called single-ion conducting polymer electrolytes,[45,48] or polyelectrolytes.[190] Being free from anion mobility assumes that polymer electrolytes based on ion-exchange membranes should prevent dendrite growth during the cycling of batteries with alkali metal anodes.[45] It was reported[217,218] that dendrites begin to grow since the metal surface is depleted of anions when the battery charges. Polymer electrolytes based on ion-exchange membranes are free from this drawback because anions are covalently bound to the polymer matrix and thus remain fixed when the battery is in operation.

Cation-exchange membranes can be based on polymers containing no electronegative atoms. Functionalization (*e.g.*, sulfonation) is achieved by attaching SO_3H groups to a finished polymer or by co-polymerization of monomers, of which one contains the necessary groups or their precursors (*e.g.*, SO_2F groups). To provide a maximum cation mobility, functional groups are often localized on the side-chain elements.[169,219] Cation-exchange membranes are mainly used in waste water treatment (membranes contact aqueous solutions)[220] and fuel cells (membranes contact moistened gases).[221] Functional groups adsorb water and form a system of pores and channels, which are filled with aqueous solution containing cations that split off from functional groups during their dissociation. This is just the reason for high ionic conductivity of cation-exchange membranes.[222] The conductivity of dry membranes is very low, first of all, due to low concentration of electronegative atoms involved in cation transport. This casts doubt on the prospects for their use in metal-ion batteries.

Various approaches have been tested to increase the ionic conductivity of the polymers in question. In particular, blends with polymers containing electronegative atoms (*e.g.*, PEO) were studied. However, blending is usually accompanied by phase separation and minor increase in the ionic conductivity.[48] One more method is to co-polymerize a functionalized monomer with monomers containing Lewis bases.[48] This can be done using polystyrene, polyethers (in particular, PEO),[223,224] polyoxyethylene,[225] polyacrylates[226] and polysiloxanes.[227]

A promising strategy is to use polymers with highly acidic functional groups that facilitate dissociation. A strong impact of the degree of delocalization of negative charge was reported.[228] Examples are provided by membranes based on a perfluorinated polymer matrix. They demonstrate high chemical stability and mechanical strength owing to high C–F bond energy.[229] In addition, electronegative fluorine atoms in the polymer chain ensure delocalization of negative charge over functional groups and facilitate their dissociation. One of the most common types of membranes are Nafion membranes representing copolymers of tetrafluoroethylene and perfluorinated sulfonated vinyl ether.[19,55,230–233]

The variety of cation-exchange materials includes polymers containing COO^-, SO_3^- and $SO_2\bar{N}SO_2$ anions.[48,169,234,235] Membranes with functional carboxylate anions are characterized by low ionic conductivity, which can be increased using a more flexible monomer or by co-polymerization with a poorly crystallizable polymer and by modifying the functional group with electronegative fragments or by doping the polymer with electronegative atoms. For instance, the use of more flexible polysiloxane instead of PEO causes a considerable increase in lithium conductivity (from 10^{-8} S cm^{-1} at 60 °C to 10^{-6} S cm^{-1} at room temperature) with retention of high transference number of lithium.[234,236] The introduction of fluorocarbon groups into fragments of a polymer chain adjacent to the functional group $CH_2OO(CF_2)_3COO^-$ causes the ionic conductivity to increase by two orders of magnitude from 10^{-8} to 10^{-6} S cm^{-1} at 60 °C.[144,234]

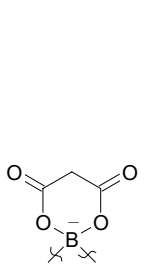
Polymers bearing sulfo groups possess higher ionic conductivity than polymers with carboxylate anions owing to higher degree of delocalization of negative charge.[48] From this point of view functional groups based on various sulfonylimides $SO_2\bar{N}SO_2$ with delocalized negative charge [they are to some extent analogous to bis(trifluoromethanesulfonyl)imide anion $TFSI^-$] seem to be the most promising. The room-temperature ionic conductivity of functionalized PEO-based polymers increases in the following order of functional groups:[235,237–239]

$$C_6H_4SO_3^- < C_6H_4SO_2\bar{N}SO_2CF_3 < C_6H_4SO_2\bar{N}SO_2F < < C_6H_4SO_2\bar{N}S(ONSO_2CF_3)CF_3.$$

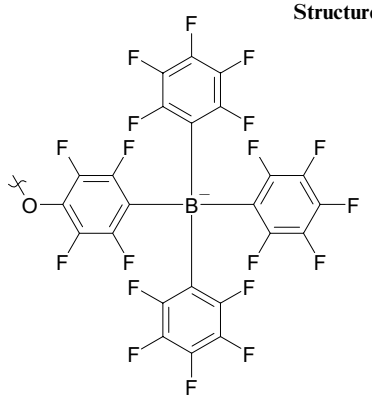
This order is consistent with the increase in the degree of dissociation of functional groups and amorphization of the polymer in the presence of a bulky substituent.[48] High acidity of the sulfonylimide functional group is confirmed by the fact that that sulfonylimide-functionalized polystyrene is used as Brønsted acid in catalysis.[240–243]

Boron-containing functional groups have been less studied. A membrane based on mono-malonato orthoborate (**1**) is characterized by a maximum ionic conductivity of 10^{-5} S cm^{-1} at room temperature.[48] The ionic conductivity of a membrane based on functional group **2** was at most 10^{-7} S cm^{-1} at room temperature in spite of high degree of delocalization of the negative charge.[244]

Structures 1, 2



1



2

At present, all ion-exchange membranes are characterized by very low conductivity at room temperature and therefore their application as electrolytes for metal-ion batteries seems to be futureless.

4.1. Gel polymer electrolytes based on cation-exchange membranes

To increase the conductivity of ion-exchange membranes, their structure should be modified to resemble that of hydrated systems. Since water cannot be used in Li-ion and Na-ion batteries, intercalation of aprotic solvents into ion exchange matrices seems to be the most promising method. The solvent filling the system of pores and channels provides the medium for cation transfer and improves the

plasticity and segmental mobility of membranes. In this connection the solvents play the role of plasticizers for ion-exchange materials. Indeed, the addition of plasticizers to solid polymer electrolytes based on cation-exchange membranes causes a considerable increase in their ionic conductivity (to 10^{-4}–10^{-3} S cm^{-1} at room temperature) with retention of high transference numbers. By analogy with gel polymer/salt electrolytes, impregnation of an ion exchange matrix with a solvent leads to an increase in the degree of dissociation of functional groups (owing to an increase in the dielectric constant of the material and cation solvation by solvent molecules) and to amorphization of the polymer matrix. In addition, solvation changes the mechanism of ion transfer from a relay one in the initial membranes (ion hopping between electronegative atoms of the membrane matrix) to the motion of metal cations through the solution confined within the system of pores and channels (by analogy to ion transfer in liquid solutions of ionic salts) in the solvated material. Note that the membrane pore walls have a negative charge due to fixed ions located on them while cations transport driven by electrostatic interaction mainly proceeds in the thin Debye layer along the pore walls.[245]

An increase in the content of solvent causes an increase in the ion mobility. In the case of ion-exchange matrices with high concentration of functional groups this also leads to significant deterioration of mechanical properties.[45] To prevent this effect, composite matrices are prepared using an ion exchange material and inert polymers (most often, PVDF or PVDF/HFP blends).[246–248] One can also use polymers with high equivalent mass (lower content of functional groups) or block copolymers.[249,250] For instance, a polymer electrolyte prepared by grafting a lithium salt of 2-acrylamido-2-methylpropanesulfonic acid and hexafluorobutyl methacrylate onto PVDF and then swollen in EC–DMC mixture was characterized by an ionic conductivity of 2.1×10^{-5} S cm^{-1} at 30 °C.[45]

Perfluorinated sulfonated Nafion membranes possess much higher ionic conductivity owing to delocalization of negative charge. For instance, lithiated Nafion-112 membranes solvated by an EC–PC mixture, which is often used in commercially available batteries with liquid electrolyte, were characterized by an ionic conductivity of 8×10^{-5} S cm^{-1} at room temperature.[251] Solvation of structurally similar Nepem membranes (China) by the same mixture lead to a much higher conductivity of 7×10^{-4} S cm^{-1}.[232] By varying the solvent composition one can achieve a higher degree of solvation and, therefore, a higher ionic conductivity.

A number of studies on the influence of the chemical composition of solvents on the ionic conductivity of polymer electrolytes based on Nafion membranes are available.[53,55,56,232,252,253] The ionic conductivity increases in the following order: DEC ≈ DMC ≈ DME ≈ ≈ THF ≈ 1,3-dioxolane ≈ acetonitrile ≈ γ-butyrolactone < < EC–DMC–DEC < PC < EC–PC < EC–DME < DMF ≈ ≈ DMSO < EC–DEC–DMA < EC–PC–DMA–THF < < EC–PC–DMA.

This order agrees with the overall effect of the viscosity and dielectric constant of the solvents and their mixtures. In most cases the lithium conductivity of gel polymer electrolytes based on ion-exchange membranes is higher than the sodium conductivity due to the higher degree of solvation of Li^+ ions having a smaller radius.[55,56,254]

As mentioned above, the ionic conductivity of a membrane depends strongly on the content of solvent. The effect can be enhanced by pre-treatment of the membrane with polar solvents including water or various low-molecular-mass alcohols (ethanol, methanol, *etc.*) and by varying the membrane conditioning techniques.[55,56,249,254–257] In the case of perfluorinated membranes, the most efficient method is solvothermal treatment, *i.e.*, sorption of solvents at elevated temperatures.[56,255,256] The organic solvent uptake of Nafion membranes can be improved by pre-treatment with methanol.[55,56] For instance, the lithium conductivity of the Nafion membranes treated at 60 °C and then solvated by an EC–PC mixture increased from 7×10^{-5} to 2.5×10^{-3} S cm^{-1} at 30 °C.[56] The influence of the pre-treatment on the subsequent uptake of aprotic solvents can be explained by the so-called membrane memory effect due to preliminary expansion of the system of pores and channels that have no time to completely relax in the course of drying prior to solvation.[258]

One more method to improve the solvent uptake is to fabricate porous membranes with a pore size of at most 1 μm to prevent the leakage of plasticizer.[45] For instance, a microporous electrolyte based on poly(arylene ether) functionalized by perfluoroethylsulfonate groups had a porosity of 47% at a micropore size in the range of 0.3–0.6 μm.[259] A gel polymer electrolyte based on this membrane and an EC–PC–DEC mixture demonstrated a high ionic conductivity at 25 °C (3.1×10^{-3} S cm^{-1}) and electrochemical stability (4.7 V).

Gel polymer electrolytes functionalized by sulfonylimide groups are characterized by higher ionic conductivity due to higher degree of delocalization of negative charge. To prepare dense nonporous polymer electrolytes, lithium poly[4-styrenesulfonyl(phenylsulfonyl)imide] and poly[lithium {4-styrenesulfonyl(phenylsulfonyl)imide]-*alt*-(maleic anhydride)} were blended with an inert polymer [PVDF (or PVDF-HFP)] and then impregnated with ac EC–PC mixture.[247,248] The room-temperature ionic conductivity of the initial polymer salt and the copolymer was 1.1×10^{-3} and 2.67×10^{-3} S cm^{-1} , respectively. Nonporous polymer electrolytes based on poly(ethylene-*b*-butylene-*b*-styrene) functionalized with sulfonic and sulfonylimide groups and plasticized by an EC–DMA mixture were reported.[250] The lithium conductivity of the electrolytes decreased in the following order:

$$R-SO_2\bar{N}SO_2CF_3 > R-SO_2\bar{N}SO_2CCl_3 \gg \gg R-SO_2\bar{N}SO_2C_6H_4NO_2 > R-SO_2\bar{N}SO_2C_6H_4CF_3 > > R-SO_2\bar{N}SO_2C_6H_5 > R-SO_3^-.$$

This order corresponds to the decrease in the degree of delocalization of negative charge of the functional group. The maximum ionic conductivity (1×10^{-3} S cm^{-1} at 25 °C) was achieved for the membrane functionalized with the sulfonyl(trifluoromethylsulfonyl)imide group $SO_2\bar{N}SO_2CF_3$.

A porous polymeric blend membrane was prepared[260] by grafting lithium sulfonyl(trifluoromethylsulfonyl)imide onto poly(ether ether ketone) and blending with poly[poly(ethylene glycol) methyl methacrylate] followed by plasticization by PC. The ionic conductivity of the gel polymer electrolyte was 2×10^{-4} S cm^{-1} at 25 °C. A gel polymer electrolyte based on 1-[3-(methacryloyl)propylsulfonyl]-1-(trifluoromethylsulfonyl)imide, poly(ethylene glycol) methyl methacrylate and poly(ethylene glycol) methyl dime-

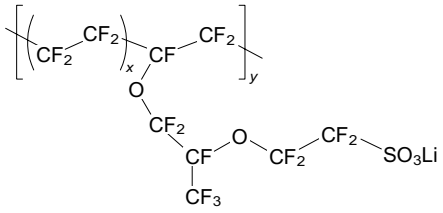
thacrylate and prepared by radical copolymerization followed by plasticization by PC possessed an ionic conductivity of 1.1×10^{-4} S cm^{-1} at 25 °C.[261] Very high ionic conductivity (5.8×10^{-3} S cm^{-1} at 28 °C) was demonstrated by a gel polymer electrolyte based on copolymer of lithium [(4-styrenesulfonyl)(fluorosulfonyl)imide], pentaerythritol tetraacrylate and pentaerythritol tetrakis(3-sulfanylpropionate) blended with PVDF and plasticized by an EC–DMC mixture.[262]

Lithium poly(1,2,3,4-butanetetracarboxylic acid borate) was blended with PVDF-HFP and plasticized by EC–PC to obtain a gel polymer electrolyte with high ionic conductivity ($\sim3\times10^{-4}$ S cm^{-1} at room temperature).[263] Covalent bonding of boron with π-conjugated systems (*e.g.*, benzene ring) allow one to increase the degree of delocalization of negative charge of the functional group. For instance, a gel polymer electrolyte based on poly(4-vinylphenol) phenolate borate and PVDF-HFP plasticized by an EC–PC mixture was characterized by an ionic conductivity of 4.4×10^{-4} S cm^{-1} at room temperature.[264]

4.2. Structural features of and ion transport in polymer electrolytes based on cation-exchange matrices

Consider structural features and ion transport in homogeneous membranes in relation to Nafion membranes and block copolymers based on sulfonated polystyrene. The former are copolymers of tetrafluoroethylene and perfluorinated sulfonated vinyl ether (structure **3**) and belong to the most commonly used and best studied homogeneous ion-exchange matrices.

Structure 3



3

The most widely used structural model for Nafion ion-exchange membranes was proposed by Gierke *et al.*[265] At present, it is used to describe the structure of all homogeneous ion-exchange membranes.[265, 266] According to this model, functional sulfo groups form spherical clusters in the hydrophobic polymer matrix. Solvation by low-molecular-mass solvents leads to connection of these clusters by ion-conducting channels whose size depends on the presence (or absence) of solvent and on the solvent type. The structure and ionic conductivity of cation-exchange membranes depend on the content of solvent. A dry Nafion cation exchanger is characterized by a low ionic conductivity of the order of 10^{-7}–10^{-5} S cm^{-1}. The reason is that functional groups form spherical clusters separated by a distance ~2.7 nm from one another (Fig. 4*a*).[267] Since these clusters are isolated, fast ion transport across functional groups is impossible. Sorption of the solvent causes the cluster size to increase owing to ion–dipole interactions (Fig. 4*b*). At low degrees of solvation, clusters remain isolated and the ionic conductivity of the membrane is low. An increase in the solvent content causes percolation and formation of channels connecting the clusters (Fig. 4*c*) and subsequent abrupt increase in the ionic conductivity by

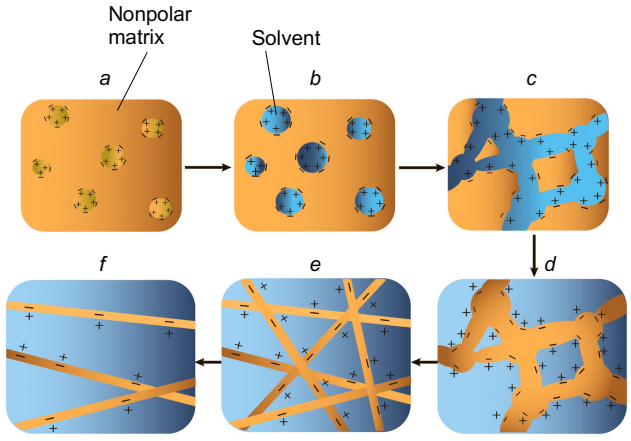
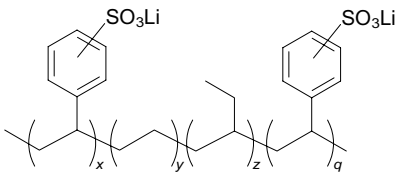


Figure 4. Structural evolution of Nafion membrane with increasing solvent content.[267]
For *a*–*f*, see text.

two or three orders of magnitude. Further increase in the solvent content in the membrane is accompanied by an increase in the pore and channel size. As the solvent content reaches a certain critical value, a phase inversion occurs and the total volume of pores and channels becomes larger than that of the hydrophobic part of the polymer (Fig. 4*d*). At even higher content of the solvent, the formation of a network of ion-conducting clusters (Fig. 4*e*) becomes energetically favourable. Electrolytes having such a structure are characterized by low mechanical strength.[73] With the solvent content still increasing, one deals with dissolution of the membrane and formation of a colloidal solution (Fig. 4*f*).

A major drawback of perfluorinated membranes is high cost; therefore, the synthesis of novel ion-exchange membranes from cheaper components and investigations of their properties are topical. It is convenient to use block copolymers based on hydrocarbons with one or more blocks functionalized with certain groups. A typical feature of such systems is phase separation. Functionalization has strong effect on structure formation and ionic conductivity of this type of materials. Consider a sulfonated poly[styrene-*b*-(ethylene-*co*-butylene)-*b*-styrene] (SSEBS) triblock copolymer (structure **4**).

Structure 4



4

At low degrees of sulfonation (content of sulfo groups is 17 mol.%–36 mol.%, which corresponds to an ion exchange capacity of 0.5–1.0 mequiv. g^{-1}), a heterogeneous system is formed. It contains ionic clusters of radius 3–4 nm, arranged within the polystyrene domains 20–30 nm in size that are distributed in the inert phase of the polyethylene and polybutylene blocks (Fig. 5*a*).[268] Here one deals with periodically arranged ordered lamellae oriented mainly along the membrane (Fig. 5*b*).[269, 270] As the

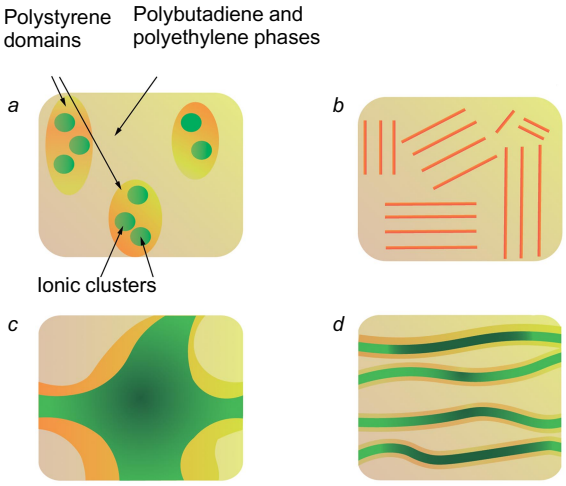


Figure 5. Structure of dry SSEBS membrane at an ion exchange capacity of 0.5–1.0 (*a*, *b*) and >1.1 mequiv. g^{-1} (*c*, *d*).[268–272]

content of sulfo groups exceeds 36 mol.% (this corresponds to an increase in the ion exchange capacity to more than 1.1 mequiv. g^{-1}), a percolation threshold is achieved, accompanied by the formation of ionic channels providing high ionic conductivity (Fig. 5 *c*). Eventually, the polymer structure represents disordered extended ionic domains (Fig. 5 *d*).

The ionic conductivity in block copolymers is strongly influenced by not only the degree of sulfonation, but also the degree of solvation and the solvent type. For instance, a study[270] on the effect of the composition of the methanol–THF mixture intercalated into a SSEBS membrane containing 27 mol.% of sulfo groups (ion exchange capacity of 0.75 mequiv. g^{-1}) on the ionic conductivity of the membrane revealed a gradual increase in protonic conductivity at a methanol content in the range of 0 vol.% — 5 vol.% followed by an abrupt increase in the ionic conductivity by an order of magnitude from 2.5×10^{-3} to 2.5×10^{-2} S cm^{-1} at higher content of methanol. The effect is also due to percolation and formation of ionic channels.[272]

Thus, the conductivity of cation-exchange membranes depends on the content of solvent, the ion exchange capacity, the nature of cations and functional groups, the polymer matrix and the degree of solvation, which is the most important parameter.[273] The structural, mechanical, thermodynamic and electrochemical properties of the cation exchanger are specified by the spatial distribution of solvent molecules, by the physical properties of the solvent and by its concentration within the membrane.

Electrolytes based on cation-exchange membranes seem to be a promising class of polymer electrolytes. Anions in these materials are covalently bound to the polymer matrix, so the electrolytes possess only cationic conductivity. Increasing the degree of delocalization of negative charge of functional groups in cation-exchange membranes by introducing electronegative substituents and forming a system of pores and channels in the polymer electrolyte by impregnating with organic solvents offers prospects for increasing the membrane conductivity. Such a modification allows the conductivity of certain electrolytes to approach the target value ($\geqslant10^{-3}$ S cm^{-1}), thus making them suitable for industrial applications.

5. Composite polymer electrolytes containing inorganic particles

Polymer electrolytes are most often modified using inorganic particles that can be divided into two groups depending on the contribution to the charge transfer processes:[28, 274]

— 'active' particles contain mobile cations that can be involved in ion transfer, *e.g.*, $Li_7La_3Zr_2O_{12}$, $Li_{1+x}Al_xGe_{2-x}(PO_4)_3$, $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$, $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}PO_{12}$, *etc.*,[49] and

— 'inert' particles not involved in ion transfer, *e.g.*, Al_2O_3, SiO_2, MgO, TiO_2, ZrO_2, *etc.*

The ionic conductivity in composite polymer electrolytes doped with inorganic particles can be increased through the interaction at the interface and by amorphization of the polymer.[192] The increase in the ionic conductivity in composite materials was for the first time reported by Liang[275] in 1973. Lithium iodide containing alumina exhibited high ionic conductivity, although the former component has low conductivity while the latter is a typical dielectric. More recently, Maier[276] proposed a theory that explained the unexpected phenomenon by sorption at the interface. According to this theory, one type of salt-forming ions is mainly adsorbed on the surface of the oxide material. This is followed by defect formation in the Debye layer nearly 1 nm thick to maintain high surface conductivity. The processes proceed at the interface, so the surface area should be as large as possible. This underlies the advantages of nanocomposites.[277] Interfacial interaction and high defect concentration enable amorphization of the conducting layer.[278]

Highly conducting layers at the oxide nanoparticle/polymer interface are formed in a similar manner. Near the surface of nanoparticles, the packing of a crystalline polymer is deformed, polymer chains become disordered and the free-volume space appears (Fig. 6). Numerous electronegative atoms present at the surface of oxygen-containing dopant particles create favourable conditions for sorption and transfer of cations, which provide accelerated ion transfer. High concentration of nanoparticles in the surface layers can induce the formation of percolation structures through which cation transport occurs.

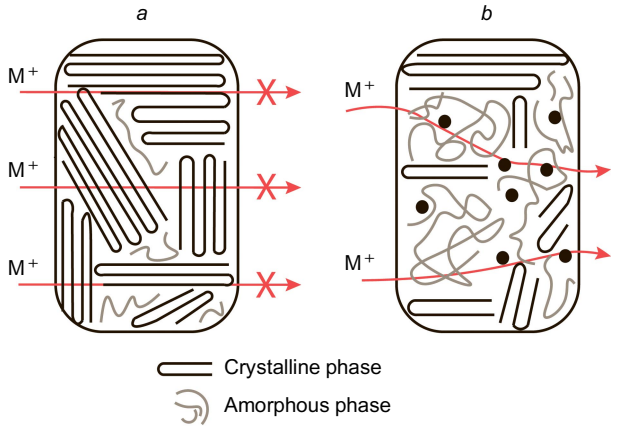


Figure 6. Formation of conducting layers and percolation structures upon doping a polymer matrix with nanoparticles: a schematic.[25] Crystalline polymer (*a*) and composite electrolyte based on the polymer doped with nanoparticles (*b*).

The ionic conductivity in polymer electrolytes is most strongly influenced by the chemical composition, size and morphology of particles.[279–281] A decrease in the particle size and corresponding increase in the particle surface area leads to a more developed interface and higher ionic conductivity of the entire system. The maximum effect is achieved upon adding nanoparticles.[281] The ionic conductivity depends on the content of inorganic particles added to the polymer matrix in a nonlinear manner. Like for other composite electrolytes, it passes through a maximum at a relatively low content of dopant particles (about 5 mass % – 20 mass % for polymer/salt electrolytes).[280, 282] Subsequent increase in the concentration of dopant particles causes a decrease in the ionic conductivity due to blocking of the ion transport pathways. The nature of nanoparticles (first of all, of their surface) has strong effect on the ionic conductivity.[283, 284]

Doping polymer/salt electrolytes with inorganic particles is followed by some increase in the transference numbers of cations, most often to 0.4–0.7 depending on the type of the dopant particles, anion and polymer matrix.[285] For instance, the conductivity of ZrO_2-doped electrolyte PEO/LiTf increased from about 10^{-7} to nearly 10^{-6} S cm^{-1} at 25 °C, while t_{Li+} increased from 0.27 to 0.42 (85 °C).[286] The electrolyte PEO/NaTFSI/x SiO_2 is characterized by $t_{Na+} = 0.39$ and 0.51 (75 °C) at $x = 0$ and 5 mass %, respectively.[287] Doping with 5 mass % SiO_2 significantly improved the mechanical properties of the electrolyte while its conductivity remained close to that of the undoped material ($\sim 10^{-5}$ S cm^{-1} at 25 °C). Doping a gel polymer electrolyte based on PVDF-HFP/NaTf/ionic liquid with $NaAlO_2$ caused its conductivity at 25 °C to increase from 4.5×10^{-3} to 6.5×10^{-3} S cm^{-1} and t_{Na+} to increase from ~ 0.32 to 0.42.[288] A considerable increase in t_{Li+} from 0.54 to 0.81 was also reported for the PEC/LiFSI system doped with titania nanoparticles (room-temperature conductivities of both materials were close to 10^{-4} S cm^{-1}).[131]

Cation transport in systems with 'active' particles can occur through both the polymer phase containing dissolved salt and the inorganic dopant phase. However, one can assume that the major contribution to the increase in conductivity comes from the interface between the polymer/salt system and the inorganic dopant.[289–292] Most authors relate the increase in conductivity to a decrease in the degree of crystallinity of the polymer,[289–294] to enhanced mobility of charge carriers at the interface between the polymer/salt system and the inorganic dopant,[290, 295, 296] and to an increase in the degree of dissociation of the salt dissolved in the polymer matrix as a result of acid-base interaction with dopant particles, which increases the concentration of charge carriers.[295, 297]

As for neutral particles, the maximum conductivity of electrolytes modified with active particles was obtained at a relatively low dopant content (5 mass % – 20 mass %).[289, 295, 296, 298–301] For instance, the maximum conductivity of electrolytes of the composition $(1-x)$ mass % [$(PEO)_8$/LiTFSI]/x $Li_{6.4}La_3Zr_{1.4}Ta_{0.6}O_{12}$ ($x = 0–80$) 1.17×10^{-4} S cm^{-1} at 30 °C was observed at $x = 10\%$.[302] For the system PC/LiTFSI/$Li_{6.75}La_3Zr_{1.75}Ta_{0.25}O_{12}$, the highest conductivity (5.2×10^{-4} S cm^{-1} at 30 °C, $t_{Li+} = 0.75$) was obtained at a 5% content of $Li_{6.75}La_3Zr_{1.75}Ta_{0.25}O_{12}$; an increase in the amount of $Li_{6.75}La_3Zr_{1.75}Ta_{0.25}O_{12}$ to 9% was followed by aggregation of dopant nanoparticles and a decrease in conductivity.[300]

It is assumed that in heavily doped systems the dopant particles can contribute largely to ion transfer.[290, 300, 302, 303] However, only a few experimental proofs are available. For instance, a ^{6}Li NMR study showed that Li-ion transport in the polymer electrolyte PEO/LiTFSI containing 50 mass % $Li_7La_3Zr_2O_{12}$ mainly occurs through the ceramic phase $Li_7La_3Zr_2O_{12}$ rather than the PEO phase or the PEO/$Li_7La_3Zr_2O_{12}$ interface.[300] More recently, having measured the dependence of the properties of PEO/$Li_7La_3Zr_2O_{12}$/LiTFSI on the content of $Li_7La_3Zr_2O_{12}$, it was concluded that an increase in the proportion of the inorganic component from 20 mass % to 50 mass % causes the ion mobility to decrease and the cation transport pathways to gradually change from the PEO phase to a network of $Li_7La_3Zr_2O_{12}$ particles.[292] Besides, a positive effect of dopant nanoparticles on the conductivity[49, 301] gives grounds to assume high conductivity of the ceramics/polymer interface.[304]

Composites containing more than 20 mass % of inorganic phase are also studied intensively, although their conductivity increases to a lesser extent or even slightly decreases on doping. Usually, these studies are aimed at improving the mechanical properties, thermal stability and stability to metallic anode.[290, 297, 302, 305–307] In some cases, an increase in the content of dopant leads to increased selectivity of ion transfer owing to reduction of anion mobility as a result of the interactions with the dopant surface. For instance, the PEO/LiTFSI electrolyte containing 40% of Al-doped $Li_{6.75}La_3Zr_{1.75}Ta_{0.25}O_{12}$ was characterized by a relatively high conductivity of 1.12×10^{-5} S cm^{-1} at 25 °C and a selectivity (t_{Li+}) of 0.58 (*cf.* 0.37 and 0.38 for PEO/LiTFSI and PEO/LiTFSI containing 20 mass % of the same dopant, respectively).[297]

The conductivity of composite electrolytes is also influenced by the shape and spatial orientation of inorganic articles. The use of nanowires, nanoplates, nanotubes or 3D porous structures as dopants favours the formation of extended ion transfer channels and allows one to obtain high-conducting materials.[290, 295, 296, 298, 308, 309] The ionic conductivity of electrolytes PEO/$LiClO_4$/40 vol.% $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$ with 200–500-nm phosphate particles randomly distributed in the PEO matrix or connected in chains oriented normal to the electrolyte plane was 1.4×10^{-6} and 6.8×10^{-6} S cm^{-1}, respectively.[303] An electrolyte based on a porous network of $Li_{6.4}La_3Zr_2Al_{0.2}O_{12}$ nanowires filled with PEO/LiTFSI ($Li_{6.4}La_3Zr_2Al_{0.2}O_{12}$ content was about 25 mass %) had a conductivity of 2.5×10^{-4} S cm^{-1} at room temperature.[290] On going from $Li_7La_3Zr_2O_{12}$ nanoparticles to the $Li_7La_3Zr_2O_{12}$ nanowires (5 mass %) the conductivity of the electrolyte PAN/$LiClO_4$/$Li_7La_3Zr_2O_{12}$ increased tenfold to 1.31×10^{-4} S cm^{-1} ($t_{Li+} = 0.3$ at 20 °C) for the material doped with the nanowires.[295] The authors of that study emphasized that obtaining a conductivity higher than 10^{-4} S cm^{-1} at room temperature requires a combination of the necessary shape and conductive properties of nanoparticles. For instance, the conductivity of PAN/$LiClO_4$ containing 5 mass % of Al_2O_3 nanowires was 1.5×10^{-5} S cm^{-1}. However, this correlation is not always observed. Indeed, a study[310] of composites prepared by doping a gel polymer electrolyte based on (PVDF-HFP)–$(PEO)_n$/$LiN(SO_2C_2F_5)_2$ with low-conductivity particles of the composition $14\,Li_2O - 9\,Al_2O_3 - 38\,TiO_2 - 39\,P_2O_5$ or

$Li_{4-x}M_xSiO_4$ (M = Ca, Mg) revealed no significant dependence of conductivity on the nature of the dopant; the conductivity reached a value of nearly 10^{-4} S cm^{-1} at room temperature.

Composite electrolytes can contain not only inorganic particles, but also various organic polymer phases that differ from the polymer host. One of the best studied examples is cellulose-modified PEO.[311–313] Often, the mechanical strength of the modified polymer electrolytes is much higher than that of the unmodified electrolytes due to the presence of hydrogen bonds between cellulose OH groups and PEO ether groups.[196] However, this is accompanied by a decrease in the ionic conductivity due to the low dielectric constant of cellulose and its interaction with the backbone, which reduces the segmental mobility of polymer chains.[314, 315] Nevertheless, a cellulose-modified composite based on PPC demonstrated good mechanical strength and high conductivity (3.0×10^{-4} S cm^{-1} at 20 °C).[316]

Thus, preparation of composite polymer electrolytes is an efficient method for increasing the ionic conductivity. Other advantages of these materials include higher thermal stability, stability of the electrode/electrolyte interface and mechanical strength.[192, 290, 297, 302, 305–307] However, this is characteristic of certain systems only. The approach is also of interest for modification of gel polymer electrolytes.

6. Application of polymer electrolytes in Li-ion and Na-ion batteries

An ideal polymer electrolyte for metal-ion batteries should meet general requirements for electrolytes, of which the most important are high cation conductivity ($> 10^{-3}$ S cm^{-1}) and high transference number of the cation, which should be as close as possible to unity. In addition, it is desired that the polymer electrolyte be mechanically strong, behave as a binder between the electrolyte and electrode material and be elastic to prevent failure due to the change in the volume of the electrode material during the alkali metal intercalation–deintercalation cycle.[317–320] Table 3 presents the conductivities and cation transfer selectivities of different types of polymer electrolytes considered in Sections 3–5 of this review.

In spite of considerable progress in the development of polymer electrolytes (especially, Li-containing ones) a system that would meet the requirements for the ideal electrolyte is still unavailable. The conductivity and cation transfer selectivity of many polymer electrolytes remain insufficient for fabrication of high-capacity metal-ion batteries. Most polymer/salt systems exhibit bipolar conductivity, which leads to their polarization in electric field. As a consequence of concentration polarization, the battery resistance increases while the voltage and capacity decreases.

Table 3. Ionic conductivities and transference numbers of cations in different types of electrolytes considered in this review (T = 25 °C).

Electrolyte	σ /S cm^{-1}	t_+
Solid electrolytes		
Polymer/salt	10^{-7}–10^{-5}	< 0.5 [a]
'Polymer-in-salt'	10^{-5}–10^{-3}	~0.6–1
Composite	10^{-5}–10^{-4}	0.15–0.8
Membranes	~10^{-7}	~1
Gel polymer electrolytes		
Polymer/salt	~10^{3}	< 0.8
Composite	~10^{3}	0.4–0.6
Membranes	~10^{-4}–10^{-3}	~1

[a] At T > 60 °C.

Nevertheless, a number of polymer electrolytes demonstrate commercially acceptable room-temperature conductivity ($\geqslant 10^{-4}$ S cm^{-1}), which gives grounds to hope for rapid progress in this field. Various laboratory models for batteries have been described and tested.[25, 78, 120, 133, 142, 162, 163, 286, 321, 322] Certain polymer electrolytes were found to be promising for low-current-density systems.[59, 120, 133, 142, 321] The electrochemical stability of PEO-based electrolytes at potentials $\geqslant$4 V is high enough for many types of batteries, *e.g.*, lithium–sulfur, sodium–sulfur and Li/$LiFePO_4$ ones. Electrolytes that are stable at potentials > 5 V, for instance, those based on some polycarbonates or polymeric ionic liquids, can be treated as promising for systems with high-voltage cathodes.[163, 323] Compatibility with metallic anode is often achieved by optimizing (i) the chemical composition of the electrolyte, which favours the formation of stable conducting SEI, and (ii) the design of the battery.[115, 120, 324–326] As an example, good contact with a lithium electrode and the formation of thin SEI was achieved using a solid electrolyte prepared by *in situ* polymerization of 1,3-dioxolane containing dissolved LiTFSI in the presence of electrodes.[325]

Electrolytes based on PEO demonstrate conductivities $\geqslant 10^{-4}$ S cm^{-1} at temperatures above the melting point of crystallites (60–80 °C, see Table 1). Taking account of this fact, cells with such electrolytes are most often cycled on heating.[120, 286] For instance, a cell with a $LiFePO_4$ cathode, a Li anode and a composite electrolyte PEO/LiFSI/Al_2O_3 delivered a high capacity and demonstrated high efficiency (> 99%) and cycling stability (160 mA h g^{-1} during 10th cycle and 156 mA h g^{-1} during 50th cycle) under cycling at 0.1 C † at 70 °C.[120] Also, doping electrolytes with inorganic particles and a proper choice of the lithium salt allows one to minimize the SEI resistance. Indeed, a cell with a $Na_3V_2(PO_4)_3$ cathode, a Na anode and PEO/NaFSI doped with $Na_{3.4}Zr_{1.8}Mg_{0.2}Si_2PO_{12}$ as electrolyte was characterized by an initial discharge capacity of 106 mA h g^{-1} at 80 °C (the capacity loss during 120 cycles at 0.1 C was insignificant).[293] Batteries with $LiFePO_4$/Li electrodes and PEO-based solid polymer electrolyte for fixed-battery energy storage systems, small electric vehicles and electric buses have been available on the market since 2011.[49, 327] They are characterized by a contracted power of nearly 100 kW h kg^{-1}, a lifespan of 3000 to 4000 cycles, an internal operating temperature interval of 60–80 °C and a range of 140–280 km (for electric buses depending on the dimensions of the electric bus and the battery).[327]

Certain polymer/salt composite electrolytes including those based on PEO are characterized by a conductivity of 10^{-4} S cm^{-1} and more at nearly room temperature. Hence, they can be used at lower operating temperatures compared to most PEO-based electrolytes.[133, 142, 163, 322] As an example, the cycling stability of a cell with Li electrodes and PAN/$LiClO_4$ electrolyte doped with $Li_7La_3Zr_2O_{12}$ nanowires was more than 500 cycles under galvanostatic cycling at a current density of 50 μA cm^{-2} (current reversal in

† The n C current density corresponds to 100% charge of the battery after 60/n min.

5 min intervals) at 20 °C.[295] An electrolyte based on porous 3D $Li_{6.4}La_3Zr_2Al_{0.2}O_{12}$ nanofibre network and PEO/LiTFSI proved itself in preventing dendrite growth. At room temperature, a cell with this electrolyte and Li electrodes demonstrated stable operation during 500 and 300 h under cycling at a current density of 200 and 500 μA cm^{-2}, respectively.[290]

Highly concentrated systems based on carbochain polymers and polycarbonates ('polymer-in-salt' electrolytes) are characterized by reasonably high, mainly cationic conductivity (10^{-5}–10^{-3} S cm^{-1}) and selectivity at room temperature.[96, 123, 124, 328, 329] However, high conductivity of highly concentrated carbochain polymers ($\sigma \approx 10^{-4}$–10^{-3} S cm^{-1}) is difficult to reproduce and these metastable materials are of limited use since methods for controlling the formation of the percolation network of ionic associates in them are unknown.[68, 96] Studies on highly concentrated electrolytes based on polycarbonates also face problems with cycling of cells containing the best-conducting materials; they are associated with poor mechanical characteristics and(or) metastable state of the electrolytes at high concentrations of the dissolved salt.[127, 162, 322] For instance, a study on the system $(PTMC)_n$/NaFSI [322] revealed a maximum conductivity of 5×10^{-5} S cm^{-1} at 25 °C for the composition $(PTMC)_1$/NaFSI; however, cycling of a cell with this electrolyte and a $Na_xFe[Fe(CN)_6]$ cathode and a metallic Na anode demonstrated a significant decrease in capacity, which was explained by instability and an increase in the resistance of the low-conducting SEI formed on the anode material. The authors of that publication also reported stable operation of a $Na/Na_xFe[Fe(CN)_6]$ cell with an electrolyte containing a lower concentration of the salt $(PTMC)_5$/NaFSI under cycling; namely, the cell delivered an average discharge capacity of nearly 90 mA h g^{-1} during 80 cycles at 0.2 *C* and 60 °C.

Various examples of successful application of modified materials based of polycarbonates are available.[49, 127, 162, 300, 316, 322] A mechanically stable electrolyte PEC/80 mass % LiFSI for Li-ion batteries was prepared[127] by supporting on macroporous polyimide substrate; however, a small conductivity loss (about 10^{-5} S cm^{-1} at 30 °C) was also reported. The discharge capacity of a cell with this electrolyte and $Li/LiFePO_4$ electrodes was nearly 120 mA h g^{-1} at 0.05 *C* during 30 cycles at 30 °C. In another study [57] the discharge capacity of a cell with a $LiFePO_4$ cathode, a Li anode and a modified electrolyte based on the poly(ε-caprolactone)–PTMC copolymer doped with LiTFSI was as high as about 120 mA h g^{-1} (>80% of the contracted capacity) at a charge-discharge rate of 0.02 *C* and about 55 mA h g^{-1} at 0.1 *C* (T = 22°C).[57] The capacity remained almost unchanged after more than 70 cycles. A cell with the PPC/LiTFSI electrolyte modified with $Li_{6.75}La_3Zr_{1.75}Ta_{0.25}O_{12}$ nanoparticles and $LiFePO_4/Li$ electrodes operated in a wide temperature range from 0 to 160 °C at charge–discharge rates to 5 *C* and demonstrated the ability to undergo long-term cycling. For instance, the discharge capacity was about 125 mA h g^{-1} at 1 *C* and 20 °C, being equal to 95% of the initial capacity after 200 cycles. A cell with the same electrolyte and $LiFePO_4/Li_4Ti_5O_{12}$ electrodes was characterized by a discharge capacity of 123, 110 and 80 mA h g^{-1} at 0.1 *C*, 1 *C* and 5 *C*, respectively; the capacity retention at 1 *C* was 95% after 800 cycles at room temperature.[300]

Tests of a cell with $LiFePO_4/Li$ electrodes and cellulose-modified composite electrolyte based on PPC/LiTFSI ($\sigma = 3.0 \times 10^{-4}$ S cm^{-1} at 20 °C) revealed a discharge capacity of 142 and 116 mA h g^{-1} at 0.1 *C* and 0.5 *C*, respectively, at 20 °C. The discharge capacity after 1000 cycles of operation at 0.5 *C* was 95% of the initial value. The cell heated to 120 °C also delivered relatively high capacity at higher charge–discharge rates, *viz.*, 139, 114 and 74 mA h g^{-1} at 1 *C*, 3 *C* and 5 *C*, respectively. The discharge capacity after 500 cycles of operation at 120 °C at 3 *C* was 95% of the initial value.[316]

The conductivity of polymer/salt systems containing plasticizer additives reaches 10^{-3} S cm^{-1} and more.[157, 160] To date, a variety of gel polymer/salt electrolyte batteries for portable devices are available.[216] However, recall that high-conductivity gel polymer electrolytes contain large amounts of liquid phase and gas release in them is possible at 50–60 °C (for plasticization with organic carbonates and ethers), which reduces the safety of batteries. A decrease in the mechanical strength of electrolytes can favour dendrite growth.[40, 48, 49, 82] The following methods are used to improve the safety and to extend the operational life of gel polymer electrolytes:

— the use of ionic liquids instead of organic solvents,[40, 177, 330–332]

— doping with inorganic particles [40, 168, 330–335] and

— support of electrolytes on porous matrices.[142, 336]

In this context, good examples are provided by cells with $LiFePO_4/Li$ and $Na_{0.9}[Cu_{0.22}Fe_{0.30}Mn_{0.48}]O_2/Na$ electrodes and hybrid gel polymer electrolytes prepared by polymerization of 1,4-bis[3-(2-acryloyloxyethyl)imidazolium-1-yl]-butane)bis[bis(trifluoromethane)sulfonimide] dissolved in the ionic liquid bis(trifluoromethane)sulfonimide-1-ethyl-3-methylimidazolium [(EMI)TFSI] containing the salt MTFSI (M = Li, Na) as additive. The electrolytes are supported on a porous membrane to improve the mechanical properties.[142] The Li cell was characterized by a capacity of 162 and 81 mA h g^{-1} at 0.1 *C* and 1 *C*, respectively, and stable operation during more than 100 cycles (the capacity retention at 0.1 *C* was 97.7%). The sodium cell was characterized by a capacity of 101 and 60 mA h g^{-1} at 0.1 *C* and 1 *C*, respectively, and the capacity retention at 0.1 *C* was 85.5% after 100 cycles.[142] A $Na_3V_2(PO_4)_3/Na$ cell with composite gel polymer electrolyte based on Al_2O_3 nanofibres and P(VDF–HFP)/$NaClO_4$ was characterized by a discharge capacity retention of 95% (nearly 100 mA h g^{-1}) at 1 *C* after 1000 charge–discharge cycles at 25 °C.[335]

Cation-exchange membranes provide high selectivity of cation transport. A number of reviews on application of these systems as electrolytes for lithium-ion batteries and batteries with Li anode have been reported.[45, 48, 49, 82, 337] Most dry cation-exchange membranes exhibit low conductivity and thus low cycling rates of batteries (<0.2 *C*) at elevated temperatures (>60°C).

Rapid selective cation transfer ($\sigma \approx 10^{-4}$–10^{-3} S cm^{-1} at room temperature, $t_{M+} \approx 1$) is possible using gel polymer electrolytes based on cation-exchange membranes. Systems that meet the requirements shown in parentheses are promising for application in metal-ion batteries including those with metallic anode.[48, 82, 338, 339] However, despite obvious advantages of selective cation transfer and thus the absence of concentration polarization, solvated membranes can have the same drawbacks as the gel polymer electrolytes based on polymer/salt systems. The drawbacks originate from the presence of the liquid phase. Note that the content

of the liquid phase in the gel polymer membranes is much lower than in liquid electrolytes.

A $LiFePO_4$/Li cell with an electrolyte based on a blend of P(VDF-HFP) and lithiated poly[(4,4′-(9-fluorenylidene)-dianiline-*co*-4,4′-dicarboxyldiphenylsulfonimide)] soaked with EC–DMC mixture ($\sigma = 6.2 \times 10^{-4}$ S cm^{-1} at room temperature) was characterized by a discharge capacity of 120 and 85 mA h g^{-1} at 1 *C* and 4 *C*, respectively.[338] No decrease in battery performance was observed after continuous operation during more than 140 cycles at 1 *C*. One more polymer electrolyte ($\sigma = 1.5 \times 10^{-3}$ S cm^{-1} at room temperature) for a Li/$LiFePO_4$ cell was prepared[340] by copolymerization of lithium bis(allylmalonato)borate and pentaerythritol tetrakis(2-sulfanylacetate) in γ-butyrolactone as plasticizer. The discharge capacity was 155 and 86 mA h g^{-1} at 0.2 *C* and 5 *C*, respectively. The capacity retention after more than 500 cycles was 91.2% of the initial value (124 mA h g^{-1} at 1 *C*). A highly conducting polymer electrolyte based on copolymer of [(4-styrenesulfonyl)(fluorosulfonyl)imide] lithium, pentaerythritol tetrakis(2-sulfanylpropionate) and pentaerythritol tetraacrylate blended with PVDF and plasticized with EC–DMC ($\sigma = 5.81 \times 10^{-3}$ S cm^{-1} at 28 °C) demonstrated a stable discharge capacity of 140 mA h g^{-1} on cycling at 0.2 *C* during more than 230 cycles.[262]

Tests of Li/$Li_4Ti_5O_{12}$–Li/$LiFePO_4$ cells with lithiated Nafion membranes solvated by PC at 0.05–1 *C* revealed stable operation durng more than 50 cycles.[341] The discharge capacities decreased with increasing charge–discharge rate and recovered at 0.05 *C*. The discharge capacity of the full cell with $Li_4Ti_5O_{12}$/$LiFePO_4$ electrodes and Nafion-Li/PC as electrolyte was 93 mA h g^{-1} for the first cycle, gradually decreased to 70 mA h g^{-1} during 25 cycles and then remained almost unchanged for the next 50 cycles at a Coulombic efficiency of 99%. The relatively low capacity values were explained by improper component ratio of the electrode materials rather than degradation of cell's materials.[341]

The possibility to manufacture a sodium battery with a polymer electrolyte based on a Nafion-Na/EC–PC membrane ($\sigma \approx 7 \times 10^{-4}$ S cm^{-1} at 30 °C), a $Na_3V_{1.9}Fe_{0.1}(PO_4)_3$/C positive electrode and a Na anode was reported.[342] The room-temperature specific capacity was about 100 mA h g^{-1} under cycling at 0.1 *C*. Taking into account the content of carbon (8.9 mass %), which shows no electrochemical activity in the range of sodium–vanadium phosphate cycling potentials, the discharge capacity was close to the theoretical value. To provide better contact between electrodes and electrolyte, electrode materials were supported on Nafion membranes used as binder instead of conventional insulator PVDF.[251,341–343]

High conductivity ($> 10^{-3}$ S cm^{-1}) in materials based on Nafion membranes was achieved at high degrees of solvation by mixtures containing amide solvents (DMA, DMF).[232,342] The absence of phase transitions enables operation of the batteries based on Nafion membranes in a wide temperature range including negative temperatures. But in spite of considerable advances certain problems are still to be solved. They are first of all associated with insufficient stability of the batteries. In particular, the capacity of sodium batteries with electrolytes based on DMA-intercalated Nafion membranes decreases during cycling due to the interaction of DMA and the metallic Na anode.[342] Compatibility of this type of membranes with electrode materials deserves further studies.

Application of polymer electrolytes in Li-S and Na-S batteries is promising. In this case, there is a severe problem associated with the formation of alkali metal polysulfides of different composition and different solubility in liquid electrolytes. Shuttle-like migration of polysulfides between electrodes causes self-discharge of the battery. The problem can be solved using polymer/salt electrolytes[49,344,345] and cation-exchange matrices,[49,346] in particular, solvated Nafion membranes for both lithium[347] and sodium systems.[348,349] For instance, a Li-S battery with a Nafion-Li/PC electrolyte was tested at 70 °C and delivered a discharge capacity of 1073 mA h g^{-1} at 0.05 *C* and 895 mA h g^{-1} at 1 *C*. The capacity retention at 1 *C* was 89% after 100 cycles.[251] The discharge capacity of a Na-S battery with a Nafion-Na membrane as electrolyte was as high as 800 and nearly 680 mA h g^{-1} at 0.1 *C* and 0.2 *C*, respectively.[348] Cycling of the cell at 0.2 *C* revealed no capacity decrease during 45 cycles. It follows that migration of alkali metal polysulfides between electrodes was efficiently suppressed.

A polymer electrolyte prepared by grafting lithium 4-aminophenylsulfonyl(trifluoromethanesulfonyl)imide onto poly(ethylene-*alt*-maleic anhydride) followed by blending with PVDF-HFP ($\sigma = 2.2 \times 10^{-4}$ S cm^{-1} at 25 °C for the blend) was then plasticized with an EC–DMC mixture.[346] The gel polymer electrolyte thus obtained was used as electrolyte for a Li-S battery characterized by a discharge capacity of 502 mA h g^{-1} at high cycling rates (2 *C*). The cell cycled at 1 *C* gave a stable capacity of 780 mA h g^{-1} after 1000 cycles, whereas the capacity of a cell with 1 M $LiPF_6$/EC–DMC as liquid electrolyte decreased from 775.2 mA h g^{-1} to 443.3 mA h g^{-1} after 1000 cycles, which corresponds to a capacity retention of 57%.

Finally, considerable advances in the application of polymer electrolytes in metal-ion batteries have been made. Research activity in this field was focused on improvement of the safety and operational stability of the batteries. Many polymer electrolyte batteries demonstrated good results and stability under actual operating conditions. However, most laboratory experimental tests were characterized by relatively low numbers of cycles.

7. Conclusion

Intensive recent research on the synthesis of polymer electrolytes for lithium- and sodium-ion batteries is driven by the desire to create a safe and stable solid-state battery. A number of electrolytes with a conductivity of at least 10^{-4} S cm^{-1} at 25 °C were prepared. Considerable advances have been made in the synthesis of solid polymer/salt electrolytes and gel polymer/salt electrolytes (including those plasticized with ionic liquids), and also composite and membrane electrolytes intercalated with aprotic solvents. However, at present it is difficult to specify a particular avenue of research as the most promising one. Each type of electrolytes has its advantages and drawbacks.

Solid polymer/salt electrolytes offer the advantage of being free from liquid organic components and thus more flame- and explosion-proof. However, most PEO-based electrolytes are still used in batteries at elevated temperatures. From the standpoint of ionic conductivity and selectivity of cation transfer, highly concentrated electrolytes based on polycarbonates seem to be the most promising polymer/salt electrolytes. In some cases low mechanical strength of gel electrolytes including highly conducting ones

($\sim 10^{-3}$ S cm^{-1}) can be improved by preparing composites doped with inorganic nanoparticles; certain composite systems demonstrated high cycling stability (up to 1000 cycles). However, in spite of considerable advances in the development of polymer/salt electrolytes including gel polymer/salt electrolytes, selectivity of cation transfer in these systems is still the most severe problem.

Materials based on cation-exchange membranes are a promising class of polymer electrolytes. These systems possess only cationic conductivity since anions are covalently bound to the polymer matrix. The ionic conductivity of such materials can be increased by increasing the degree of delocalization of the negative charge over functional groups of the cation-exchange membrane by introducing electronegative substituents and by solvating the membrane matrix in organic solvents. As a result, the conductivity of certain modified gel polymer electrolytes based on cation-exchange membranes exceeds a value of 10^{-3} S cm^{-1}. Optimization of the membranes and the composition of organic solvents can lead to significant extension of the range of operating temperatures and the application fields of batteries based on the electrolytes in question.

Currently, gel polymer electrolytes based on cation-exchange membranes are studied intensively and the available results of cycling of laboratory model batteries undoubtedly deserve attention. Obvious advantages of this type of polymer electrolytes give grounds to hope for rapid progress of studies on their synthesis and commercialization.

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