Russian Chemical Reviews **71** (4) 329 – 346 (2002) © 2002 Russian Academy of Sciences and Turpion Ltd

DOI 10.1070/RC2002v071n04ABEH000706

The state-of-the-art and prospects for the development of rechargeable lithium batteries

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Abstract. The state-of-the-art of investigations into the development and perfection of the most promising class of chemical power sources, namely, rechargeable lithium batteries, is considered. The main problems of designing the batteries with a metallic lithium electrode are formulated and the use of alternative negative electrodes is substantiated. Special attention is paid to the studies dealing with the principles of the performance of lithium-ion batteries as well as the key directions for the perfection of these devices, which mainly concern the elaboration of new materials for lithium-ion batteries. A separate section is devoted to the consideration of polymeric electrolytes for lithium and lithium-ion batteries. The bibliography includes 390 references.

I. Introduction

A new type of chemical power source, namely, lithium cells with aprotic electrolytes appeared for the first time in the early 1970s and later gained wide acceptance.[1, 2] Thus, a long-standing idea of scientists, *viz*., to build a chemical power source with the most active reductant, *i.e*., an alkali metal, was materialised. The use of such a reductant allowed one to enhance both the operational voltage of a power source and its energy density.

In contrast to primary cells (one-shot cells) with lithium anodes, which were developed relatively quickly and successfully and are used now as the power sources in portable devices of every-day and special equipment, the history of the development of rechargeable lithium batteries has been very dramatic.[3, 4]

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Received 10 December 2001
Uspekhi Khimii **71** (4) 378 – 398 (2002); translated by T Ya Safonova

II. The main problems in the development of rechargeable batteries with lithium anodes.

Primary cells designed for operation under ordinary conditions can be divided into two classes: cells with liquid and solid cathodes. For liquid cathodes-oxidants, thionyl chloride and sulfur dioxide, which simultaneously form the basis of the electrolytes, are used most often. Exhibiting high values of power and energy densities and operating in a wide range of temperatures, the cells with liquid oxidants represent, however, a fire hazard and are explosive and, hence, are used only in special equipment. For cells with solid cathodes, oxides of manganese, copper and certain other metals serve as the active cathodic materials, together with iron sulfide and fluorocarbons. Electrolytes in such cells represent solutions of certain lithium salts (perchlorate, hexafluoroarsenate, tetrafluoroborate, *etc*.) in organic nonaqueous aprotic solvents (propylene carbonate, dimethoxyethane, tetrahydrofuran, γ-butyrolactone and various mixtures). Depending on the cathodic material type, the working voltage of the cells can approach 3 V (for manganese dioxide and fluorocarbons) or 1.5 V (for copper oxide and iron sulfide); in the latter case, lithium cells and conventional cells based on the manganese dioxide – zinc system are interchangeable. It is the primary cells with aprotic electrolytes that are considered as the analogues of rechargeable (secondary) cells.

The reactions which proceed in primary cells with aprotic electrolytes are similar to those in secondary cells. In both types of cells, the discharge involves the same processes, *viz*., the anodic dissolution of lithium and the cathodic insertion of lithium into the lattice of the positive electrode material. The charging in a secondary cell represents the reverse processes. The materials for positive electrodes on which the cathodic insertion and anodic extraction (in other words, cathodic intercalation and anodic deintercalation) of lithium proceed reversibly were found back in the late 1970s. Titanium and molybdenum disulfides can serve as examples of such compounds.

The main problem arisen concerns the choice of the negative electrode material. Its discharge, *i.e*., cathodic deposition of lithium poses complications typical of electroplating practice. It is known that the lithium surface in aprotic electrolytes is coated with a thin passive film (its thickness does not exceed several nanometres) as a result of chemical reactions with the electrolyte components, namely, the organic solvent and anions. This film has the properties of a solid electrolyte with conduction in lithium

ions and adequately protects lithium from the reactions with the electrolyte (*i.e.*, prevents self-discharge).

On the cathode, the deposition of lithium results in the formation of dendrites and, in many cases, the film formed during charge–discharge cycles envelopes individual lithium microparticles preventing their electric contact with the support. Such a phenomenon called 'encapsulation' manifests itself in the fact that every charging step removes a part of lithium from the further operation. That is why, the secondary cells with metallic lithium electrodes should contain lithium in amounts exceeding (from 4- to 10-fold) its stoichiometric value; hence, the specific capacity decreases from the theoretical value of 3828 to 380–800 mA h g^{-1}. Moreover, the formation of dendrites increases the probability of short-circuiting and, hence, makes the cells inflammable and explosive.

Various methods for the treatment of the cathodic surface and a search for additives to the electrolyte that would prevent the dendrite formation during cathodic deposition of lithium yielded positive results. For example, it was shown that, being added to a propylene carbonate electrolyte, even trace amounts of hydrogen fluoride favour lithium deposition as a dense fine-grain continuous layer rather than in the form of dendrites.[5,6] The beneficial effect achieved by treating the lithium surface with carbon dioxide (or, simply, by adding either CO_2 as such or substances evolving CO_2 into the electrolyte upon their reactions with lithium) has been repeatedly mentioned.[7,8] It was suggested[9] to modify the lithium surface by applying monomolecular layers of non-ionic surfactants, particularly, dimethyl ether of poly(ethylene glycol) and a dimethylsiloxane–propylene oxide copolymer. Electrolytes that prevent the dendrite formation even in the absence of additives were also found. For example, a solution of lithium hexafluoroarsenate in 1,3-dioxolane (this solution also contained tributylamine which prevents dioxolane polymerisation).[10–12]

III. Practical developments in the field of metallic lithium cells.

Despite the fundamental obstacles in the development of secondary cells with metallic lithium electrodes, attempts were made to establish their commercial production. Thus in 1987, Moli Energy Ltd (Canada) started serial production of AA-size batteries (which corresponds to the Russian size of 316)† with positive electrodes made of molybdenum disulfide. The cells possessed the following characteristics: an initial voltage of 2.3 V, a capacity of 600 mA h for a discharge at a current of 0.2 A up to the final voltage of 1.3 V. In certain cases, the discharge to the final voltage of 1.1 V allowed one to reach a discharge capacity of 800 mA h. According to the reports by manufacturers, their cells had a cycle life of several hundred charge–discharge cycles; however, these results were disputed by some experts and consumers. In fact, a cycle life of 100 charge–discharge cycles could be claimed. In 1989, a modernised version of a secondary cell was developed which contained a positive electrode of molybdenum sulfide with a composition of Mo_6S_8. This cell had a higher discharge voltage (from 2.3 to 1.8 V) and a higher capacity (up to 1000 mA h) and allowed a high-current discharge (up to 1 A).

The characteristics of the secondary cells fabricated by Moli Energy Ltd could have been considered adequate even despite a considerable voltage decrease during the discharge and a short real cycle life, but the reliability of the cells proved to be insufficient. In the summer of 1989, incidences of ignition of primary lithium cells were observed, as well as failures of the secondary cells produced by this firm, which made them stop the production.

At the Jet Propulsion Laboratory of the California Institute of Technology (USA), secondary cells with positive electrodes of titanium disulfide have been developed; however, no attempt has been made to organise their serial production mainly due to their low cycle life, namely, 100–200 charge–discharge cycles. The same situation was observed with the cells developed by Honeywell, Eveready Battery Co. Inc. (USA) and the United Design and Technology Bureau 'Orion' at the Novocherkassk Polytechnical Institute (Russia). Engineers of Matsushita Electric Industrial Co. (Japan) have developed AA-size rechargeable batteries of a higher quality using manganese dioxide as the active substance for positive electrodes. The batteries had a discharge voltage in a range from 3.2 to 2.0 V and a capacity of 800 mA h at the beginning of cycling and 600 and 450 mA h after 60 and 200 charge–discharge cycles, respectively.

At present, Tadrian (Israel) is engaged in the development of rechargeable batteries with matallic lithium electrodes; however, the prospects of their application are still vague. It was reported[13] that, for AA-size cells, the gravimetric power density of 125–140 W h kg^{-1} and the volumetric power density of 280–315 W h dm^{-3} at a service life of 250 full depth charge–discharge cycles were achieved.[13] [The depth of discharge (dod) or the cycling depth of a battery is the capacity fraction realised during the discharge from the total capacity designed into a rechargeable battery.] The reliability of these cells was not confirmed, but it was reported that explosions are ruled out even for substantial overcharges. However, in certain cases, the cells mildly leaked (without explosions) due to overheating.

IV. Materials alternative to metallic lithium

The attempts to solve the problems associated with the use of metallic lithium in negative electrodes involved substitution of lithium alloys for lithium. Lithium–aluminium alloys were assumed to be the most promising candidates. On such an electrode, the lithium concentration decreases during the discharge (lithium is etched out of alloys) and increases during the charge. The chemical activity of lithium in an alloy is somewhat lower as compared with that of metallic lithium; hence, the potential of an alloy-based electrode is more positive (by ~0.2–0.4 V) than the potential of an electrode of pure lithium. This results, on the one hand, in a decrease in the working voltage and, on the other hand, in a weakening of the alloy interaction with the solvent, *i.e.*, reduces the probability of self-discharge.

Disk-shaped rechargeable batteries of the VL 2020 model developed by Matsushita Electric Industrial Co. involved negative electrodes made of a lithium–aluminium alloy and positive electrodes of vanadium oxide. Such batteries were characterised by a rated capacity‡ of 20 mA h being discharged from 3.2 to 2.0 V, their cycle life was ~1000 charge–discharge cycles for a 10% dod and ~450 cycles for a 20% dod. At the Jet Propulsion Laboratory of the California Institute of Technology (USA), specimens of cells were built with advanced characteristics: their cycle life reached 600 charge–discharge cycles at 50% dod.

Indeed, the small dod values typical of these batteries make their specific characteristics inferior as compared with secondary cells with lithium electrodes. A principal drawback of lithium–aluminium alloys consists in the fact that they change substantially their specific volumes during the cycling. A deep discharge can result in embrittlement and crumbling of the electrode. That is why, no further progress was observed in the field using lithium–aluminium alloys as the material for negative electrodes.

† In Russia, the sizes of cylindrical cells may be designated in accordance with three types of nomenclature: the GOST (State Standard) (three-digit numbers: 283, 286, 314, 316, 373, *etc.*), the recommendations by the International Electrotechnical Commission (R06, R03, R4, R6, R20, *etc.*) and the USA nomenclature (AAA, R, AA, D, *etc.*). Thus a cell with a diameter of 14.5 mm and a height of 50.5 mm may be designated as AA, 316 and R6; a cell of a diameter of 34.2 mm and a height of 61.5 mm may be designated as D, 373 and R20. Tables comparing different designations of cell sizes are available (*e.g.*, in Ref. 2, p. 216).

‡ The rated capacity is a capacity realised in a 5 h discharge to a final voltage of 2.5 V.

Lithium alloys with heavy metals (such as the Wood's alloy) change their specific volumes during cycling to a lesser extent as compared with lithium–aluminium alloys. Matsushita Electric Industrial Co. has developed several versions of secondary cells with electrodes based on lithium alloys with heavy metals. Specific characteristics of these batteries were very low, and these alloys were considered to be of little promise.

V. Lithium-ion rechargeable batteries

1. General information

The publications reporting the secondary cells with negative electrodes of carbon materials developed in Japan marked a revolution in the field of rechargeable lithium batteries.[14—17] Carbon was shown to be a very convenient matrix for intercalation of lithium. The specific volumes of many graphitised materials changed by no more than 10% upon insertion of sufficiently large amounts of lithium.[18]

The potential of carbon electrodes which contain moderate amounts of intercalated lithium can be 0.5–0.8 V more positive than the lithium electrode potential. To make the cell's voltage sufficiently high, Japanese researchers used cobalt oxide as the active material for positive electrodes. The potential of lithiated cobalt oxide was ~4 V *vs.* lithium electrode; the working voltage of the cell was 3 V.

During the discharge of this cell, lithium is deintercalated from the carbon material (on the negative electrode) and is intercalated into the oxide (on the positive electrode). The charge involves the reverse processes. Thus, the system contains no metallic (zero-valent) lithium, and its charge and discharge processes simply involve the transfer of lithium ions from one electrode to another. These rechargeable batteries were named lithium-ion,[14] 'rocking-chair' [19] and 'swing' [20] cells.

Figure 1 shows the scheme of performance of a lithium-ion battery. On the left, a negative graphite electrode is shown. Its structure is characterised by the presence of layers (conditionally shown as hexagonal fragments) between which lithium ions (black points) can be inserted. On the right, the positive electrode of lithium manganese spinel with a structure that can intercalate lithium ions is shown. Lithium salts in non-aqueous solvents are used as the electrolyte. During the charging of the cell, in the external circuit, an electronic current flows from the positive electrode to the negative one, whereas inside the cell, an ionic current flows also from the positive electrode to the negative one.

Since the appearance of first publications on the development of lithium ion batteries,[14–17] active research into the intercalation of lithium into carbon and the other materials commonly used for the positive electrodes has started. To date, the publications on this subject number in the hundreds and involve several reviews.[19,21–28]

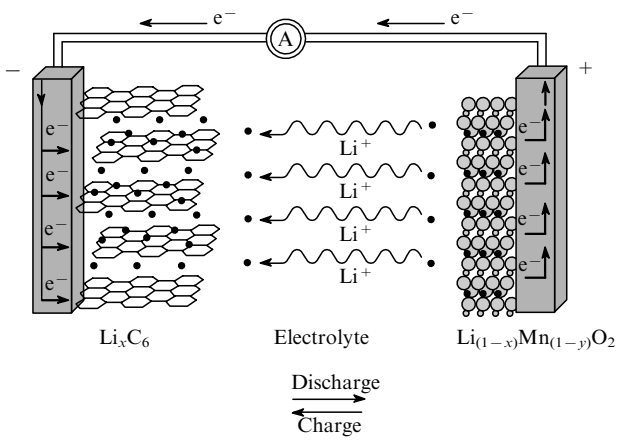


Figure 1. A scheme of performance of lithium-ion rechargeable batteries.

2. Examples of lithium-ion batteries

In 1991, Moli Energy Ltd elaborated the specimen of lithium-ion batteries shaped as disks (coins).[29] A cell of the 1225 size § had a capacity of ~7 mA h and a cycle life of ~300 charge–discharge cycles at a discharge current of 1 mA and a charge current of 0.5 mA.

Of Japanese firms, the leading position in the production of lithium-ion cells belongs to Sony which produces lithium-ion cells of various types, not only coin cells but also cylindrical ones of a spiral design and prismatic cells. Its annual production exceeds 10 million cells.[30] Sanyo Electric Co. holds the second position. Matsushita Electric Industrial Co. also has a large-scale production. In addition, six to eight other Japanese firms have just entered the market of lithium-ion batteries.

Since 1994, Sony has arranged the production of rechargeable batteries with sufficiently stable characteristics. The cells of AA size (according to Japanese nomenclature, US 14500) with a weight of 19 g, a rated capacity of 500 mA h at a voltage of 3.6 V are most representative. The manufacturer guarantees their performance in temperature ranges from −20 to +60 °C (discharge) and from 0 to +45 °C (charge). The energy density of these cells was ~95 W h kg^{-1} or 222 W h dm^{-3}. Cells of larger sizes had somewhat higher energy densities: *e.g.*, for cells of size 16 630 and 18 650 the energy densities were 105 and 126 W h kg^{-1} (or 250 and 290 W h dm^{-3}), respectively. Under the usual storage conditions, the self-discharge of the cells was ~10% in three months.[21]

The greatest rated capacity equal to 2800 mA h was demonstrated by a cylindrical cell of the size 26 650 weighing 83 g.

A discharge under a 1 h high-current mode reduced the capacity of Sony cells only insignificantly. The manufacturer guarantees cycle life of 500 charge–discharge cycles at only a 20% capacity fade.

In Japan, in addition to the development of lithium-ion cells of small sizes, attention has focused on elaboration of large-size rechargeable batteries, which can be used for both electrical vehicles and load distribution between autonomic nets. Since 1992, the studies have been carried out in accordance with the 'New Sunshine' program, which was intended to be accomplished in ~10 years with a total financing of ~$140 mln (USA). This programme scheduled the development of two versions of rechargeable cells, *viz.*, batteries with medium energy densities (up to 140 W h kg^{-1}) designed for long-term service (the cycle life of 3500 charge–discharge cycles) and batteries intended for a short cycle life (500 charge–discharge cycles) but displaying enhanced energy densities (up to 180 W h kg^{-1}).[31,32]

In other countries, the industrial output of lithium-ion batteries ranks far below that in Japan; however, certain companies intend to substantially increase the production of these secondary cells.

In the USA, the engineers of Rayovac Corp. have developed specimens of both coin and cylindrical cells.[22] Coin cells of the 1225 size were characterised by energy density of 35 W h kg^{-1} or 115 W h dm^{-3}. These characteristics rank substantially below those of the cylindrical cells produced by Sony, which is explained by the fact that the effectiveness of using the cell's mass and volume are different for small and large batteries (the share of casings and other structural elements in the cell's total weight is higher in coin cells as compared with cylindrical cells). The monthly self-discharge in these cells is ~5%, which is comparable with the characteristics of Japanese cells. Engineers of Rayovac

§ The designations of sizes of coin cells comprise the numbers that signify their diameters (in millimetres) and heights (thickness, in tenths of a millimetre). For instance, a cell of the 1225 size has a diameter of 12 mm and a thickness of 2.5 mm.

Corp. intend to organise the production of prismatic cells with an energy density approaching ~ 130 W h kg^{-1}. Being designed for a long-term discharge (and charge) by small currents, the first version of these cells should demonstrate an enhanced capacity. The second version is designed to have a lower capacity and withstand high-current discharges and charges.

Bellcore (USA) has undertaken great efforts in the development of lithium-ion batteries.[33, 34] Their cell prototypes of the AA size with a capacity of 380 mA h (*i.e.*, lower as compared with similar batteries made by Sony) were, however, capable of discharging in a 20-min mode¶ without substantial capacity loss ($< 20\%$).

Prismatic lithium-ion batteries developed by Yardney Corp. (USA)[35] exhibited capacities of 3 A h and energy densities of 87 W h kg^{-1} or 225 W h dm^{-3}.

SAFT (France) have completed the preliminary stage in the production of lithium-ion batteries to be used in both communication facilities and electric vehicles.[36, 37] The energy density of such a battery was 125–150 W h kg^{-1} with discharge by low currents and 90–135 W h kg^{-1} at a high-current discharge. In the latter case, the power density was 190–200 W h kg^{-1}. A decrease in the temperature to -30 °C resulted in a 20%–25% decrease in the capacity, the cycle life was assessed to be ~ 400 charge–discharge cycles.

Large-size lithium-ion batteries (capacity from 40 to 100 A h) are being elaborated by engineers of VARTA (Germany).[38] The characteristics of the developed prototypes are still not too high: the energy density of a cell with a capacity of 100 A h was 50–70 W h kg^{-1} for a 2 h discharge mode and ~ 30 W h kg^{-1} for a 30 min discharge mode. The capacity of the cells substantially decreased with cycling, which, apparently, is associated with the scale factor.

VI. The main problems in the development of lithium-ion batteries.

1. Materials for negative electrodes

The lithium-into-graphite intercalation compounds (layered graphite compounds) have been known for a long time (see, *e.g.*, Ref. 39). In the 1970–1980s, the reversible intercalation of lithium into graphite and certain other materials from lithium salt solutions in aprotic solvents was extensively studied.[40–46] The very first studies on the reversible lithium intercalation have shown that lithium intercalation into carbon materials is a complex process with the mechanism and kinetics largely dependent on the choice of carbon material and the electrolyte. Whereas the effect itself was quite evident, however, the results of different authors on its mechanism appear to be extremely contradictory. Even now, an important question remains open as to which properties (structure, electronic structure, the presence of impurities, *etc.*) of carbon materials determine the intercalation and deintercalation processes.

Despite the uncertainty mentioned above, certain simple relationships and phenomena have been established unambiguously. Thus it was found that, upon the first contact of an aprotic electrolyte with a carbon material (irrespective of its structure), the latter acquires a potential in the range from 2.5 to 3.5 V *vs.* lithium electrode, the value being determined by the presence of compounds with certain chemical groups (first of all, oxygen-containing groups) in the electrolyte. At a cathodic polarisation, the potential shifts to negative values, and slow intercalation of lithium begins. Simultaneously, the electrolyte is reduced (both the solvent and different impurities), and this reaction proceeds much more easily (at less negative potentials) on the surface of carbon material as compared with the metallic lithium surface. Being partially insoluble, the reduction products form a film of the carbon material surface. This film is similar in composition and properties to the passive film formed on the lithium surface. Thus, during the first charge, electricity is consumed in both lithium intercalation and passive-film formation. A completely formed film prevents direct contact between the electrolyte and carbon, thus virtually eliminating further reduction of the electrolyte.

The second undeniable fact is that the carbon material structure affects the mechanism of lithium intercalation. As a rule, intercalation of lithium into well pronounced graphite structures results in the formation of a thermodynamically stable compound, namely, LiC_6. In this compound, the lithium activity is equal to unity, *i.e.*, the potential of such a compound is equal to that of a lithium electrode. The majority of authors represent intercalation–deintercalation by the following equation:

$$x\,Li^+ + x\,e + 6\,C \rightleftharpoons Li_xC_6\,. \qquad (1)$$

The dependence of the Li_xC_6 potential on the degree of intercalation x (*i.e.*, the charge curve of a graphite electrode) was shown to have several almost horizontal steps corresponding to the following compounds: LiC_6, $Li_{0.5}C_6$, $Li_{0.33}C_6$, *etc.*[45] Intercalation of lithium into graphite structures occurs at negative potentials (the main part of lithium is intercalated at a potential more negative than 0.5 V), *i.e.*, the activity of lithium in such intercalates is sufficiently high. On the one hand, this is an advantage, because the cell voltage increases; however, on the other hand, this is a drawback, because the reduction of electrolytes on these intercalates proceeds more actively than on non-graphitised samples. Moreover, intercalation of lithium into graphite structures is often accompanied by co-intercalation of the solvent, which leads to swelling and exfoliation of graphite.

Intercalation of lithium into amorphous structures occurs at more positive potentials, as a rule, in the range from 0.9 to 0.0 V. In this case, x *vs.* potential plots represent smooth curves typical of uniform systems. Nongraphitised structures do not exfoliate during intercalation of lithium.

Numerous studies were devoted to elucidation of how the potential variation depends on the degree of intercalation x (thermodynamics of the intercalation process) (see, *e.g*, Refs 18, 29, 45–48). It was shown that the dependence of the activity of intercalated lithium on its content has a complex form, its mechanism still being a subject of speculation.

Different scientists tried to find a correlation between the structure of carbon materials and their abilities to intercalate lithium reversibly. This correlation is still not established conclusively. Controversial assumptions have been drawn on this subject. For instance, it was supposed[49] that reversible intercalation is possible exclusively into materials with the well pronounced graphite-type crystal structure and is unfeasible for amorphous materials. In contrast, it was also proposed[50] that lithium is intercalated only into amorphous materials. Probably, the optimum materials should possess amorphous matrices with mesophase inclusions, *viz.*, nuclei of graphite crystals. These materials are represented by various cokes, pyrographite and pyrolysis (carbonisation) products of different polymers. This assumption was confirmed by the results of studying the possibility of lithium intercalation into the same substances preliminarily pyrolysed at different temperatures. The optimal pyrolysis temperature was found to correspond exactly to the formation of the hypothesised mesophase materials.[51, 52]

The research practice employs various carbon materials, whereas in the industry only certain specific materials which ensure adequate characteristics of negative electrodes for lithium-ion cells are used. Of the latter, a material produced by Osaka Gas Co. (Japan) which is called mesocarbon microbeads (MCMB) was employed most extensively. This material is the product of pitch carbonisation carried out under certain temperature conditions.[53, 54] It was assumed that fibrous materials are also promising for fabrication of anodes.[55–59]

¶ A discharge with such a current that the total designed capacity is realised in 20 min.

Carbon materials (obtained by pyrolysis of certain organic substances, *e.g.*, poly(*p*-phenylene), phenol–formaldehyde resin, soluble phenol–formaldehyde resin and even sucrose) with the intercalation capacity exceeding 372 mA h g^{-1}, which corresponds to the LiC_6 limiting composition, have been described. Their real intercalation capacity could reach 600–700 mA h g^{-1} (see Refs 60–71).

Naturally, elucidation of the reason for such an enhanced capacity became a challenge for scientists. It was found that lithium ions intercalated into graphite can occupy different sites in the graphite lattice, *viz.*, in interstitials (proper intercalation), at the edges and on surfaces of graphite crystals.[72] These sites differ in the types of bonds formed between the lithium ions and carbon. In amorphous matrices, lithium appears to be dissolved and uniformly distributed. Materials of the MCMB type are considered as the mixtures of pure graphite and a certain amorphous (turbostratic) material.[67,73] Furthermore, it was assumed that excessive lithium ions can be incorporated into nanosize microcavities.[56,65,74] Strongly disordered structures contain isolated graphite sheets (a 'house of cards' structure) both sides of which can adsorb the incorporated lithium. Such an intercalation mechanism doubles the intercalation capacity. Moreover, a definite correlation has been found between the intercalation capacity and the content of residual hydrogen in the carbon material.[75,76] The formation of hydrogen–lithium bonds was hypothesised.[65] Further studies have shown that the characteristics of disordered materials gradually deteriorate so that their enhanced intercalation capacity is observed only at the beginning of their operation. These studies are being continued, however, without any definite hopes for success.[77–80]

Passive films formed on the carbon material surface during the first cathodic charge have a great effect on intercalation–deintercalation processes. The problem of formation of passive films on carbonaceous materials has been extensively studied, being probably the central question in the development of lithium-ion cells. A vast number of studies were devoted to the elucidation of the formation mechanism, composition, structure and properties of these films. As was stressed above, the passive films on carbon material resemble those formed on the surface of pure lithium with respect to their composition and properties (see, *e.g.*, Refs 21, 81–89). They result from irreversible reduction of electrolyte components and serve as a natural barrier that prevents the further process. Thus, the carbon material surface catalyses the electrolyte reduction. The data on the kinetics of this process are contradictory.

Propylene carbonate is reduced most actively, hence, it is recommended not to use propylene carbonate-containing electrolytes in lithium-ion batteries. The electrolyte reduction during the first discharge consumes a charge which is comparable with the specific capacity of the material and represents the irreversible capacity of the negative electrode. To reduce this quantity, it is desirable to add different substances to the electrolyte, *e.g.*, carbon dioxide, crown ethers, sulfur dioxide, ethylene sulfite, nitrogen dioxide, vinylene carbonate, *etc.*[83,90–96] Later, different procedures of surface treatment were proposed for carbon materials themselves, which includes deposition of certain protective coatings. For instance, it was proposed to oxidise[65,97] the graphite material surface, silver-plate its particles[98] and vacuum spray fine tin films.[99] Coating of fine graphite particles with still finer nickel particles (in essence, coating of graphite with a porous nickel film) seems more practicable.[100] Such a treatment favours a decrease in the irreversible capacity from 310 to 40 mA h g^{-1} and a simultaneous increase in the reversible capacity. A similar result was achieved by applying a thin layer of non-graphitised carbon on the surface of graphite particles.[101,102] Judging from the deposition method used, *viz.*, a fluidised bed treatment of graphite with a mixture of nitrogen and toluene vapour at 1000 °C, the resulting coating represented pyrolytic carbon. It was shown[102] that such a coating eliminates completely the irreversible capacity in such electrolytes as propylene carbonate (PC) and ethylene carbonate (EC). Finally, an original proposal to precoat the surfaces of graphite materials with protective films which resemble the film usually formed during the first cathodic polarisation in the working electrolyte deserves mentioning. Such protective films can be formed using chemical (treatment with butyllithium)[103] and electrochemical[104] procedures.

It follows from above that in the elaboration of negative electrodes, attention is mainly focused on carbon materials; however, attempts have been made to study different substances. At one time, carbon compounds with nitrogen and boron were assumed to be promising.[105–109] It was found that although their starting capacities (the capacity in the first cycles) are comparable with those of carbon materials, these decreased substantially during the cycling. The most promising results looked with carbon–silicon compositions.[110–112]

In the late 1990s, the attention of many researchers has been attracted by the materials based on tin oxides.[113–128] When negative electrodes made of such materials were used, lithium was intercalated into metallic tin formed during the initial cathodic polarisation of the electrode

$$SnO_2 + 4\,Li^+ + 4\,e^- \longrightarrow Sn + 2\,Li_2O \qquad (2)$$

rather than into the tin oxide.

Subsequent insertion of lithium into tin formally proceeds in the same fashion as its intercalation into carbon

$$x\,Li^+ + Sn + x\,e \rightleftharpoons Li_xSn, \qquad (3)$$

but, for tin, the coefficient x can be sufficiently high, *i.e.*, reach 4.4 (for intercalation into graphite, $x = 1/6$). For $x = 4.4$, the theoretical specific capacity of a tin electrode is 991 mA h g^{-1} or 7234 mA h cm^{-3}. Such high values of specific capacity (especially the volumetric one) are responsible for the keen interest paid to these materials. Even being calculated with respect to the initial oxide SnO_2 rather than to tin (into which lithium is intercalated), the resulting values of specific capacity still remain sufficiently high, *viz.*, 781 mA h g^{-1} and 5428 mA h cm^{-3}. However, the use of tin oxides and other tin compounds entails a number of problems.

The common (and the main) drawback of all metal electrodes is the substantial change in their specific volumes upon lithium intercalation. During lithium intercalation, the specific volume of an alloy formed (or, more precisely, a binary system) substantially increases, which results in high internal stresses and, as a consequence, the electrode cracking. In turn, this results in the appearance of a high ohmic resistance at the boundaries of individual metal particles and a sharp polarisation rise. While, for primary cells, this factor cannot play any significant role, for a secondary cell (rechargeable battery), it is the determining factor. (It should be borne in mind that the specific volume changes induced by cycling were the reason for the failure of numerous attempts to create a negative electrode based on aluminium and certain alloys like the Wood alloy.)

Tin is a remarkable material because it can be obtained in a fine-grain form with a characteristic particle size of several nanometres using different technological procedures. Dispersion of tin occurs in particular owing to its formation in the lithium oxide matrix by Eqn (2). In several studies,[115–190] this was considered to be the key factor.

Yet another principle for the preparation of highly dispersed particles is the use of tin alloys and intermetallic compounds.[121–130] However, in this method too, the stability of a finely dispersed phase of either tin or its intermetallic compound is favoured by the presence of another (inactive) phase. A relatively complex procedure of fabrication of negative electrodes based on tin, *viz.*, chemical deposition of tin into pores of a polymeric membrane has been proposed.[127] Such a membrane (a polycarbonate filter) has a system of monodispersed cylindrical pores with diameters of 50 nm. Prior to deposition of tin, the membrane was applied on a current collector made of foil. In the end, the membrane was burnt out to give a brush of tin hairs, which are

oxidised in air to give crystalline SnO_2. The electrodes thus prepared exhibited highly stable characteristics and were capable of discharging by huge currents (a complete discharge in 1 min!).

A two-phase system consisting of mixed powders of tin and a tin–antimony intermetallic compound (SnSb) was suggested [128] for the fabrication of negative electrodes. The ultradispersed powders can be obtained by chemical reduction using borohydride. Being inserted into such a two-phase system, lithium occurs first in the intermetallic compound, the tin phase playing the role of a stabilising matrix. Following completion of this process, intercalation of lithium into tin begins. Thus, the tin 'matrix' is not inert (in contrast to Li_2O) but makes an additional contribution to the capacity. The use of these electrodes allowed a specific capacity of 360 mA h g^{-1} to be maintained for 200 charge–discharge cycles. It was proposed [126] to prepare a Ni_3Sn_2 intermetallic compound by a mechanochemical method, *viz*., by processing nickel and tin powders in a ball mill. Electrodes based on such an intermetallic compound exhibited specific capacities up to 327 mA h g^{-1} or 2740 mA h cm^{-3}. The same method was proposed for fabricating an intermetallic compound of indium with antimony (InSb).[129] Despite their adequate characteristics, the electrodes made of this compound have several drawbacks, *viz*., the high cost of indium and the toxicity of antimony. Later, copper was substituted for indium and tin was substituted for antimony.[130, 131]

A Cu_6Sn_5 intermetallic compound was also shown to be quite plausible as a matrix for intercalation of lithium. In the potential range from 2.0 to 0.2 V, lithium intercalated successfully to give a $Li_{13}Cu_6Sn_5$ compound. True enough, such an intercalation was accompanied by a noticeable increase in the specific volume; however, this effect can be eliminated by decreasing the size of intermetallic compound particles. A proposal [132] to prepare a microcomposite material from the Cu_6Sn_5 intermetallic compound and metallic copper was more successful. This material was prepared by the so-called mechanical alloying of an equiatomic mixture of copper and tin powders in a high-speed planetary mill in an argon atmosphere. The electrodes made of this material withstand more than 80 charge–discharge cycles with a specific capacity of 200 mA h g^{-1}.

An interesting approach was suggested [133] for the preparation of a $Sn-LiO_2$ nanocomposite by a reaction of tin oxide with lithium nitride in a ball mill in an argon atmosphere. This reaction

$$2\,Li_3N + 3\,SnO \longrightarrow 3\,Sn + 3\,Li_2O + N_2\uparrow \qquad (4)$$

was carried out for 5 days. However, in reward, this method produced a ready-for-use composite; hence, there was no need to spend the charge in the primary reduction of tin by reaction (2).

Amorphous oxides of silicon and tin $SiO \cdot SnO$ (see Ref. 134) are also considered as promising materials for negative electrodes. Powders of these oxides were also obtained in a planetary ball mill from the starting monoxides. Electrodes of these materials had the initial capacity of $\sim$600 mA h g^{-1} which decreased to 350 mA h g^{-1} during the initial 20 charge–discharge cycles.

Recently, in addition to most popular tin-containing compounds, other materials were proposed for use as negative electrodes in lithium-ion batteries. The following examples may be mentioned: the KC_8 intercalation compound;[135] magnesium silicide Mg_2Si (the starting capacity of 1370 mA h g^{-1} which, however, smoothly decreased to 100 mA h g^{-1} in the initial 10 charge–discharge cycles);[136] a complex nitride $Li_{2.6}Co_{0.4}N$ (the starting capacity was 760 mA h g^{-1} and also decreased with time);[137] a sodium–molybdenum bronze of the $Na_{0.25}MoO_3$ composition which exhibited an intercalation capacity in lithium of 940 A h kg^{-1} (or 4000 mA h cm^{-3}).[138] However, the application field of lithium-ion batteries with electrodes of this bronze is rather narrow, because their potential changes within a very wide range, *viz*., from 3 to 0.005 V during the discharge. It was proposed to use a material based on $Li_4Ti_5O_{12}$ (Refs 139, 140) and a lithium–zinc alloy [141] for negative electrodes. The latter material can be obtained by controlled vapour codeposition of individual metals, the vapour mixture being condensed on a titanium current collector cooled by dry ice. The microstructure formed makes it possible to carry out cycling at high current densities.

Lithium is known to form alloys with silicon up to the $Li_{4.4}Si$ composition, which corresponds to a theoretical specific capacity of 4000 mA h g^{-1}. However, intercalation of lithium into silicon is accompanied by great changes in the specific volume. A laser-induced method was applied for the preparation of silicon powder from silane.[142] The particles measuring only $\sim$80 nm did not destroy during cycling. Electrodes fabricated from a mixture of such a silicon powder with carbon black demonstrated the capacity values of 1700 mA h g^{-1} after the tenth cycle and 1300 mA h g^{-1} after the twentieth cycle.

Nanocomposites of silicon microparticles in a titanium nitride matrix were also used for negative electrodes.[143] In this case, lithium gets intercalated into silicon. For a 33% silicon content, the composite capacity reached 300 mA h g^{-1} and remained unchanged for 20 cycles (no data on long-term cycling is available). The Si/TiN nanocomposites were also fabricated in a high-speed ball mill.

Mention should be made of important problems of the technology of negative electrodes such as the difficulties in the development of binding materials and current collectors, the imperfect technology for the fabrication of the electrodes themselves that gives no way of providing their uniform (small) thickness, the questions associated with corrosion of electrodes, *etc*.

2. Materials for positive electrodes

The choice of the material for the positive electrode in rechargeable lithium-ion batteries is restricted to lithiated cobalt, nickel and manganese oxides. Electrodes based on lithiated cobalt oxide are characterised by the lowest polarisation and the highest specific capacity. The performance of a positive electrode is reduced to deintercalation of lithium during the cell discharge and intercalation of lithium during the charge

$$LiCoO_2 \rightleftharpoons Li^+ + e + CoO_2. \qquad (5)$$

The operational characteristics of high-potential electrodes (*i.e*., the electrodes with open-circuit potentials of $\sim$4 V *vs*. lithium electrode, which maintains the discharge voltage at a level above 3 V) are approximately the same. The choice of the active substance for positive electrodes was arbitrary to a certain extent. Japanese scientists prefer cobalt oxides which are much more expensive than other materials; however, their industrial synthesis is relatively simple and reproducible.

In France and Canada, preference is given to cheaper nickel oxide. Lithiated nickel oxides operate at a less positive potential than cobalt oxide. This mitigates to a certain degree the requirements of the stability of the electrolyte to oxidation during charging. At the same time, the discharge curve of a nickel-oxide electrode is steeper, *i.e*., the voltage variations during the discharge in a cell with nickel-oxide electrodes are greater as compared with cells equipped with electrodes of manganese and cobalt oxides. The USA industry mainly uses the materials based on manganese oxides (lithium–manganese spinels) which seem to be more attractive economically and environmentally safe (see, *e.g*., Ref. 144).

Electrochemical characteristics of positive electrodes depend to a great extent on the technology used in their synthesis. Most publications were largely devoted to technological problems, and the questions of mechanisms of processes on these electrodes have received less attention. The technology of synthesis of lithiated oxides is based on the use of various high-temperature (sintering) and low-temperature (sol–gel, ion exchange, deposition from solutions) processes. Lithiated cobalt oxide was mainly prepared by a low-temperature technology,[145] whereas lithiated nickel oxide was fabricated by sintering.[146, 147]

Numerous studies aimed at the perfection of positive electrodes for lithium-ion cells are largely limited to improvement of their

structures. This is achieved by both technological methods and the introduction of different modifiers.

For example, it was shown that lithium cobaltate with the *O*2 structure has a more pronounced layered structure (suitable for reversible intercalation of lithium) as compared with conventional lithium cobaltate with the *O*3 structure.[148] The modification with the *O*2 structure can be prepared, for instance, by ion exchange from a solution of sodium cobaltate ($Na_{2/3}CoO_2$) and lithium bromide in hexanol. Although the materials with the *O*2 and *O*3 structures hardly differ in many parameters, the former material is more cycling-stable. Yet another technology used in the preparation of lithium cobaltate with a good texture (preferential crystal orientation along a lithium intercalation direction) consists in radiofrequency magnetron sputtering of thin films on various conductive supports,[149] which also facilitates the reversible cycling, *i.e.*, increases the battery life. To obtain highly dispersed $LiCoO_2$ powders with enhanced reversibility degrees, an original method of supercritical aqueous synthesis was put forward.[150] For this purpose, the aqueous solutions of LiOH, $Co(NO_3)_2$ and H_2O_2 were fed under a pressure of 30 MPa to an electric furnace at 400 °C, where the synthesis was completed in 30 s.

A method of emulsion drying was used for the preparation of highly dispersed $LiCoO_2$ powders.[151]

As was mentioned above, a sufficiently high discharge potential of a positive electrode at which the lithiation occurs is one of the merits of lithium cobaltate. However, this property is simultaneously a drawback, because the charging of a positive electrode occurs at still higher positive potentials at which the electrolyte can be oxidised on the catalytically active surface of cobaltate (or on a carbon additive used for increasing the active-layer conductivity). To overcome this disadvantage, an original method for modifying the electrode surface by applying a very thin (no thicker than 0.1 μm) layer of diamond-like carbon by plasma spraying from ethylene has been proposed.[152] The resulting electrodes could be cycled in the potential range from 3.0 to 4.2 V with a specific capacity above 200 mA h g^{-1}.

It is known that, being heated, lithium cobaltate decomposes to evolve oxygen. This reaction is especially fast for highly dispersed powders. To enhance the cycling stability of the lithium cobaltate structure, the latter was coated with a SnO_2 film using a sol–gel technology and then annealed.[153]

A similar method was used for modifying a $LiSr_{0.002}Ni_{0.9}Co_{0.1}O_2$ mixed compound.[154] A powder of this compound was coated with a $Mg(OH)_2$ layer and then annealed. The annealing resulted in the formation of a MgO coating which prevented electrolyte oxidation during the discharge, increased the discharge capacity from 145 to 160 mA h g^{-1} and enhanced the cycling stability (the capacity fade did not exceed 0.4 mA h g^{-1} per cycle).

A $LiMn_2O_4$ coating was applied on the $LiCoO_2$ powder to protect the electrolyte from oxidation during the charge and to enhance the thermal stability of lithium cobaltate.[155]

The use of mixed oxides, particularly, cobalt and nickel oxides, substantially improves the characteristics of lithiated oxides. Although the materials for such compounds were proposed for this use long ago, they are still being refined.[156–159] Complex mixed oxides are also of great interest. Thus in addition to $LiSr_{0.002}Ni_{0.9}Co_{0.1}O_2$ mentioned above, a material with the composition $Li_8(Ni_5Co_2Mn)O_{16}$ remarkable for its sufficiently high specific capacity (~150 mA h g^{-1}) and cycling stability (a capacity fade was ~0.4 mA h g^{-1} per cycle) deserves mention.[160] This material can be obtained by fine synthesis from solutions of salts of the corresponding metals in methanol and tetrahydrofuran, which is followed by controlled annealing.

Materials of the compositions $LiAl_yCo_{1-y}O_2$ have also attracted attention of scientists.[161, 162]

The promising mixed materials with a composition described by the general formula $LiCo_{1-y}Fe_yO_2$ should be also mentioned. The cost of lithium-ion batteries based on these materials could be substantially decreased by partial substitution of cheap iron for extremely expensive cobalt.[163, 164] First specimens contained low ($y < 0.1$) iron fractions; however, later, materials with $y = 0.24$ were developed. Unfortunately, the resulting materials were characterised by too fast a capacity fade during cycling.

The main drawback of lithium nickelates used as the materials for positive electrodes is the impossibility of complete deintercalation of lithium. As a rule, compounds Li_xNiO_2 are cycled only in the range of $0.5 < x < 1.0$. A deeper deintercalation results in irreversible structural changes. At the same time, it was found that a material with a violated stoichiometry with the composition $Li_xNi_{1.02}O_2$ can be cycled reversibly in the whole range of x (*i.e.*, $0 < x < 1$).[165]

An extension of the cycle range for nickelates can be also achieved by using mixed oxides. Lithiated nickel and cobalt mixed oxides (at a small content of the latter, see, *e.g.*, Refs 166–168) are gaining in acceptance. A mixed oxide material with a layered *O*2 structure and a composition described by the formula $Li_{2/3}(Ni_{1/3}Mn_{2/3})O_2$ has been proposed.[169] In the structural aspect, this material resembled the layered cobaltate modification[148] and was also obtained by ion exchange from a sodium bronze $Na_{2/3}(Ni_{1/3}Mn_{2/3})O_2$ [or, more generally, from $Na_{2/3}(Ni_yMn_{1-y})O_2$]. The discharge capacity of this material was ~180 mA h g^{-1} but the discharge curve demonstrated two steps: at a potential of ~3.9 V, which corresponded to electron transfer to the 3*d* level of nickel, and at 2.9 V where manganese changes its valence from +4 to +3.

A series of magnesium-modified lithium nickelates with the general composition $Li_{1+x}NiMg_yO_{2+2y}$ has been described.[170] An introduction of magnesium resulted in stabilisation of the nickelate structure, which, on the one hand, allows its deeper delithiation, *i.e.*, increases the specific capacity and, on the other hand, reduces the capacity fade during cycling. A material with $x = 0.15$ had a specific capacity of ~145 mA h g^{-1}, which even increased a little during the first 30 cycles. Lithiated nickel–magnesium oxides with layered structures (and approximately the same characteristics) have been described.[171, 172]

Lithiated nickel oxides are much cheaper than lithiated cobalt oxides; however, partial substitution of iron for nickel is believed to be economically warranted. Attempts[173, 174] for such a substitution were made, which, however, were not too successful: only the materials with the $Li_xNi_{1-y}Fe_yO_2$ composition, where $y < 0.1$, could be cycled reversibly.

Among lithiated manganese oxides, spinels with compositions similar to $LiMn_2O_4$ were used most often for fabrication of positive electrodes. Intercalation of lithium into such a material (*i.e.*, during a discharge of the lithium-ion battery) resulted in formation of compound $Li_{1+x}Mn_2O_4$. Such electrodes had a rated potential value of ~3 V. In the lithium deintercalation (the formation of $Li_{1-x}Mn_2O_4$), the potential value approached ~4 V. Various technologies for the preparation of spinels of different compositions ($LiMn_2O_4$, $Li_2Mn_4O_9$, $Li_4Mn_5O_{12}$, *etc.*) were described.[175–184] The best results were obtained using low-temperature 'wet' technologies which allow finely dispersed materials to be obtained,[177, 183, 184] although plausible high-temperature versions are known.[179]

In studying spinels, the main attention was paid to their lattice parameters. Intercalation of lithium into a spinel was accompanied by a decrease in the a_0 parameter of the cubic lattice[180, 182, 185] and a linear decrease in the phase-transition temperature, which was attributed to disproportionation of the spinel and a loss of a certain amount of oxygen.

A substantial decrease in the capacity during cycling, especially at high temperatures, is a drawback of lithium–manganese spinels (as well as their low specific capacity as compared with cobaltates and nickelates). The reasons for deterioration of characteristics of spinel electrodes were discussed in Ref. 186. Fourier-transform IR spectroscopic studies[187] have shown that self-discharge of spinel electrodes is accompanied by simultaneous oxidation of the solvent on particles of a carbon conducting additive.

Recently, attention of researchers has been attracted to non-spinel metastable and disordered lithium–magnesium structures including their monoclinic and orthorhombic modifications.[188–195] Good characteristics of these materials are associated particularly with the high defect densities at their grain boundaries and the small sizes of grains themselves (5–20 nm). Doping spinels with small amounts of other elements, such as aluminium [192–195] and potassium was recommended [196] to obtain such structures. For example, a monoclinic modification of $LiAl_{0.25}Mn_{0.75}O_2$ had a capacity of 130–150 mA h g^{-1}, being cycled in a potential range from 2.0 to 4.4 V.[192] A material of the composition $LiAl_{0.05}Mn_{0.95}O_2$ had a specific capacity of 150 mA h g^{-1} for its orthorhombic modification and ~200 mA h g^{-1} for the monoclinic modification.[194] Moreover, for these materials, the capacity faded by ~0.05% per cycle, whereas for common spinels this value exceeds ~0.5% per cycle.

Yet another way of enhancing the cycling stability of positive-electrode materials is the synthesis of amorphous (or amorphised) materials, *e.g.*, complex compounds such as $Li_{1.5}Na_{0.5}MnO_{2.85}I_{0.12}$ (see Refs 197–199). Its first 40 cycles not only showed no sign for the capacity fade but also resulted in its increase from 120 to 125 mA h g^{-1}. It was suggested [200] to use an amorphous modification of manganese dioxide Li_xMnO_2 as a starting material that can be cycled to the depth of over 400 mA h g^{-1}, which corresponds to a change in x from 0 to 1.6. It is evident that the capacity of these electrodes should be lower but are quite acceptable (260 mA h g^{-1} in a range from 4.0 to 2.5 V).

Yet another approach to the preparation of stable materials is the use of sol–gel technology. Its version using supercritical drying is the most interesting. For example, a technology was described [201] in which, first, a hydrogel was obtained from an aqueous solution of potassium permanganate and lithium fumarate, after which water was exchanged for acetone and then hexane. The hexanogel thus obtained was dried under conditions close to critical ones. In the process, the surface tension was eliminated, and an extremely fine-grain structure retained. An electrode made of this material with the composition $Li_{0.9}MnO_{2.5}$ had a capacity of ~440 mA h g^{-1} at a discharge up to 2.9 V. It should be noted that such electrodes could be discharged by very high currents. Thus a discharge with a current of 270 mA g^{-1} gave a capacity of 200 mA h g^{-1} and a discharge at 100 mA g^{-1}, *i.e.*, in a 2.5C mode,† resulting in a capacity of 150 mA h g^{-1} (the maximum load tested for these electrodes corresponded to the 7.5C mode, *i.e.*, a total discharge took 8 min). A material with the composition $LiAl_{0.24}Mn_{1.76}O_{3.98}S_{0.02}$ was obtained [202] using the sol–gel method. Having a well defined spinel structure, this material could be cycled without any noticeable capacity loss; its capacity was 230 mA h g^{-1}. A similar material (with sulfur partially substituted for oxygen) has been described.[203] A $LiAl_xMn_{2-y}O_{4-z}F_z$ material [204] exhibited a high cycling stability; this was attributed to the presence of a small amount of fluorine in the oxygen sublattice.

In addition to lithium–manganese spinels doped with aluminium, materials with chromium atoms partly substituted for manganese were reported to show promise for using them in lithium-ion batteries.[205–207]

A sample of lithium–manganese spinel with a well pronounced crystalline structure (with coarse crystals) was synthesised.[208] This material exhibited cycling stability, although its capacity was not too high (less than 80 mA h g^{-1}).

As was noted above, cobaltate particles were coated with a thin layer of manganese oxides to protect electrolytes from oxidation and enhance the thermal resistance of electrode materials.[155] The same group of authors have proposed a 'reverse' version, *viz.*, deposition of lithium cobaltate on the particles of a lithium–manganese spinel.[209] Such a coating was applied as a gel consisting of lithium and cobalt acetates, which was followed by annealing of the specimen. This procedure allowed the authors to reduce the capacity fade from 1.1 to 0.06 mA h g^{-1} per cycle.

The use of certain cobalt–manganese mixed spinels provides a discharge at very high potential ratings, *viz.*, ~5 V. The use of such material poses very severe requirements to the electrolyte (which should not be oxidised at a potential of ~5.3 V). In principle, the possibility of enhancing the battery voltage is a challenge. 'Five-volt' materials are being elaborated for several years.[210–212] To date, two of these materials have been described, *viz.*, $Li_2CoMn_3O_8$ and $LiCoMnO_4$.

In addition to lithiated cobalt, nickel and manganese oxides, other materials were suggested for use as positive electrodes, *e.g.*, lithiated chromium oxides (the capacity of ~200 mA h g^{-1}),[213] $LiCo_yNi_{1-y}VO_4$,[214] $LiVOPO_4$ [215] and $LiFePO_4$.[216–219] The latter compound exhibits a theoretical specific capacity of 170 mA h g^{-1}. The prospects of using these materials are still unclear, although the use of such a cheap compound as $LiFePO_4$ as the active material for positive electrodes seems to be challenging.

The materials based on vanadium oxides exhibited sufficiently high specific capacities; however, their voltage changed with the discharge in a very wide range, which cannot be tolerated in chemical cells designed for power supply of electronic equipment.

3. Electrolytes for lithium and lithium-ion rechargeable batteries

In lithium-ion rechargeable batteries, liquid electrolytes, which represent solutions of lithium salts in aprotic organic solvents, were used.[220, 221] As was mentioned above, in rechargeable batteries with metallic lithium electrodes, the use of liquid electrolytes poses certain problems; hence, the efforts of researchers were focused on the search for solid polymeric electrolytes (SPE). The processes of dendrite formation and encapsulation were assumed to be eliminated at the metal lithium/SPE interface. At the same time, the possibility of using polymeric electrolytes in lithium-ion batteries was also widely discussed.

An electrolyte for a lithium-ion rechargeable battery should exhibit high conductivity. As a rule, liquid electrolytes have a conductivity in the range from 0.001 to 0.01 S cm^{-1}. The electrolyte should be resistant toward oxidation and reduction, in other words, have a wide 'electrochemical window'.‡ The potential range of electrolyte stability is ~5 V. As was mentioned above, the stability of electrolytes largely depends on the formation of passive films on the electrode surface. These films are conductive with respect to lithium ions and do not prevent their intercalation and deintercalation. At the same time, the films should exhibit a minimum electronic conductivity to avoid corrosion (self-discharge) of the electrode. For this very reason, the film material should not dissolve in the electrolyte. Moreover, these films should be sufficiently elastic to avoid destruction during electrode volume changes in the discharge and charge processes.

Various combinations of solvents (both individual and mixed) and lithium salts intended for use as the electrolytes were described; however, only some of them are applied in practice.

Propylene and ethylene carbonates (PC and EC) are commonly used as the solvents. Solvents based on PC are reduced on graphite negative electrodes; hence, EC was proposed as the substitute for PC. At the same time, PC has a number of advantages over EC: the solubility of lithium salts is higher in PC, its freezing point (−54 °C) is substantially lower than the freezing point of EC (+36 °C). Moreover, in certain cases, the use of PC is preferential for improvement of positive electrode characteristics. As a rule, PC and EC are used as their mixtures

† If a cell is completely discharged in 1 h, this mode is designated as 1C; if a cell is discharged in 2 h, the mode is designated as 0.5C or C/2; if the total discharge takes 0.5 h, then the mode is 2C, *etc.*

‡ The difference between the potential of the beginning of anodic oxidation and the potential of the beginning of cathodic reduction.

with less viscous, although less polar, solvents such as 1,2-dimethoxyethane, dimethyl carbonate and diethyl carbonate.

Lithium hexafluorophosphate and tetrafluoroborate are used most often as lithium salts; the possibilities of using lithium hexafluoroarsenate and perchlorate were also examined. Merck (Germany) produces ready-for-use electrolytes for lithium-ion batteries of the following types: LP20, LP30 and LP40, where electrolytes represent 1 M $LiPF_6$ solutions in the following solvent mixtures: PC – diethyl carbonate (1 : 4), EC – dimethyl carbonate (1 : 1) and EC – diethyl carbonate (1 : 1), respectively.

In recent years, the following lithium salts were proposed for use as lithium-ion batteries, *viz*., lithium trifluoromethanesulfonate (triflate), bis(trifluoromethylsulfonyl)imide and tris(trifluoromethylsulfonyl)methanide and their derivatives. The derivatives involved such compounds as cyclic imides $Li[N(SO_2)(CF_2)_n(SO_2)]$, where $1 < n < 4$,[222,223] an asymmetrical methanide $Li[C(SO_2CF_3)_2(SO_2C_4F_9)]$ and bismethanide $Li_2[(C_2(SO_2CF_3)_4(S_2O_4C_3F_6)$,[224] imides with long fluoroalkyl chains,[225] lithium hexafluorotrimethylenebis(sulfonyl)di[bis(trifluoromethylsulfonyl)methanide],[226] *etc*.

Boron-containing compounds, particularly, different borates and chelatoborates were used in lithium-ion batteries as the additives that extend the potential range of electrolyte stability, increase the solubility of salts and decrease the corrosive action of the electrolyte on the current lead material (*e.g*., aluminium).[227–235] Of great interest is the hexamethoxycyclotriphosphazene $[NP(OCH_3)_2]_3$ additive, which favours a decrease in the inflammability of lithium-ion batteries.[236]

VII. Polymeric electrolytes for lithium-ion batteries

Among solid ionic conductors which can be used at ambient temperature, the SPE with a relatively fast ion transfer are most promising. Thin films fabricated of these polymeric electrolytes are characterised by elasticity (mobility), adequate mechanical properties, a low electronic conductivity (10^{-14} S cm^{-1} at room temperature), a wide electrochemical window of stability (3–4 V) and are compatible with the electrodes of alkali metals.

At the same time, the use of SPE is limited due to the following reasons: first, they have a low ionic conductivity at ordinary temperatures (from 10^{-5} to 10^{-8} S cm^{-1}); second, not only lithium ions, but also anions take part in the charge transfer, which can give rise to concentration polarisation; third, like liquid electrolytes, they can form a transition layer with a high resistance upon contact with the electrode (both positive and negative) material.

Armand *et al*.[237] were the first to propose the use in lithium cells of a complex of a lithium salt with a polymer [poly(ethylene oxide), PEO]. The conductivity of such a PEO – LiSCN complex system at room temperature was 10^{-8} S cm^{-1}.[237,238] These rechargeable batteries could operate only at temperatures above 60 °C, because it was only under these conditions that the conductivity of the electrolyte solution had acceptable values for practice. Nonetheless, the interest in these electrodes was so high that the extensive research undertaken has soon produced polymeric electrolytes with conductivities of $\sim 10^{-3}$ S cm^{-1} at room temperature, which is comparable with the conductivity of liquid electrolytes.

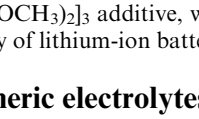
An important requirement to SPE is their mechanical strength, because, to decrease the resistance, these electrodes are mainly used as thin films with thicknesses of 0.0025–0.005 cm commensurable with the thicknesses of porous separators based on polypropylene and polyethylene, which divide the electrodes in lithium batteries with liquid electrolytes. A solid polymeric electrolyte should also withstand the pressures induced by morphological changes in the electrode material during the lithium cell cycling. Thus, SPE, on the one hand, should provide ionic conduction typical of liquid electrolytes and, on the other hand, should be spatially stable, *i.e*., retain their solid shapes. Modern SPE fulfil all these requirements.

We can single out two large classes of polymeric electrolytes with conductivities above 10^{-5} S cm^{-1} at room temperature. The first class involves 'solution-free' SPE. In addition to polymers, these SPE contain lithium salts. The second class comprises SPE 'with solvents', which, in addition to polymers and lithium salts, contain liquid solvents called plasticisers. These two SPE classes may have polymeric matrices with different structures.

1. Solid electrolytes with the polymer – lithium salt composition

Solid electrolytes based on crystalline polymers have low conductivities, whereas those based on amorphous polymers exhibit higher conductivities. Thus, the SPE conductivity can be increased by decreasing the degree of crystallinity of a polymer by changing its structure. Table 1 lists the characteristics of certain polymers; Table 2 lists the SPE conductivities.

Table 1. Properties of certain polymers used as the electrolyte matrices.[239]

Polymer [a]	Polymer unit	T_g /°C	m.p. /°C
PEO	$-CH_2CH_2O-$	−64	65
PPO	$-CH(Me)CH_2O-$	−60	see [b]
POO	$-(CH_2O)-(CH_2CH_2O)-$	−66	13
MEEP		−83	see [b]
PDMS	$-Si(CH_3)_2O-$	−127	−40
PAN	$-CH_2CH(CN)-$	125	317
PMMA	$-CH_2C(Me)(CO_2Me)-$	105	see [b]
PVC	$-CH_2CHCl-$	82	see [b]
PVDF	$-CH_2CF_2-$	−40	171

[a] The following abbreviations were used: PEO, poly(ethylene oxide); PPO, poly(propylene oxide); POO, poly(oxymethylene oligooxyethylene); MEEP, poly{bis[2-(2-methoxy)ethoxy]ethoxy}phosphazene; PDMS, poly(dimethylsiloxane); PAN, poly(acrylonitrile); PMMA, poly(methyl methacrylate); PVC, poly(vinyl chloride); PVDF, poly(vinylidene difluoride). [b] Amorphous polymer.

Table 2. Composition and bulk conductivity with respect to Li^+ ions for solid polymeric electrolytes.[237,238,240]

Electrolyte	Conductivity at 20 °C /S cm^{-1}
$(PEO)_8LiClO_4$	10^{-5}
$(PPO)_8LiClO_4$	10^{-8}
$(POO)_{25}LiCF_3SO_3$	3×10^{-5}
$(MEEP)_4LiBF_4$	2×10^{-5}

Back in 1979, it was pointed out[238] that PEO exhibits good solvating ability towards those Li^+ ions and ions of other metals located in a favourable position relative to the donor oxygen atoms of the polymeric chain. By changing the oxygen atom position in the chain, the solvating ability and the temperature transitions in the polymer can be changed. For example, PEO can form polymeric electrolytes with salts of alkali and transition metals.[241] Moreover, the existence of various PEO complexes with $LiBF_4$, $LiPF_6$ and LiB_4,[242] $LiAsF_6$,[243] LiSCN,[244] $LiCF_3SO_3$ and $LiClO_4$,[245] $LiN(CF_3SO_2)_2$[246,247] has been reported.

The use of inorganic additives in the form of fine powders of Al_2O_3 or $LiAlO_2$ was proposed to enhance the mechanical strength of an electrolyte based on PEO and a lithium salt.[248–254] Such additives, first, prevent crystallisation of the polymer and, second, can absorb water, which allows one to

reduce the lithium electrode passivation. At room temperature, the ionic conductivity of an electrolyte with the composition $(PEO)_8LiClO_4$ was 10^{-5} S cm^{-1}, whereas the conductivity of the $(PEO)_8LiClO_4$ + 10 mass % $LiAlO_2$ composition was 10^{-4} S cm^{-1}.

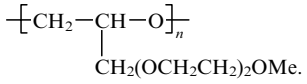
It was proposed [255] to modify a polymeric electrolyte based on PEO and $LiBF_4$ using finely dispersed Al_2O_3 powders with ~10 μm particles as well as by modified particles measuring 1.3×10^{-2} μm. The conductivity of the latter SPE was higher by an order of magnitude as compared with SPE modified by 10 μm particles.

Introduction of γ-$LiAlO_2$ to a polymeric electrolyte based on PEO and $LiN(CF_3SO_2)_2$ resulted in a substantial decrease in the degree of crystallinity and an increase in the stability of the Li/electrolyte interface.[256]

The effect of various types of fine powders added to a polymeric electrolyte on the conductivity and mechanical strength of PEO-based SPE was also studied.[257, 258]

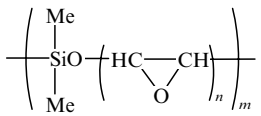
Using $LiClO_4$ complexes with a number of aliphatic polyesters (PEst) synthesised by a reaction of poly(ethylene glycol) (PEG) (M_w = 300, 1000) with diacid chlorides ($ClOC[CH_2]_nCOCl$, n = 3–8, 10) as the examples, the effect of the polymer structure on its ionic conductivity was studied.[259] The general composition of these complexes can be expressed by the formula PEst(m,n), where m is the number of ethylene groups and n is the number of methylene groups; *e.g.*, PEst(6,8) is $[-(OCH_2CH_2)_6O-CO(CH_2)_8CO-]$. In contrast to the PEO–$LiClO_4$ system with a degree of crystallinity of 0.4, the PEst(m,n)–$LiClO_4$ systems are totally amorphous, and their ionic conductivity varies in the range from 2.5×10^{-5} to 4.1×10^{-5} S cm^{-1}. The degree of crystallinity of PEO can be reduced by shortening its chain and decreasing its molecular mass;[260] however, low-molecular PEO with short chains represent viscous liquids even after the formation of complexes with lithium salts and could not form SPE.

With the aim of decreasing the degree of crystallinity, comb-like polymers with short PEO side-chains attached to the main chain were synthesised, *e.g.*, poly[2-(2-methoxy)ethoxy]ethyl glycidyl ether

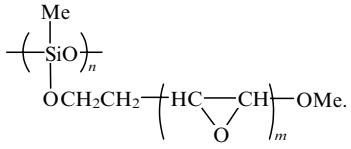


A complex of this amorphous polymer (T_g = −57 °C) with $LiClO_4$ had a conductivity of an order of magnitude of 10^{-5} S cm^{-1} at room temperature.

A search for amorphous polymers has produced materials with highly mobile inorganic skeletons based on polysiloxanes $(-SiR_2O-)_n$ and polyphosphazenes $(\geq P=N-)_n$. Siloxane polymers can be exemplified by poly(dimethylsiloxaneoligoethylene oxide)



and poly{[ω-methoxyoligo(ethylene oxide)ethoxy]methylsiloxane}

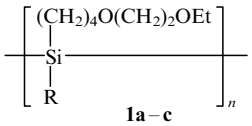


A maximum conductivity achieved using electrolytes of these types (which also represent viscous liquids) is 10^{-4} S cm^{-1} (Refs 261, 262). Cross-linking of polymers decreased the conductivity to 10^{-5} S cm^{-1} at room temperature. The drawback of these polymers is the sensitivity of Si–O–C bonds to hydrolysis and their structural degradation with time. This problem can be solved, *e.g.*, by synthesising copolymers with stable Si–C bonds, which has been achieved by grafting PEO to polysiloxanes.[263]

Electrolytes based on such a polymer (−77 °C < T_g < −54 °C) exhibited conductivities of 10^{-5} S cm^{-1} at room temperature.

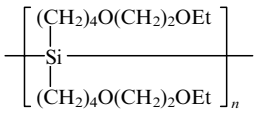
A modified polymeric electrolyte based on MEEP (see Table 1) was described.[264] Complexes of MEEP with lithium salts had a low stability. The authors proposed to add $LiAlCl_4$ to such an electrolyte, which allowed them to fabricate MEEP–$(LiAlCl_4)_n$ films. The mechanical properties of spatially unstable MEEP–lithium salt complex systems were substantially improved as a result of formation of complexes with such polymers as PEO, PPO, poly(ethylene glycol diacrylate) and poly(vinylpyrrolidone). An electrolyte containing 55 mass % MEEP + 45 mass % PEO–$[LiN(CF_3SO_2)_2]_{0.13}$ had a conductivity of 6.7×10^{-5} S cm^{-1} at room temperature. Such electrolytes remained stable up to 4.5 V. A Li/TiS_2 cell with these electrolytes had a cycle life exceeding 200 charge–discharge cycles.

Results [265] obtained in line with these studies should be considered as less successful. The authors have obtained a number of polysilane polymers: **1a**–**c**, **2** and **3**

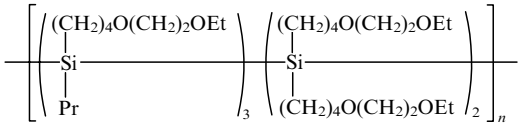


1a–**c**

R = Me (**a**), Pr (**b**), C_8H_{17} (**c**).



2



3

Polymers **1b** and **2** with 8 oxygen atoms per lithium ion exhibited a maximum ionic conductivity equal to 1.9×10^{-7} S cm^{-1}.

The degree of crystallinity can be reduced by cross-linking the polymers. Such polymeric nets exhibited relatively high conductivities (1.5×10^{-5} S cm^{-1} at 25 °C for a $LiClO_4$ salt) and an acceptable mechanical strength. This approach was put forward in Refs 266–268 and involved cross-linking of low-molecular PEO (M_w = 600, 1000, 2000) and block-copolymers PEO–PPO–PEO with urethane and cyclosiloxane. Polymeric electrolytes based on PEO with M_w = 2000 which contained either $LiCF_3SO_3$ or $LiN(CF_3SO_2)_2$ and electrolytes with the composition PEG–$LiCF_3SO_3$ with an addition of poly(ethylene glycol dimethyl ether) (PEGDME) with M_w = 500 were studied.[269] The following electrochemical properties of these three electrolytes were examined: ionic conductivity, electrochemical stability window, reduction and the resistance and stability of the lithium electrode/electrolyte interface. Moreover, prototypes of lithium cells with composite cathodes based on $LiMn_2O_4$ were tested with the aim of studying the performance of these electrolytes in solid lithium batteries. In SPE containing $LiN(CF_3SO_3)_2$, a conductivity of 10^{-4} S cm^{-1} required for their practical application was achieved only at 60 °C. An addition of PEGDME decreased the resistance of the lithium electrode/electrolyte interface and trebled the specific capacity (90 mA h g^{-1}).

A new method of SPE preparation by dissolving the polymers with high glass transition temperatures (T_g > 90 °C) in a $LiCF_3SO_3$ melt has been described.[270, 271] Such polymers as poly(*N*,*N*-dimethylacrylamide), poly(acrylonitrile) (PAN), poly-

(vinylpyrrolidone) and its copolymer with vinyl acetate were studied. At 45 °C, the conductivity of a PAN–$LiCF_3SO_3$ (75 mass %) electrolyte did not exceed 10^{-6} S cm^{-1}.

2. Plasticised polymeric electrolytes

In contrast to SPE with the polymer–salt composition, plasticised polymeric electrolytes contain organic solvents which are confined within the swollen polymeric matrix so that these electrolytes resemble rubber in their consistency. Plasticised electrolytes are also called polymeric gel-electrolytes (PGE). They can be obtained by adding plasticisers, *viz*., polar aprotic solvents with high boiling points and high dielectric constants to SPE. Table 3 shows typical solvents-plasticisers.

Table 3. Certain organic solvents used as plasticisers.[272]

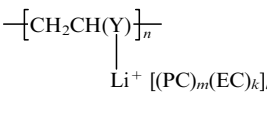
Solvent-plasticiser	m.p. /°C	b.p. /°C	Dielectric constant at 25 °C	Viscosity /10^{-3} Pa s
Ethylene carbonate	36	248	95.3	1.9
Propylene carbonate	−70	240	65.1	2.53
γ-Butyrolactone	−43.5	204	39	1.75
Dimethylformamide	−61	153	36.7	0.8
1,2-Dimethoxyethane [a]	−70	85	5.5	0.46

[a] Used only as mixtures with high-boiling plasticisers added to decrease the viscosity.

The conductivity of PGE depends on the solvent content, its viscosity and dielectric constant. Polar solvents with low viscosities such as *N*-dimethylformamide (DMF) and γ-butyrolactone (BL) substantially increase the conductivity in lithium ions. The activation energy of conductivity decreases dramatically with an increase in the solvent-to-lithium salt molar ratio. In fact, lithium ions travel in the liquid electrolyte confined by a polymeric matrix. Hence, to obtain a PGE with an acceptable conductivity, the amount of DMF required should be only a third of that required for more viscous PC.

Solvents-plasicisers solvate Li^+ ions facilitating their transport (this phenomenon was not observed for polyethers in which an ion travels along the polymer chain). The 'degree of assistance' to the ionic transport probably depends on the rate at which the ions form complexes with the polymeric chain rather than with the solvents-plasticisers.

The structures of plasticised polymeric electrolytes are still not clearly understood. The PEG structure in which Li^+ forms a complex both with the polymeric network and the solvent has been hypothesised [273] for electrolytes based on PAN (Y = CN) and PVC (Y = Cl) in a mixture of propylene carbonate–ethylene carbonate (PC/EC) solvents



To date, a large number of PGE that consist of lithium salts and plasicising organic electrolytes are known. The important advantage of PGE as compared with SPE is their high ionic conductivities at room temperature, which approaches the conductivity of liquid electrolytes. However, in practical applications of PGE, a number of other characteristics should be taken into account, *e.g*., their ability to confine electrolyte, mechanical strength and conductivity in a wide temperature range. In particular, for multicomponent PGE, solvent losses due to leakage and vaporisation can hardly be avoided.[274,275] This results in a decrease in the cell resistance and impairs the electrolyte–electrode contact. The main parameter that characterises the solvent confinement in the PGE is the affinity between the polymeric matrix and the organic solvent. This parameter also affects the mechanical strength of the PGE film and its conductivity in a wide temperature range, especially in thin-film cells which contain electrodes with high surface areas. Low degrees of affinity between a polymer and an electrolyte can result in separation of PGE into predominantly polymeric and solvent-enriched microphases. As a consequence, the mechanical strength can increase due to the formation of a polymeric network. The electrolyte electrochemical stability in lithium chemical power sources can be increased if highly polar, easily freezing solvents are used (*e.g*., ethylene carbonate with m.p. = 36 °C). It may be assumed that an increase in the degree of solvent–polymer affinity will allow one to eliminate the problem of the increase in the PGE resistance with a decrease in the temperature, because the interaction of solvent molecules with the polymer will prevent their ordering during freezing.

Properties of PGE which contained PVDF, a copolymer of vinylidene fluoride with hexafluoropropylene (PVDF–HFP), PAN (M_w = 150 000) and PMMA (M_w = 12 000) as the polymeric components were compared,[276] which revealed the following features. The solvent-loss rate increased in the order PMMA ⩽ PAN ≪ PVDF–HFP ⩽ PVDF in accordance with the increase in the solvent affinity to the polymer and the increase in the degree of crystallinity. Polymers with low degrees of crystallinity swelled more easily and better confined the solvent, the latter being uniformly distributed throughout the polymeric matrix.

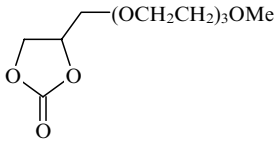
In some studies,[277,278] PGE based on chemically cross-linked PEO and $LiBF_4$ and $LiN(CF_3SO_2)_2$ were plasticised by PC and BL, then their ionic conductivities were compared to the conductivities of liquid electrolytes without polymers. Although the degree of dissociation of salts in PGE was higher, the conductivity appeared to be lower due to specific capture of lithium ions by the polymeric matrix.

Itoh *et al*. [279] dissolved $LiN(CF_3SO_2)_2$ in PEGDME (M_w = 400–500) and then added γ-$LiAlO_2$. The solution obtained was mixed with PEO (M_w = 4 000 000) and a liquid electrolyte was added. The compositions thus prepared contained different amounts of the following liquid components: dimethyl carbonate (DMC), diethyl carbonate (DEC), EC and PC. These reagents were used for increasing the amorphous phase fraction in the polymeric composite membrane. Impedance measurements have shown that the maximum stability with respect to Li electrodes was observed for the following compositions (mass %): 13.6 PEO + 77.3 lithium salt solution in PEGDME + 9.1 γ-$LiAlO_2$ (I) and 18.2 PEO + 54.5 lithium salt solution in PEGDME + 18.2 DMC + 9.1 γ-$LiAlO_2$ (II). At the same time, composition (II) displayed a high ionic conductivity, *viz*., 2×10^{-3} S cm^{-1} (for composition I, the ionic conductivity was 0.09×10^{-3} S cm^{-1}).

The main disadvantage of using PC and oligomeric ethers as the plasticisers is the low stability of the resulting films due to the solubility of the linear PEO in these solvents. To solve this problem, two approaches were suggested: (1) plasticisation of cross-linked polymeric nets which involve $-CH_2CH_2O-$ units; (2) plasticisation of polymers which do not involve such units but are either insoluble or poorly soluble in plasticisers.

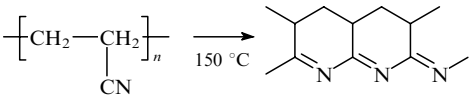
It was shown [277] that the problem of solubility of chemically linked PEO in PC can be solved using the first approach. Although the cross-linked polymer studied was amorphous and contained the $-CH_2CH_2O-$ unit, a non-plasticised polymeric electrolyte on its basis with addition of $LiCF_3SO_3$ had a conductivity of 1.4×10^{-6} S cm^{-1} at 25 °C. Addition of 50 mass % PC increased the conductivity of the system to 8×10^{-4} S cm^{-1}, while the mechanical properties allowed its application as a film.

A new plasticiser, *viz*., a modified carbonate (MC), was synthesised,[280] by addition of three ethylene oxide groups to propylene carbonate.



The conductivity of a PEO–$LiCF_3SO_3$ complex rapidly increased to 5×10^{-5} S cm^{-1} at room temperature upon introduction of 50 mass % MC. It was assumed that this plasticiser increases the conductivity throughout the complex system bulk, in contrast to common plasticisers that provide conduction only in the liquid phase. It was assumed that MC favours a deeper dissociation of the salt as compared with PC.

A large number of studies were devoted to PAN-based PGE obtained by heating the polymer, plasticiser and lithium salt to 130–150 °C, which resulted in cross-linking along the C—N bonds



Although the amount of PAN did not exceed 20 mass %, the electrolyte obtained resembled rubber in its consistency.

Table 4 shows the conductivities of PGE based on PAN with additions of lithium salts such as $LiClO_4$, $LiAsF_6$, $LiCF_3SO_3$, $LiN(CF_3SO_2)_2$ and $LiPF_6$ (Refs 273, 281). PC, EC, BL, *N*-methylpyrrolidone (*N*-MP) and their mixtures were used as plasticisers.

Table 4. Conductivities of electrolytes based on PAN at 20 °C.

Electrolyte composition (mol.%)	Conductivity at 20 °C /S cm^{-1}
21 PAN + 38 EC/33 PC + 8 $LiClO_4$	1.7×10^{-3}
21 PAN + 38 EC/33 PC + 8 $LiAsF_6$	2.1×10^{-3}
16 PAN + 68 PC + 16 $LiClO_4$	8.6×10^{-4}
21 PAN + 18 BL/20 EC/33 PC + 8 $LiClO_4$	2.3×10^{-3}
21 PAN + 40 EC/36 PC + 3 $LiN(CF_3SO_2)_2$	1.5×10^{-3}
21 PAN + 61 EC/13 PC + 5 $LiCF_3SO_3$	1.1×10^{-3}
21 PAN + 61 EC/13 PC + 5$LiBF_4$	3.5×10^{-4}
21 PAN + 33 PC/30 BL/8 *N*-MP + 8 $LiPF_6$	2.2×10^{-3}

Polymeric gel-electrolytes based on PAN were also modified by introducing crown ethers such as 15-crown-5 and benzo-15-crown-5.[282] Earlier, the effect of these crown ethers as well as 2,4-dioxo-16-crown-5 on the conductivity of PEO-based solid electrolytes was studied.[283] It was found that the introduction of 15-crown-5 and 2,4-dioxo-16-crown-5 increases the ionic conductivity of a film electrolyte approximately by an order of magnitude, whereas the addition of benzo-15-crown-5 does not affect this electrolyte characteristic. A gel-electrolyte with the following composition: 8.5 mass % PAN + 81 mass % PC + 3 mass % $LiClO_4$ + 7.5 mass % 15-crown-5 had a conductivity of 10^{-3} S cm^{-1} at 20 °C.[282]

Films prepared of a composite polymeric electrolyte involving zeolite powder dispersed in a PAN-based gel with an addition of $LiAsF_6$ were studied.[284] Gel-electrolytes based on a mixture of PC/EC and PAN with addition of $LiAsF_6$ had ionic conductivities exceeding 10^{-3} S cm^{-1} at room temperature. The addition of zeolite powder increased the ionic conductivity at low temperatures due to high degrees of amorphousness of the composites. The lithium electrode/electrolyte interface was studied using the impedance spectroscopy technique. The resistance of charge transfer across the Li/PGE interface was found to decrease, which indicates a decrease in the area occupied by the passive film on the surface of lithium. According to results of cyclic voltammetry, for Li/$LiCoO_2$ cells, an introduction of PAN and zeolite powder into a PC/EC electrolyte containing $LiAsF_6$ did not change the window of electrochemical stability, and, at a current density of 0.5 mA cm^{-2}, the capacity loss during cycling did not exceed the corresponding values for liquid electrolytes.

A highly conducting PAN-based PGE was prepared[285] using EC/DMC solutions of either $LiPF_6$ or $LiC(CH_3SO_2)_3$ as the plasticisers. The PGE preparation involved the following stages:

(1) dissolution of a lithium salt in EC/DMC;

(2) addition of PAN to the solution obtained and stirring for several hours at room temperature;

(3) casting of the resulting liquid solution on an aluminium support preheated to 90 °C for no longer than 30 s for cross-linking of PAN;

(4) cooling of the gel obtained to room temperature.

A $LiPF_6$ + EC + DMC + PAN composition with a molar ratio of 4 : 60 : 20 : 16 had a conductivity of 5.9×10^{-3} S cm^{-1} and a break-down voltage of 4.5 V.

Ionic conductivity of a polymeric electrolyte based on PAN and lithium methacrylate (PAN–LiMA) with an addition of EC-dissolved $LiClO_4$ was 2.4×10^{-4} at 10 °C and 1.9×10^{-3} S cm^{-1} at 25 °C.[286]

A copolymer of acrylonitrile with butadiene had an ultimate strength of 3.0 MPa and a conductivity of 10^{-3} S cm^{-1}.[287]

A new copolymer of PAN with bis[2-(2-methoxyethoxy)-ethyl]itaconate (PANI) was synthesised.[288] The maximum conductivity, namely 1.9×10^{-3} S cm^{-1}, was found for a gel-electrolyte of the following composition: 25 mass % PAN + 10 mass % PANI + 50 mass % EC/BL + 15 mass % $LiClO_4$.

Polymeric electrolytes were also prepared based on PVC.[289] They were obtained by dissolution of PVC in THF and subsequent addition of plasticisers with lithium salts. Then, the solution was cast on a support and dried at room temperature up to complete evaporation of THF. For an electrolyte of the following composition: 15 mass % PVC + 40 mass % PC + 40 mass % EC + 5 mass % $LiClO_4$, the conductivity of 1.2×10^{-3} S cm^{-1} was reached at room temperature. Attempts to prepare an electrolyte by dissolving PVC directly in PC and EC have failed,[290] because these polymers do not dissolve PVC even at elevated temperatures. This obstacle was bypassed using THF which dissolves all the electrolyte components.

The use of PVDF and PC-solutions of $LiClO_4$ as the polymeric matrix and the plasticiser, respectively, made it possible to obtain PGE with a conductivity in the range from 10^{-5} to 10^{-3} S cm^{-1} at room temperature.[291]

In recent years, the active search for polymeric composites as well as binary and ternary copolymers which can be used as polymeric matrices for electrolytes has been in progress.[292–299]

It was shown[282, 300, 301] that, being used as effective protective coatings for lithium electrodes, the polyacetylene (PA)/porous polyethylene (PE) and PA/polypropylene composites play the additional role of electrolyte carriers and conductors, because PA present in their compositions exhibit both ionic and electronic conductivity.

A constantly increasing number of publications devoted to synthesis of new PGE using photopolymerisation have appeared in recent years.[302, 303] For example, this method was used for the synthesis of poly(ethylene glycol diacrylate). Synthesis of a gel-electrolyte by UV-irradiation of a mixture of oligo(urethane methacrylate) and poly(ethylene glycol monomethacrylate) has been reported;[304, 305] the PGE conductivity was of an order of magnitude of 10^{-3} S cm^{-1}.

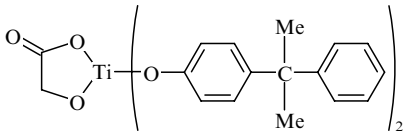
An ethylene oxide/propylene oxide (80 : 20) copolymer with acrylate groups at the macromonomer's termini that could be cross-linked under the action of UV-radiation was synthesised.[306] EC/PC (1 : 1, by volume); EC/BL (1 : 1, by volume); PC; PC/BL (1 : 1, by volume); BL and $LiBF_4$ (1 M) were used as the plasticisers. The polymeric films obtained exhibited good mechanical properties in a wide range of concentrations of additives to liquid electrolytes. Their shear moduli decreased with an increase in the liquid component content, however, remaining sufficiently high, *viz*., 10 MPa even for a liquid content of 90 mass %. The ionic

conductivity of a composition with 1 M $LiBF_4$/BL decreased from 3 to 1×10^{-3} S cm^{-1} with a decrease in the temperature from +20 to −20 °C.

Recently, it was proposed to use ternary copolymers as the polymeric gel-electrolytes.[307] For example, ternary polymeric electrolytes were prepared by casting from a solution of a homogeneous mixture containing 18 mass % poly[(acrylonitrile)(methyl methacrylate)styrene] [poly(AMS)], 73 mass % 1 M $LiClO_4$ solution in EC/DMC (1 : 1, by volume) and 9 mass % silica. The Li/PGE/carbon cell had a reversible capacitance of 305 mA h g^{-1} in a voltage range of 0.01 – 1.5 V and a cycling efficiency of 99%.

The next work by the same authors [308] dealt with a PGE which contained 12 mass % poly(AMS), 75 mass % plasticiser and 13 mass % SiO_2. The plasticiser represented a 1 M solution of $LiBF_4$ in either EC/DMC (1 : 1, by volume) or EC/DMC/BL (5 : 4 : 1, by volume) (BL was added to increase the ionic conductivity). $LiCoO_2$ was used as the cathodic material. Indeed, the $LiBF_4$ + EC + DMC + γ-BL electrolyte added to the polymer has demonstrated a somewhat higher ionic conductivity (6.1×10^{-3} S cm^{-1}) as compared with the $LiBF_4$ + EC + DMC electrolyte (5.2×10^{-3} S cm^{-1}). The PGE films obtained were 60 – 80 μm thick and had satisfactory mechanical properties.

Composite electrolytes based on a mixture of lithium-ion-conducting ceramics $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ and a poly(ether urethane) electrolyte have been proposed.[309] Electron microscopy studies have shown the ceramic and polymeric phases to be divided by ~1 μm interlayers. The conductivity of a dry composite did not exceed that of the initial polymeric electrolyte. Under the action of solvent vapour (DMF, acetonitrile, water), the conductivity increased substantially as compared with a polymer subjected to a simpler plasticisation procedure. Treatment of the ceramics with a compatibilising agent



improved the adhesion on the polymer – ceramics interface but decreased the total conductivity of the specimen studied.

A polymeric matrix has a strong effect on the dendrite formation in PGE. Inhibition of lithium dendrite formation in a PAN-based electrolyte was studied.[310] The electrolytes used were obtained by dissolving PAN (up to 17 mass %) in a PC/EC solvent mixture (1 : 1, by volume) containing $LiClO_4$ (1 M) at 120 – 140 °C with subsequent cooling to −15 °C for 16 h. Upon electrodeposition of lithium for 1 h from liquid electrolytes containing up to 3 mass % PAN, dendrites were observed to be formed on the lithium/electrolyte interface, whereas in a gel-electrolyte (5 mass % – 17 mass % PAN) their formation was suppressed. Taking into account the increase in the bulk resistance with an increase in the PAN content, its optimal concentration in the electrolyte was found to be 5 mass % – 10 mass %.

A metallic lithium electrode in contact with a gel-like PAN-based electrolyte which contained two lithium salts ($LiBF_4$ and $LiPF_6$) was precycled to decrease the bulk resistance.[311] The cycling was carried out in the range from +0.5 to −0.5 V at 20 °C immediately after the Li/PGE/Li cell was assembled. For cells with $LiBF_4$-containing PGE, the impedance values measured after storage for 230 days at 20 °C were below 100 Ω. Cells with $LiPF_6$ needed to be precycled at the potentials > 0.5 V and at 60 °C. The impedance values at 10 kHz that determine the bulk resistance of the gel-electrolyte were the same for both types of cells and remained unchanged during storage. This was also confirmed by the example of a Li/PGE/(1,3,4-thiadiazole-2,5-dithiol + polyaniline-based composite cathode) cell. According to XPS data, only a LiF – LiOH layer was retained upon cycling in a gel-electrolyte containing $LiBF_4$, whereas, in a gel-electrolyte containing $LiPF_6$, a dense and thin LiF interlayer was 'incorporated' into the LiF – LiOH mixed layer. It was assumed that the layer containing LiF and LiOH formed during preliminary cycling stabilises the Li/PGE interface.

Electrolyte based on the following polymers were studied:[312] dimethyl ether of tetra(ethylene glycol) (tetraglyme), dimethyl ether of poly(ethylene glycol) (M_w = 400) and poly(methylene ethylene oxide). The study was aimed at elucidation of the kinetics of decomposition of liquid and solid polyether electrolytes, which contained either $LiPF_6$ or complexes based on this salt and exhibited high thermal stability and advanced electrochemical properties resembling those of a pure salt. Lithium bis(diglyme) hexafluorophosphate [313] and lithium (pentamethyldiethylenetriamine) hexafluorophosphate [314] were shown to exhibit advanced thermal stability and conductivity in nonaqueous media.[315]

In recent years, attention is focused on electrolytes based on the PVDF – HFP copolymer called Kynar in the industry. Using $LiClO_4$, $LiPF_6$ [316] and $LiN(CF_3SO_2)_2$,[317] as well as the EC/ethyl methyl carbonate plasticising mixtures, the PVDF – HFP electrolyte films with advanced mechanical and electrochemical properties were obtained. In another study,[318] PVDF – HFP membranes were first cast using such solvents as acetone, THF, ethyl methyl ketone and *N*-MP and then impregnated with a 1 M solution of $LiBF_4$ in PC. The polymeric electrolytes obtained had a conductivity of an order of magnitude of 10^{-3} S cm^{-1}.

Syntheses of new gel-electrolytes based on PVDF [319 – 321] and PVDF – HFP [322 – 327] have been reported.

The search for new polymeric electrolyte compositions for lithium-ion cells is in progess. About 100 publications on this subject appear annually. For a deeper insight into the state-of-the-art of this field, the readers are directed to the reviews [239, 328, 329] and the book.[242]

VIII. Conclusion

In the past decade, lithium-ion rechargeable batteries have occupied a significant place in the power source market. They are extensively used in portable electronic devices. At present, active research on the development of large batteries, particularly, for electric vehicles is in progress. Success achieved in elaboration of lithium-ion cells is determined by the progress in the research fields of intercalation processes and development of high-performance intercalation materials. Despite the evident achievements, many problems remain to be solved.

While this review was in the stage of preparation, interesting publications devoted to lithium rechargeable batteries have appeared. For example, interesting information can be found in the Proceedings of the 10th International Meeting on Lithium Batteries which took place in Como (Italy) in 2000 (see Refs 330 – 353) as well as from the materials of the Joint Meeting of the International Society of Electrochemistry and the Electrochemical Society (USA) held in San-Francisco (USA) in 2001.[354 – 390] The studies that deal with nanomaterials (such as fullerenes and nanotubes) used for negative electrodes in lithium-ion cells [384] and, as a consequence, the new developments in the technology of nanosize materials [341, 346, 354, 373, 390] deserve attention.[384] The research aimed at the development of new materials for both negative [347, 349, 350, 364, 382, 386, 387] and positive electrodes [332, 360 – 362, 368, 370] as well as for electrolytes [330, 345, 362, 375] is noteworthy. Finally, generalising reviews [329, 335, 340, 376] should be mentioned.

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