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New Lithium Salts in Electrolytes for Lithium-Ion Batteries (Review)[1]

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Abstract—The properties of electrolyte systems based on standard nonaqueous solvent composed of a mixture of dialkyl and alkylene carbonates and new commercially available lithium salts potentially capable of being an alternative to thermally unstable and chemically active lithium hexafluorophosphate $LiPF_6$ in the mass production of lithium-ion rechargeable batteries are surveyed. The advantages and drawbacks of electrolytes containing lithium salts alternative to $LiPF_6$ are discussed. The real prospects of substitution for $LiPF_6$ in electrolyte solutions aimed at improving the functional characteristics of lithium-ion batteries are assessed. Special attention is drawn to the efficient use of new lithium salts in the cells with electrodes based on materials predominantly used in the current mass production of lithium-ion batteries: grafitic carbon (negative electrode), $LiCoO_2$, $LiMn_2O_4$, $LiFePO_4$, and also solid solutions isostructural to lithium cobaltate with the general composition $LiMO_2$ (M = Co, Mn, Ni, Al) (positive electrode).

Keywords: lithium-ion batteries, liquid nonaqueous electrolytes, new lithium salts, dipolar aprotic solvents, physicochemical properties, compatibility with electrode materials, prospects of practical application

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INTRODUCTION

Lithium electrochemical systems demonstrate the highest energy capacity among the wide diversity of existing versions, because lithium has the most negative redox potential among all metals and the smallest electrochemical equivalent owing to its position in the periodic system. The lithium power sources are characterized by the highest nominal voltage (which can reach the record-breaking value of 5 V) and also by the maximum theoretical specific capacity and the high specific energy which exceed many times the characteristics of other types of batteries [1–3]. Lithium-ion batteries (LIBs) which appeared in the market relatively recently occupy the leading position among high-capacity batteries for portable electronic devices (cellular phones, notebooks, etc.) [2–5]; moreover, LIBs form a considerable part of market's segment of rechargeable batteries for electric tools. According to prognoses, the same should be observed for high-power batteries used in electric and hybrid vehicles, backup systems, systems for leveling peak loads, systems for energy storage and redistribution at the power stations working on renewable energy (solar, wind, etc.) as well as in distributed power generation, etc. However, this has not yet happened despite the pressing demand of the market for such power sources. High-power batteries for electric vehicles should retain their performance for no less than 15 years [6, 7] even when working in a temperature range wider that the range available so far (from –20 to +50°C [7]). However, the modern mass-production LIBs demonstrate the even if gradual but inevitable loss in their capacity and power capability at temperatures above 60°C [2]. For a high-power LIBs, the main life-shortening factor is not even the loss in capacity but the power loss associated with the increase in the internal resistance with time [6]. Moreover, when the high charge/discharge current flows, the problems such as

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fire and explosion safety become pressing and are still unsolved in modern LIBs [8, 9]. This keeps down the production of high-power LIB and substitution of other types of batteries for them, in contrast to low-current LIBs designed for portable electronics. Ultimately, there is the problem of safe and efficient operations of batteries under the conditions of negative temperatures (down to –40°C), which is especially pressing in Russia.

The majority of modern mass-production LIBs use carbon (mostly grafitic) as the active material of the negative electrode [3, 5, 10]. As the material for the positive electrode in LIBs, three classes of compounds [3, 11–20] are used: (1) layered lithium transition-metal oxides with the general composition $LiMO_2$ (M = Co, Mn, Ni, Al); (2) lithium transition-metal oxide spinels with the general composition LiM_2O_4 (M = Mn, Ni); (3) compounds based on complex phosphates with the polyanion structure and the general composition $LiMPO_4$ (M = Fe, Co, Mn, Ni). Among them, lithium cobaltate $LiCoO_2$ is the most popular material [3, 11, 12, 16–18] preferentially used in LIBs for portable electronic devices and electric tools [15]. The attempts to increase the specific capacity and raise the operating voltage of a cell and also to improve the electrode kinetics and increase the resistance to degradation have led to commercialization of mixed layered oxides based on lithium nickelate. In the LIBs production, the solid solutions $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (NCM) and $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA) (their quantitative composition can be varied) are the most popular [3, 12, 16, 18, 20]. It is the latter that are used preferentially in lithium-ion rechargeable batteries for electric and hybrid transport [3, 17, 18], although the problems of their safety, high cost, and limited service life are still topical [18, 20]. The obvious advantages of lithium-manganese spinel are its cheapness, availability, and nontoxicity on retention of the acceptable level of specific capacity and sufficiently high discharge voltage as well as its higher thermal and structural stability [3, 20]. However, the wide commercialization of the high-power LIBs with the positive electrode of lithium-manganese spinel is hindered by its limited cycle life sharply decreasing even at temperatures above 40°C due to irreversible degradation of this electrode [14, 16]. This is why the LIBs with spinel-based positive electrodes have the limited working temperature interval, demonstrating their best performance at low temperatures. Recently, the real alternative to complex-oxide materials for the positive electrode in high-power batteries was provided by lithium iron phosphate $LiFePO_4$ with the polyanionic structure of olivine, which has the lower operating potential (~3.5 V against ~3.8–5 V) but exhibits quite a number of advantages: low price, availability, safety, and relatively high capacity [11–13, 15, 16, 19]. This material has found wide application in high-power LIBs [3]; however, their characteristics are far from being perfect so far.

In many aspects, the problems of high-power LIB as regards their reliability, lifetime, safety, operation in a wide temperature range, and acceptable costs correlate with those of presently used electrolyte systems. In connection with this, the necessity of optimizing the composition of standard liquid and gel electrolytes with lithium-ion conductivity is quite evident. One of the most important research directions in this field is the search for alternative lithium salts with the more stable anion [7, 9] as the substitute for conventional lithium hexafluorophosphate $LiPF_6$ on retention of the basic composition of the mixed organic solvent. However, as correctly noted by the authors of a review [21], despite the acuteness of the problem, much less attention was paid to the development of new lithium salts as compared with the development of new cathode [3–5] and anode [3, 5] materials. Nonetheless, in the past 15–20 years, several tens of lithium salts potentially suitable for LIB electrolyte systems were synthesized and studied, the corresponding information can be found in reviews [2, 3, 10, 21–26].

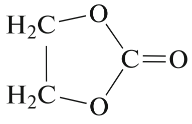
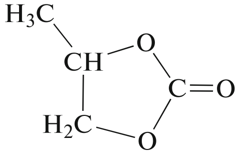
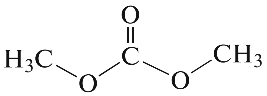
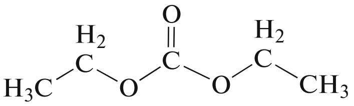
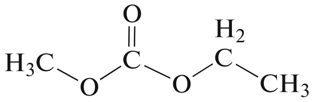
This review is aimed at summarizing the available information on the properties of conventional carbonate-based electrolyte systems comprising new commercially available lithium salts and also on the prospects of their use in commercial LIBs, first of all, in high-power rechargeable batteries. In connection with this, attention is focused on the effect of the nature of lithium-salt anion on characteristics of electrochemical cells with electrode materials commonly used in modern LIBs.

SOLVENTS AND SOLID ELECTROLYTE INTERFACE (SEI) ON THE CARBON ELECTRODE SURFACE

The main components of liquid and gel electrolytes of mass production are a lithium salt LiX and a mixed organic solvent based on dipolar aprotic solvents. The electrolyte composition was chosen such to provide the fast transport of lithium ions, adequate impregnation of the electrode and separator bulk, good wetting of granules of electroactive materials, and also to form solid electrolyte interface (SEI) on the carbonaceous electrode surface during the first few (forming) cycles, which provides long-term cycling. Moreover, the electrolyte should stabilize the surface of the positive electrode material.

The choice criteria of dipolar aprotic solvents for LIBs electrolytes are described in detail in reviews and monographs [2, 3, 10, 21, 22, 27–29]. At present, it is the family of organic esters of carbonic acid with the linear or cyclic structure, namely, dialkyl and alkene carbonates, that are used virtually exclusively for this purpose. This is associated with the combination of

Table 1. Properties of cyclic and linear carbonates used in LIB electrolyte systems [2]

Name	Structure	$T_{m.p}$, °C	$T_{b.p}$, °C	ε (25°C)
Ethylene carbonate (EC)		36.4	248	89.78
Propylene carbonate (PC)		–48.8	242	64.92
Dimethyl carbonate (DMC)		4.6	91	3.107
Diethyl carbonate (DEC)		–74.3	126	2.805
Ethylmethyl carbonate (EMC)		–53	110	2.958

their good solvating ability with respect to lithium ion and the high electrochemical stability and also with the ability to form a stable protective layer on the carbon electrode surface [2, 3, 30]. Insofar as neither of individual carbonates combines the high dielectric permittivity (required for dissolution and dissociation of lithium salt) with the low viscosity (necessary for the fast transfer of lithium ions and impregnation of LIB components), their mixtures are used. Although the exact composition of a mixed solvent produced by different manufacturers may vary, the basic mixture should involve ethylene carbonate (EC) with the cyclic structure and one or more dialkyl carbonates with the linear structure: dimethyl carbonate (DMC), diethyl carbonate (DEC), and ethylmethyl carbonate (EMC). Sometimes, the mixed solvent composition is supplemented by ethers or carboxilic esters with various structures, but the latter play the secondary role. Table 1 shows the key properties and the structures of the main components of mixed solvents. The ionic conductivity (σ_{ac}) of a lithium-salt solution in a mixed solvent should be at the level of (5–10) × 10^{-3} S cm^{-1} near room temperature; this provides the LIB operations at temperatures from –30 to +60°C [10].

It is well known [27–29] that the ability of a carbonaceous electrode to be cycled for a long time is associated with the formation of SEI (passive film) on its surface from the reduction products of electrolyte components. The reactivity of lithium-carbon intercalation compounds is extremely high, differing only slightly from that of metal lithium; the electrolyte solution components are also chemically active. The SEI forms a barrier between these components, spatially separating the reagents from one another. This layer serves simultaneously as a "sieve," permitting the passage of only Li^+ cations involved in the electrochemical reaction and preventing the penetration of other molecules (including the solvation shells of Li^+ ions) and also holding, like a "glue," the graphene sheets together, preventing exfoliation (Fig. 1a) [10]. Moreover, SEI blocks the electron transfer thus preventing the self-discharge of LIBs associated with formation of short-circuited elements. The ability to form the high-quality SEI is one of the most important criteria for the choice of mixed solvent components.

Figure 1b illustrates the mechanism of SEI formation. According to modern views [10, 28, 30–32], the formation of SEI proceeds on cathodic polarization of the carbon electrode during the first charging cycle (or several cycles). First, at potential <1.5 V, the solvated Li^+ cations are incorporated into the graphite interlayer space through the lateral surface. (From here on, the potentials are related to Li^0/Li^+.) This induces local expansion of the graphite lattice along its crystallographic axis *c* (Fig. 1b); this effect was

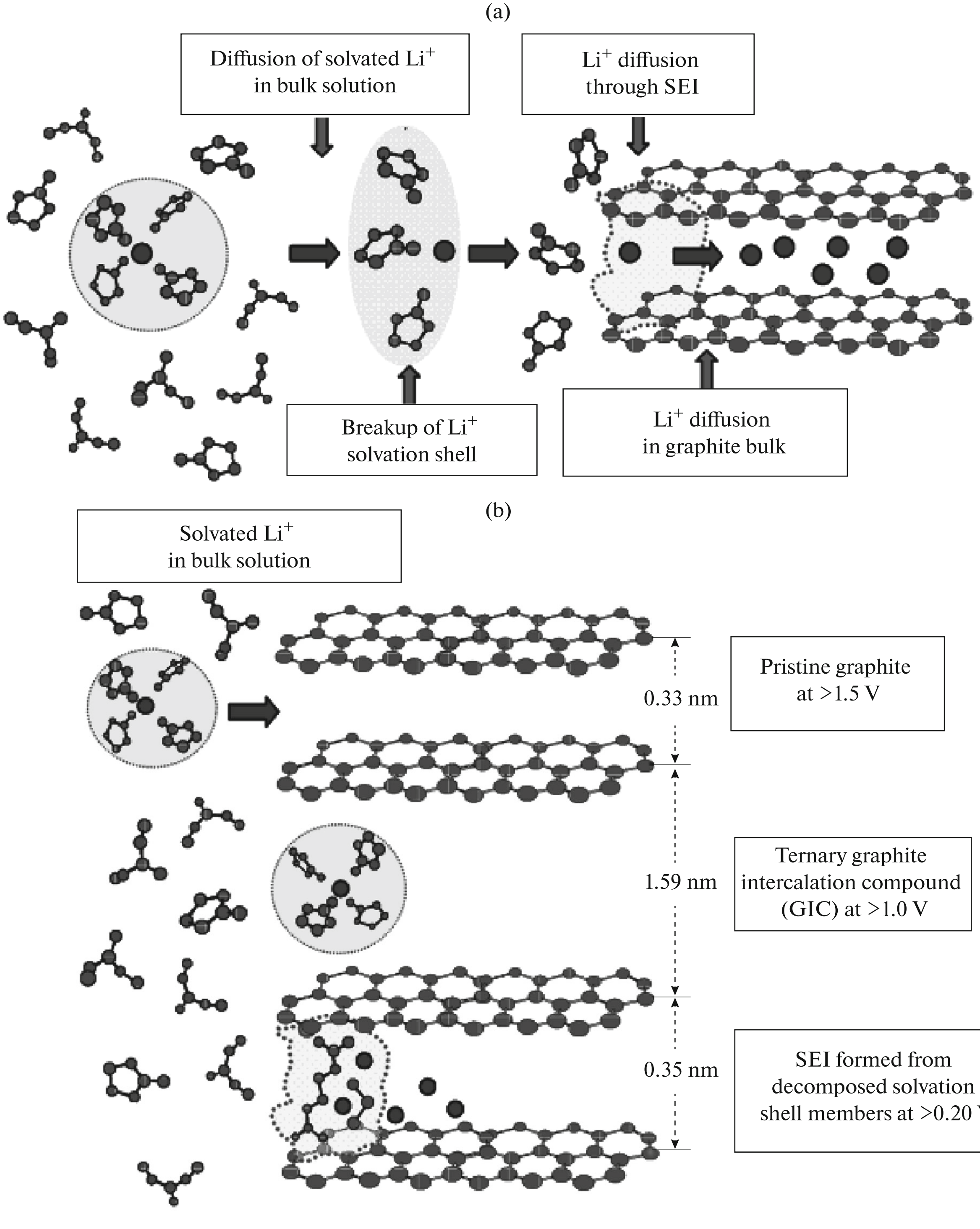
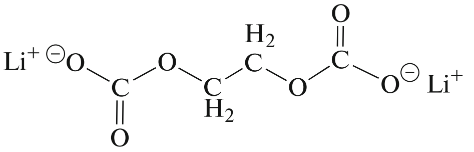
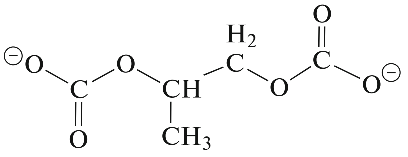
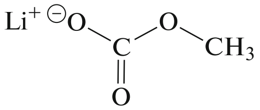
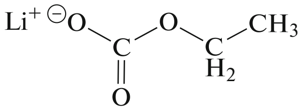


Fig. 1. Illustration of (a) intercalation of lithium ions into the graphite structure through the SEI layer and (b) the role of solvation shell of Li^+ ions in the formation of SEI on the graphite anode surface on cathodic polarization in the first charging cycle [31].

observed experimentally above 0.7 V [31]. Further, the electrochemical reduction of carbonate molecules takes place to produce unsoluble products that form the SEI. In the potential range of <0.3 V, lithium ions stripe of their solvation shells and incorporate into graphite through the SEI layer to form intercalation compounds (Fig. 1a); the lithium-saturated composition of the latter is LiC_6. According to this scheme, the charge transfer resistance of the graphite electrode (R_{ct}) is associated with two activation processes:

Table 2. Unsoluble reduction products of dialkyl and alkylene carbonates (in the presence of Li^+)

Solvent	Reduction product	Initial temperature of thermal decomposition, °C*
EC	 LEDC	~150
PC	 LPDC	~150
DMC	 LMC	~210
DEC	 LEC	~210
EMC	LMC + LEC	

* According to [30].

(1) desolvation of the lithium cation and (2) its transition through the SEI layer [32].

It was found [10] that it is lithium ethylene dicarbonate (LEDC) (Table 2), the only solid product of EC electrochemical reduction in the presence of Li^+ cations through single-electron pathway, that is responsible for the sought properties of SEI [33]. The linear carbonates DMC, DEC, and EMC can also produce the similar unsoluble products, lithium alkylcarbonates, as a result of electrochemical reduction in the presence of Li^+ [34] (Table 2); nonetheless, the main role in the SEI formation belongs to EC. This is associated with the preferential solvation of Li^+ cations by EC molecules. It was shown [31] that electrochemical reduction involves first of all those solvent molecules that take part in the Li^+ solvation shell, whereas the linear carbonates exhibit much weaker ability to solvate lithium ions as compared with cyclic carbonates. Moreover, it is LEDC that forms the dense layers strongly bound with the granule surface. In contrast to EC, its nearest homolog, propylene carbonate (PC) which is reduced at ~0.8 V, is incapable of forming the high-quality SEI layer; when cycled in PC-based electrolytes, the graphitic electrode quickly fails due to exfoliation [2, 10, 35, 36]. That is why the electrolytes of LIBs mass-production do not include PC or its use is limited, despite its high dielectric permittivity and the low melting point (Table 1) important for LIBs operation at negative temperatures. The observed dramatic difference between the related and chemically close cyclic carbonates EC and PC as regards their ability to stabilize the graphitic electrode is still the subject of debates [10]. One of the most convincing and substantiated versions concerns the specific properties of lithium propylene dicarbonate (LPDC), the product of single-electron reduction of PC in the presence of Li^+ (Table 2). Due to steric hindrances associated with the presence of the side methyl group, this compound, in contrast to LEDC, cannot form a closely packed layer strongly bound with the graphite surface and hence exhibit enhanced solubility in the electrolyte [10].

The products of the electrochemical reduction of all main components of the mixed solvent in the presence of Li^+ ions (Table 2) were also synthesized as individual compounds [30]. This provided the reference data required for their identification (IR spectra, X-ray photoelectron spectra) and investigation of their physicochemical properties [30]. It was found that the reduction products of linear carbonates LMC and LEC are characterized by the higher (by 60–100°C) temperatures of thermal decomposition as compared with the corresponding derivatives of cyclic carbonates LEDC and LPDC (Table 2) but are significantly below LEDC as regards their resistance to dissolution in the electrolyte. The comparative assessment of solubility of various products in the mixed solvent EC/EMC (3 : 7 (mass)) has shown that solubility of LEDC is much lower as compared with LPDC and LEC which have the close solubility. It is this difference in solubility that explains the different ability of EC and PC to prevent exfoliation of graphene layers in graphitic electrodes [37].

The scheme of SEI formation described above is rather simplified and ignores the influence of real stepped morphology and sufficiently complicated surface chemistry of graphite particles as a result of which their different regions may be involved in the reaction to the different extent and at different rates, making the SEI formation a step-wise process and the film itself nonuniform as regards its composition and structure [32, 38]. Nonetheless, this scheme provides the required general insight into the mechanism of SEI formation and can be applied to carbonaceous materials with different degrees of graphitization and also to disordered carbons in which the similar processes may occur [2, 10, 39]. The scheme is very important for understanding the criteria of choice of electrolyte components.

Lithium salt anions also undergo electrochemical reduction on the graphitic electrode surface and contribute to the SEI formation; this process usually (but not necessarily) occurs in the same potential range. Despite the fact that stabilization of the graphitic electrode surface is determined first of all by the formation of LEDC [2, 10], the nature of anion influences strongly the composition, morphology, and physicochemical properties of SEI, allowing their variation in the wide limits.

Besides the ability to form SEI, the mixed solvent components should be stable against oxidative decomposition up to the potential ≥5.0 V [2, 10]. All dialkyl and alkylene carbonates shown in Table 1 satisfy this condition, being electrochemically stable up to ≥6.0 V (at high degrees of cleaning from impurities) [27].

LITHIUM SALT

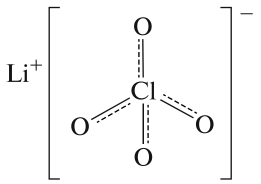
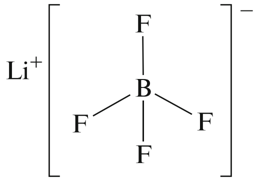
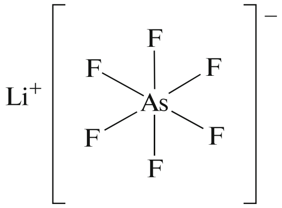
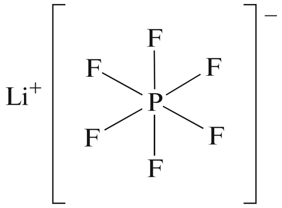
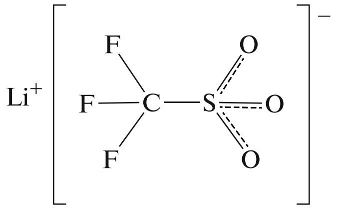
The choice of the lithium salt is of no less significance for the battery performance than the choice of solution components. Ideally, the lithium salt should dissolve readily in carbonate solvents shown in Table 1 and its anion X^- should be sufficiently stable against electrochemical oxidation and reduction on battery electrodes, chemically inactive, and insusceptible to hydrolysis and thermal decomposition. Moreover, the reduction products of X^- should not affect the transport properties and also the thermal and chemical stability of SEI in the working temperature range of the battery [2, 21, 22]. Finally, the lithium salt should be available, cheap, and nontoxic.

The extremely important and even decisive criterion of applicability of a lithium salt in the LIBs mass production is the ability of electrolyte on its basis to protect the aluminum foil surface from corrosion. This material serves as the current collector in mass-production LIBs and has no alternative [2, 25, 40–42]: Al exhibits high conductivity and low density, being also cheap and available. During the operation of a lithium-ion battery, the Al foil is constantly subjected to considerable anodic polarization (>4 V); under these conditions, the anodic dissolution of aluminum accompanied by pitting may occur. Because the foil is very thin (down to 10 μm), the corrosion may lead to complete disintegration and fragmentation of the current collector [2]. The corrosion phenomena reduce the battery capacity and shorten its lifetime. The aluminum foil surface is passivated either as a result of appearance of an efficient protective layer formed by its chemical or electrochemical reaction with electrolyte components or, at least, due to retention of the film already present on the foil surface which consists of Al_2O_3, oxyhydroxide, and hydroxide (~50 nm) [2]. The efficient passivation does provide the operation of the aluminum current collector even at the anodic polarization far exceeding the thermodynamic potential of aluminum dissolution (1.39 V) [2].

The lithium salt should not only exhibit sufficient thermal stability as such but also provide the necessary level of thermal stability for the electrolyte solution. It was shown that the temperature of the beginning of exothermic processes in the electrolyte which induce its self-heating depends strongly on the nature of lithium salt anion and can be shifted to one or another direction; the rate of these processes also changes substantially [22, 43–49]. However, LiX plays the secondary role in the electrolyte inflammation. It was shown [50] that irrespective of the nature of lithium salt anion, the first stage of combustion is solely governed by the most volatile components of the mixed solvent, namely, linear carbonates which have the burning rate higher as compared with cyclic carbonates. The effect of the lithium salt anion manifests itself only in the second stage. The combustion enthalpy is also determined by the mixed solvent, being independent of LiX. However, the toxicity of burning products depends on the nature of X^- anion and, only to the small extent, on the organic solvents [50].

The electrochemical stability of the lithium salt anion should be sufficient for its use in combination with the positive electrode materials in modern LIBs, taking into account their working interval: 2.0–4.0 V

Table 3. Lithium salts of the first generation used in electrolytes of commercialized lithium electrochemical systems

Chemical composition, name	Structure	M_w	Application field [1]
$LiClO_4$ lithium perchlorate		106.4	Primary Li cells
$LiBF_4$ lithium tetrafluoroborate		93.9	Primary Li cells; thin-film LIB (limited)
$LiAsF_6$ lithium hexafluoroarsenate		195.9	Primary Li cells (limited)
$LiPF_6$ lithium hexafluorophosphate		151.9	Mass-production LIB
$LiCF_3SO_3$ lithium trifluoromethanesulfonate (triflate)		155.9	Primary Li cells

for $LiFePO_4$; 3.0–4.2 V for $LiCoO_2$ and isostructural solid solutions NCM and NCA; 3.0–4.4 V for $LiMn_2O_4$ [51, 52]. The quantitative characteristic of electrochemical stability of anion is its oxidation potential (E_{ox}) on the inert electrode (usually Pt or glassy carbon).

The anion X^- is the only degree of freedom of a lithium salt; thus, its nature is of the key importance for the performance of the electrochemical cell as a whole. The lithium salt has a strong influence on the composition and morphology of SEI, thus determining the thermal stability of the graphite electrode and its impedance. Moreover, LiX takes part in interfacial chemical reactions in the cathode half-cell leading to the formation of surface layers of unsoluble products which contribute to the impedance of the positive electrode [2, 53, 54]. In its turn, the impedance of the positive electrode is responsible for the increase in the internal resistance of the whole lithium-ion battery in time [2].

ELECTROLYTES BASED ON LITHIUM SALTS OF THE FIRST GENERATION

The electrolytes of primary and secondary electrochemical systems which were commercialized even before the appearance of LIBs included most often the salts $LiClO_4$, $LiBF_4$, $LiAsF_6$, $LiPF_6$, and $LiCF_3SO_3$ as their ionogenic component [2, 21–25, 55–58]. Table 3 shows structures and application fields of these salts attributable to the first generation.

All lithium salts of the first generation have their own advantages and drawbacks and, hence, satisfy the requirements imposed on LiX only to one or another degree. Electrolytes containing cheap and available

Table 4. Properties of lithium salts of the first generation and electrolyte solutions on their basis

LiX	Properties of individual salts			Properties of electrolyte solutions* (at 25°C)		
	$T_{\mathrm{m.p}}$, °C	T_{decomp}, °C	stability against hydrolysis	σ_{ac}**, S cm^{-1}	E_{ox}***, V	passivation of Al
$LiClO_4$	236 [2]	>236 [2]	Stable [2]	~10^{-3}–10^{-2} [2]	4.6 [2]	Yes [2, 64]
$LiCF_3SO_3$	~420 [65] >300 [2]	430 [66]	Stable [2]	~10^{-3} [60, 67]	5.0 [2]	No [60–63]
$LiAsF_6$	340 [2]	240 [68]	Stable in nonaqueous solutions [2]	~10^{-2} [2, 23]	5.1 [2]	Yes [2]
$LiPF_6$	190 [43] 200 [2]	≥50 [69, 70]	Unstable [2]	~10^{-2} [2, 7, 27, 60]	4.2 [71, 72] 4.25 [73] 4.4 [74] 4.5 [75]	Yes [2, 7, 42]
$LiBF_4$	293 [2] 305 [76]	~160 [76] 132 [77] ~300 [78]	Unstable [2, 62]	~10^{-3} [2, 7, 77]	5.2 [77]	Yes [2, 7, 79, 80]

* In mixture of cyclic and linear carbonates.

** On alternating current.

*** On the surface of inert Pt electrode.

$LiClO_4$ exhibit high conductivity and good thermal stability, can passivate Al and efficiently form SEI on the negative-electrode surface. However, the highest oxidation state of chlorine makes the ClO_4^- anion a very strong oxidizer; under extreme operation conditions (enhanced temperature or high current density), $LiClO_4$ can enter into intense chemical interaction with the organic solvent, which brings about the explosion hazard [2, 21, 23, 24, 43]. Indeed, 1 M $LiClO_4$ solution in the mixed carbonate solvent EC/DEC/DMC (2 : 1 : 2 (vol)) explodes at 220°C [43]. $LiAsF_6$ is also thermally stable, forms electrolyte solutions with the very high conductivity, passivates Al, and provides good cycling behavior of electrochemical cells with the graphitic electrode [2, 59]; however, the wide use of lithium hexafluoroarsenate is limited by the high toxicity of arsenic and its compounds [21, 24, 55]. $LiBF_4$ has the lower thermal stability and is less resistant to hydrolysis in nonaqueous solutions as compared with $LiAsF_6$, demonstrating also the lower conductivity; on the other hand, the electrolytes on its basis have the lowest viscosity at negative temperatures [2, 24, 25]. $LiPF_6$ forms electrolyte solutions with the highest conductivity, efficiently passivates Al, and forms SEI with the lowest resistance, but exhibits the lowest thermal and hydrolytic stability among all salts under consideration [2]. Lithium triflate $LiCF_3SO_3$ demonstrates thermal and hydrolytic stability; however, its solutions in carbonate mixtures exhibit relatively low conductivity and fail to protect Al from corrosion (according to different sources, this process begins at 2.8 V [60, 61], 3.3 V [62] or 3.8 V [63]). Moreover, $LiCF_3SO_3$ forms the SEI with poor properties on the negative electrode [2, 24, 25, 55, 58]. Table 4 compares the characteristics of lithium salts of the first generation and electrolyte solutions on their basis.

The vast majority of commercialized electrolytes for lithium-ion batteries represent solutions of lithium hexafluorophosphate [2, 10, 21]. The use of $LiPF_6$ is the result of compromise because this salt does not completely meet all the requirements to lithium salt [2, 3, 21, 22]. $LiPF_6$ ranks below $LiAsF_6$ as regards conductivity of electrolytes and susceptibility to oxidative decomposition, below $LiBF_4$ as regards mobility of ions, below $LiClO_4$ and $LiCF_3SO_3$ as regards hydrolytic stability and also has the lowest thermal stability of all salts considered here. However, none of lithium salts of the first generation satisfies as much the multifaceted requirements as $LiPF_6$ does [2]. The main advantage of $LiPF_6$-based electrolytes is that they easily form the protective layer on the aluminum surface [23, 42, 64].

NEW LITHIUM SALTS AS AN ALTERNATIVE TO $LiPF_6$

Lithium Phosphates

When studying the properties of electrolytes and the characteristics of electrochemical cells with other versions of lithium salts, the $LiPF_6$ solution in the same solvent (individual or mixed) is used as a rule as the reference point and the advantages of the new electrolyte are compared with this standard electrolyte. This is why it seems reasonable to mention the main characteristics of the conventional electrolytes based on $LiPF_6$ before considering various versions of

Table 5. Commercially available alternative lithium salts

Short name	Complete name	Chemical formula	M_w	CAS	Manufacturer
LiFAP	Lithium *tris*(pentafluoroethyl)trifluorophosphate	$LiPF_3(CF_2CF_3)_3$	452.0	–	Merk (USA)
LiBOB	Lithium *bis*(oxalato)borate	$LiB(C_2O_4)_2$	193.8	244761-29-3	Sigma-Aldrich (USA); Chemetall (USA); BASF (Germany);
LiDFOB	Lithium difluoro(oxalato)borate	$LiBF_2(C_2O_4)$	143.8	409071-16-5	Central Glass (Japan); Fujian Chuangxin Science and Technology Development (China); Dongguan Shanshan Battery Materials (China)
LiTFSI	Lithium *bis*(trifluoromethyl sulfonyl)imide	$LiN(CF_3SO_2)_2$	287.1	90076-65-6	Sigma-Aldrich (USA); Chemodex (Germany)
LiBETI	Lithium *bis*(perfluoroethyl sulfonyl)imide	$LiN(SO_2CF_2CF_3)_2$	387.1	132843-44-8	3 M (USA) Chempur (Poland)
LiFSI	Lithium *bis*(fluorosulfonyl)imide	$LiN(SO_2F)_2$	187.1	171611-11-3	Suzhou Fluolyte (China) HQ (Canada); Huasheng Chemical (China); HSC Corporation (USA); Chempur (Poland) Nippon Shokubai (Japan)
LiTDI	Lithium 4,5-dicyano-2-trifluoromethyl-imidazolide	$Li[C_3N_2(CN)_2CF_3]$	192.0	–	Alfa Aesar (USA) Arkema (France)

commercially available lithium salts (Table 5) and assessing their advantages.

$LiPF_6$ dissolves in carbonate solvents up to very high concentrations; according to [81], even in individual DMC with the very low dielectric permittivity (see Table 1) 5 M $LiPF_6$ solution can be obtained. At 25°C, the maximum conductivity of these solutions approaches 10^{-2} S cm^{-1} and corresponds to 2 M concentration [81]. The electrolyte conventionally used in lithium cells represents 1–1.5 M $LiPF_6$ solution in a mixed carbonate solvent with the conductivity of ~10^{-2} S cm^{-1} at room temperature [2].

The main drawbacks of $LiPF_6$ is the thermal and hydrolytic instability of its complex anion. Even for crystalline $LiPF_6$, its thermal decomposition to LiF and PF_5 was observed even at 50°C [69, 70]. According to calculations carried out in [82], $LiPF_6$ is thermodynamically unstable even at room temperature; the equilibrium concentration of decomposition products increases with heating. The decomposition of the unstable complex lithium fluoride $LiPF_6$ proceeds still easier in electrolyte solutions where the thermal decomposition is supplemented by its hydrolysis to yield HF and POF_3 [2, 29, 83]. This affects adversely the battery characteristics, because HF enters into side chemical reactions with the positive electrode material and also induces the formation of the LiF layer on the negative electrode surface, thus blocking the transfer of Li^+ ions [21, 84, 85]. The high hydrolyzability of $LiPF_6$ necessitates the strict control over the residual water present inevitably in the electrolyte solution (usually ≤20 ppm). This complicates the production, transport, and storage of electrolytes and raises the costs. It deserves mention that water can be formed in electrolyte itself during the battery operation as a result of chemical reactions involving organic components [2]. Furthermore, the degradation products of the hexafluorophosphate anion, namely, PF_5 and POF_3 are the Lewis acids capable of initiating the autocatalytic decomposition of electrolyte components [2, 23]. Many of these reactions are exothermic, contributing the LIB self-heating and thermal runaway [2, 86]. The reactions in electrolyte are accompanied by intense gas evolution, creating the risk of explosion. The buildup of pressure in electrolytes containing $LiPF_6$ is observed already at 170°C (in the heating mode); at 200°C the first exothermic process of electrolyte decomposition to form gaseous products begins, and at 240°C the second more

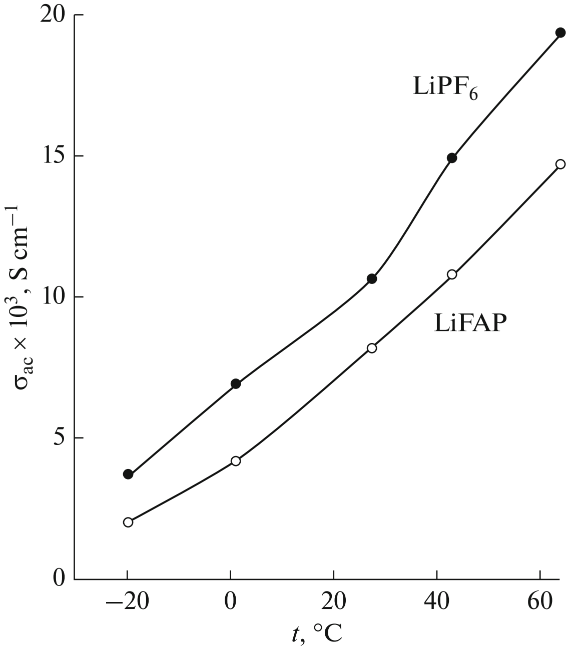
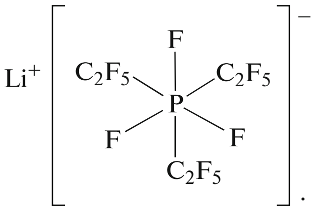


Fig. 2. Temperature dependence of conductivity of 1.0 M solutions of LiFAP and LiPF$_6$ in the mixed solvent EC/DMC (1 : 1 (mass)) (according to [75]).

intense process to form preferentially gaseous products starts [43, 86].

In the presence of LiPF$_6$, a dense and uniform SEI layer is formed on the graphitic electrode surface [87], which exhibits good protective properties [59] and low resistance [7, 52]. This makes possible long-term cycling of the graphitic electrode virtually without loss of capacity (close to theoretical) in the vicinity of room temperature [2, 59]. However, at elevated temperatures the behavior of graphitic electrode in electrolytes with LiPF$_6$ is far from perfect; the electrolyte rapidly degrades even at 60°C [71]. This is associated with instability of SEI in contact with electrolyte solution [88]. The destruction of SEI or the break of its continuity is a result of partial dissolution of its constituents in the electrolyte [2, 10]. According to investigations, if the SEI itself on the graphitic electrode (after washing from electrolyte and drying) remains stable up to ~250°C [54] (which well correlates with the data in Table 2), then the exothermic reaction of the graphitic electrode (in its lithiated state) in contact with electrolyte begins already at 70–80°C and is accompanied by active formation of gaseous products [49, 83, 88].

Insofar as LiPF$_6$ proved to be a sufficiently successful version for LIBs electrolyte systems, the attempts to modify the chemical structure of the complex phosphate anion in order to overcome its thermal and chemical instability and simultaneously strengthen its advantages seem to be quite reasonable. Modifying the anion structure by substituting mono and/or bidentate organic ligands for a part of fluorine atoms with the aim of stabilization yielded a family, albeit not too big, of new lithium salts; some of these modified lithium phosphates demonstrated interesting properties [10, 23]. At present, only one member of this family, lithium *tris*(pentafluoroethyl)trifluorophosphate $LiPF_3(CF_2CF_3)_3$ (LiFAP) is commercially available (Table 5):



LiFAP

As follows from its structural formula, the anion of this salt contains three perfluorinated alkyl groups in place of three fluorine atoms. Insofar as similar to fluorine atoms, the perfluoroalkyl substituents exhibit strong electron-withdrawing properties, the thus modified phosphate retains its chief advantages, namely, good solubility in organic solvents [2] (we failed to find any quantitative data in the literature) and high ionic conductivity of its solutions in carbonate solvents. The conductivity of LiFAP solutions is only insignificantly lower than that of LiPF$_6$ solutions [75] (Fig. 2). Furthermore, the replacement of fluorine atoms by more voluminous perfluoroethyl groups suppresses the anion susceptibility to hydrolysis, as experimentally proved in [75].

It is shown that modification of the phosphate anion structure gives only insignificant advantage in the thermal behavior of electrolytes with LiFAP: the onset of intense gas evolution (in heating mode) corresponds to 180°C, which is only 10°C higher as compared with LiPF$_6$; in the interval of 210–290°C some intense exothermic processes occur and the self-heating rate of the LiFAP-based electrolyte proves to be one order of magnitude higher as compared with LiPF$_6$ [43].

As regards its stability against oxidative decomposition on the electrode surface on anodic polarization, the anion FAP$^-$ is on the level of PF_6^-: intense anodic current can be observed only at ~5.0 V, although at potentials above 4.0 V a certain increase in the background current was noted (these data were obtained on the inert Pt electrode) [2, 71, 75]. The recent study [73] carried out in the LF30 electrolyte solution produced by Merk (1 M LiFAP in EC/DMC (1 : 1), content of H_2O ≤20 ppm, HF ≤50 ppm) revealed a little lower limit for the electrochemical stability window of FAP$^-$: ~4.5 V.

Table 6 summarizes the physicochemical properties of LiFAP and electrolytes on its basis together with the data for other alternative lithium salts.

Table 6. Properties of alternative lithium salts and electrolyte solutions on their basis

LiX	Properties of individual salts			Properties of electrolyte solutions* (at 25°C)		
	$T_{\text{m.p}}$, °C	T_{decomp}, °C	resistance to hydrolysis	σ_{ac}**, S cm^{-1}	E_{ox}***, V	passivation of Al
LiFAP	No data	No data	Stable [2]	~10^{-3} [75]	4.5 [73] 5.0 [2, 71, 75]	Yes **** [44, 71]
LiBOB	350 [76]	290 [76] 302 [89, 90] ~300 [78]	Unstable [62, 91]	~10^{-3} [91]	4.3 [2] 4.5 [91]	Yes [2, 78, 92]
LiDFOB	272 [76]	240 [78] 200 [76] ~280 [62]	Unstable [62]	~10^{-3} [62, 78, 93, 94]	4.35 [95] 4.5 [74] 5.57 [72]	Yes [78]
LiTFSI	236 [2, 68] 233 [96]	360 [2, 68] 365 [66] 384 [96]	Stable [2, 61, 97]	~10^{-3}–10^{-2} [2, 25, 58, 60, 98]	5.3 [2]	No [2, 42, 60, 61, 63, 99–101]
LiBETI	No data	≥400 [97]	Stable [97]	~10^{-3} [102]	>5.5 [23, 71]	No [2, 41, 61]
LiFSI	132 [103] 135 [25] 142 [81]	>180 [81] >200 [25, 99]	Stable [42]	~10^{-2} [81, 99, 103]	5.6 [103]	Yes***** [99]
LiTDI	–	250 [40] 285 [104]	Stable [40]	~10^{-3} [40, 105]	4.8 [40]	Yes [40, 104]

* In a mixture of cyclic and linear carbonates.

** On alternating current.

*** On the surface of Pt electrode.

**** Indirect data.

***** For salt with high purity.

The SEI are formed on the graphitic electrode in LiFAP solutions in the potential range the same as for $LiPF_6$ solutions; moreover, for LiFAP this process is completed already in the first cycle [44, 45, 71]. The SEI layer thus formed consists preferentially of the reduction products of solvents [106]; its resistance is only insignificantly higher as compared with $LiPF_6$ [71]. In electrolytes based on LiFAP, the graphitic electrode is cycled very well: its capacity is quickly stabilized at a level considerably higher as compared with $LiPF_6$ [44, 45, 71, 106]. However, cycling at 60°C has shown that after several tens of cycles, the graphitic electrode capacity begins to decrease gradually. Although the electrode degradation proceeds much more slowly than in electrolytes with $LiPF_6$ [71], this suggests the insufficient stability of SEI at elevated temperatures.

Cycling the cathode half-cell based on $LiMn_2O_4$ in the vicinity of room temperature has demonstrated that electrolytes with LiFAP can provide the higher discharge capacity and the faster electrode stabilization as compared with $LiPF_6$, although the capacity decreases virtually similarly with the increase in the cycle number [71, 75]. The surface of $LiMn_2O_4$ is covered with a passivating layer formed preferentially by the oxidation products of solvents [106]. The impedance of the positive electrode in LiFAP solutions considerably exceeds the impedance observed in $LiPF_6$ solutions, which can affect adversely the electrode kinetics; the increase in impedance is associated with the surface layer formation [71].

Thus, despite its good solubility in alkyl carbonates and conductivity close to that of $LiPF_6$ solutions and also the high electrochemical stability, LiFAP is not fully competitive with $LiPF_6$ in electrolytes based on mixtures of carbonate solvents. Unfortunately, modifying the PF_6^- anion by substituting fluoroorganic residues for fluorine failed to improve the stability of LiFAP-based electrolytes toward self-heating and even dramatized the problem of fire and explosion safety. Moreover, the use of LiFAP in place of $LiPF_6$ is economically unprofitable: first of all, this salt is rather costly and, second, taking into account the difference in molecular masses (M_w) (see Tables 3 and 5), the mass of LiFAP salt needed to prepare 1 M solution is three-times larger as compared with $LiPF_6$.

Lithium Borates

The progenitor of this family of lithium salts, $LiBF_4$ was considered as an alternative to $LiPF_6$ back in the

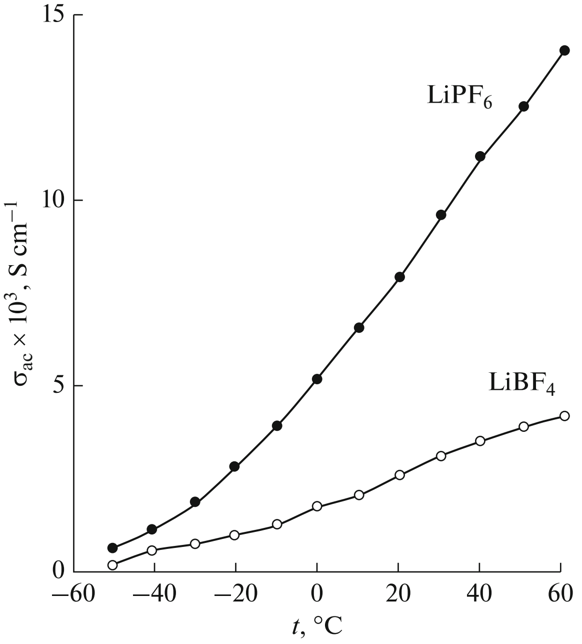


Fig. 3. Temperature dependence of conductivity of 1.0 M solutions of $LiBF_4$ and $LiPF_6$ in a mixed solvent EC/EMC (3 : 7 (mass)) (according to [7]).

early 2000s; the electrochemical cells with electrolyte on its basis demonstrate enhanced characteristics not only at elevated temperatures (up to 50°C) but also, quite unexpectedly, at low temperatures also [2, 24, 107].

Solutions of $LiBF_4$ in mixed carbonate solvents demonstrate characteristics much inferior as compared with $LiPF_6$ solutions as regards conductivity [7]; however, below 0°C these differences are leveled (Fig. 3). According to the authors of [108], it is possible to select the mixed solvent for $LiBF_4$ in such a way as to enhance substantially the conductivity at negative temperatures and obtain a good electrolyte for low-temperature applications. As regards their ability to passivate the surface of Al foil, the electrolytes based on $LiBF_4$ surpass those based on $LiPF_6$ [7, 79, 80]. $LiBF_4$ is much more thermally stable as compared with $LiPF_6$ (Table 4); although the data by different authors substantially deviate, the decomposition of this salt to LiF and BF_3 begins at temperatures above 130°C [76–78]. The anion BF_4^- is also more stable against hydrolysis than PF_6^- and has the wider electrochemical stability window (Table 4).

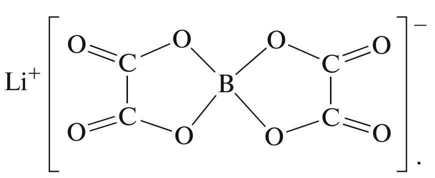
Taking into account the enhanced stability of $LiBF_4$, one could consider the relatively low conductivity of electrolytes based on this salt as acceptable provided that the SEI properties on the graphite electrodes do not degrade [7]. According to investigations, the SEI formation in electrolytes with $LiBF_4$ proceeds at the potential <1 V as for $LiPF_6$ [54]. SEI formed in $LiBF_4$ solutions have the granular structure and are denser as compared with $LiPF_6$ [87]. The impedance of the anode half-cell near room temperature is considerably higher as compared with $LiPF_6$ (~2 times) but quickly decreases with temperature [52].

Comparative studies carried out [7] for the anode half-cell with graphitic carbon, the cathode half-cell with a solid solution based on lithium nickelate (its composition is omitted), and also for the full lithium-ion cell have shown that at room temperature the results on cycling of all three cell versions with electrolytes containing $LiBF_4$ and $LiPF_6$ are virtually identical; the cycling behavior of cells based on $LiBF_4$ was unaffected by the presence of water in the amount of 620 ppm. On cycling at the enhanced temperature (60°C), the cells with $LiBF_4$ retained the Coulomb efficiently >98% even in the presence of 80 ppm of water. The fast loss of capacity was observed only at 80°C [7]; this is probably associated with the fact that SEI formed in solutions with $LiBF_4$ are unstable in contact with the electrolyte solution above 60°C [49]. The studies of low-temperature behavior of such cells carried out by the same authors [107] have shown that the relatively low conductivity of electrolytes with $LiBF_4$ is not the limiting factor below 0°C. The substitution of $LiBF_4$ for $LiPF_6$ resulted in a decrease in charge-transfer resistance and considerably increased the discharge capacity in the region of negative temperatures corresponding to the homogeneous liquid electrolyte.

Thus, $LiBF_4$ is an acceptable alternative to $LiPF_6$, which extends the LIB working range of temperatures and somewhat weakens the requirements to the residual water content in the electrolyte.

In attempts to improve the properties of LiX, a whole family of new lithium borates was developed, which is the largest among the families of new lithium salts; a recent individual review was devoted to this family [24]. Besides $LiBF_4$, two more representatives of this family are commercially available (Table 5).

Lithium *bis*(oxalato)borate $LiB(C_2O_4)_2$ (LiBOB) contains a complex anion formed by boron atom and two organic bidentate ligands—residues of oxalic acid



LiBOB

LiBOB is the best studied of all the new lithium salts. This nontoxic compound with acceptable cost was first synthesized in the early 1990s and patented in 1999 and 2003 as a conducting electrolyte component for lithium-ion batteries [109]. Like $LiBF_4$, LiBOB is unstable with respect to hydrolysis [62, 91]; however, in view of the absence of fluorine, its hydrolysis products are not so aggressive and chemically active as compared with hydrolysis products of lithium complex fluorides [2]. In contrast to $LiBF_4$, the solubility of LiBOB in carbonate solvents is not too high. Thus, the solubility of LiBOB in PC is only 0.362 M (at 25°C). At the same time, the conductivity of such saturated solutions is sufficiently high being equal to 6.76×10^{-3} S cm^{-1} [91], which is close to the values typical of 1 M $LiPF_6$ solutions in the same solvent. The more concentrated solutions of LiBOB (up to 1 M) can be prepared in the mixtures of EC with linear carbonates (DEC, DMC, EMC) or with other dipolar aprotic solvents, although their conductivity is somewhat lower as compared with analogous solutions of $LiPF_6$; however, at temperatures above 0°C, it is of the order of magnitude of 10^{-2}–10^{-3} S cm^{-1} [89, 110, 111] (Fig. 4).

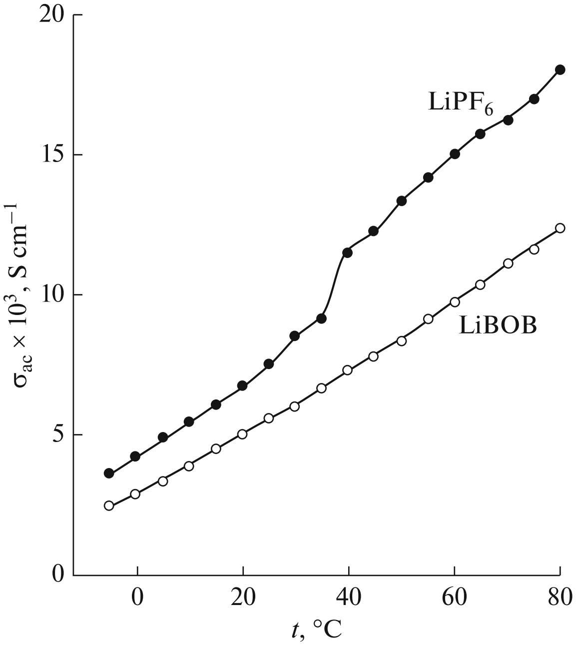


Fig. 4. Temperature dependence of conductivity of 1.0 M solutions of $LiPF_6$ and LiBOB in a mixed solvent EC/EMC (1 : 2 (mass)) (according to [110]).

The crystalline salt LiBOB exhibits the much higher thermal stability as compared with $LiBF_4$ and begins to decompose by a complicated mechanism only in the vicinity of 300°C (Table 6). Owing to the latter, the electrolyte solutions on its basis are also characterized by enhanced thermal stability: even after the 4-month storage at 85°C, no indication of degradation was observed for 0.7 M LiBOB solution in the EC/DEC/DMC mixture (1 : 1 : 1) [112]. As regards the electrochemical oxidation of its anion, LiBOB is close to $LiPF_6$ but ranks far below $LiBF_4$ (Table 6). The electrochemical stability window of BOB^- is 4.2–4.5 V (depending on the mixed solvent composition) [2, 24, 91]; this is sufficient for using such electrolytes in combination with commercialized materials of positive electrodes but too narrow for promising electrochemical systems with high-voltage materials [4].

According to the studies carried out in [92], the BOB^- anion can passivate the freshly prepared Al surface as efficiently as PF_6^- or BF_4^-. The high stability of aluminum current collectors (up to 6.0 V [2]) is associated with the fact that electrolytes with LiBOB do not destroy completely the protective oxide layer already present on the Al foil surface [113, 114] and can supplement the latter with a layer consisting of $AlBO_3$ [115].

One peculiarity of electrolyte solutions containing LiBOB is the peculiar mechanism of the SEI protective layer formation on the graphitic electrode surface at its cathodic polarization in the first (forming) charge cycle; this is illustrated by dependences of the differential capacity of electrochemical cells Li|LiBOB (sol)|graphite on the potential shown in Fig. 5. In electrolytes with LiBOB, the SEI formation involves two stages and begins already at 1.8–1.6 V being a result of electrochemical reduction of oxalate ligands [8, 24, 36, 52, 54, 87, 116]. On the other hand, in the conventional $LiPF_6$-based electrolyte and also in electrolyte solutions with $LiBF_4$ the SEI formation is observed only at ~(0.7–0.8) V (Fig. 5), which is typical of the electrochemical reduction of nonaqueous solvents in the presence of Li^+ ions [36, 52, 87]. The higher potentials of the electrochemical reduction point to the first-priority involvement of the lithium salt anion (in this case, LiBOB) in the SEI formation. This means that on the graphitic electrode surface during the first cathodic polarization, before the beginning of carbonate solvents reduction (~0.8 V), the protective layer has already been formed from the anion reduction products and is capable of preventing the intercalation of solvated lithium cations into graphite. The completion of such SEI as a result of further EC reduction improves its properties; however, it was found that LiBOB can form a high-quality SEI even in the absence of EC in the mixed solution composition [2, 36, 117]. This fact is of great importance because in this case, one can add PC to electrolyte composition (and even use PC as individual solvent), totally omitting EC [2, 36, 108]. Here, the benefit lies in the possibility of considerably extending the liquid range of electrolyte solution (PC melts at –48.8°C and EC atmelts at +36.4°C, see Table 1) thus improving the electrochemical behavior of cells at negative temperatures [2, 108]. It deserves mention that in this respect LiBOB and related LiDFOB (see below) are unique; their solutions are the only that can provide stable cycling behavior of the graphitic electrode when PC is used as individual solvent [2, 78, 93]. Morphology studies have shown that SEI formed in LiBOB solutions are dense, thin, and smooth [8, 87]. Such

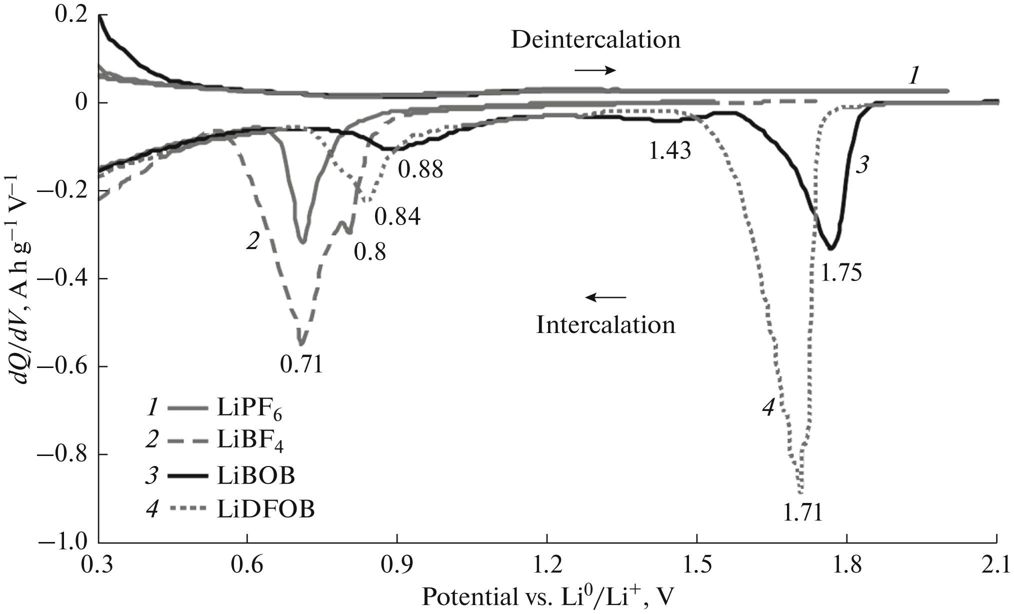


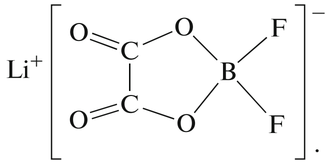
Fig. 5. Fragments of differential capacity curves of electrochemical cells Li|LiX (sol)|graphite with different electrolytes (1.2 M $LiPF_6$, 1.0 M LiDFOB, 1.0 M $LiBF_4$, and 0.7 M LiBOB in EC/EMC mixture (3 : 7 (mass)) in the potential range corresponding to SEI formation [54].

SEI comprising the reduction products of dioxalatoborate anion [87] exhibit the enhanced thermal stability: exothermic reactions between Li_xC_6 ($0 \leq x \leq 1$) and the electrolyte (as a result of destruction of the SEI barrier) begin higher than 170°C (in the heating mode), whereas, as was noted above, such processes for $LiPF_6$ and $LiBF_4$ begin already near 60–80°C. Unfortunately, the gain in the thermal stability for LiBOB is accompanied by the considerably higher resistance of such SEI [52].

Although as regards its hydrolytic stability, LiBOB ranks below $LiBF_4$ [62], the formation of HF is ruled out due to the absence of fluorine in the anion structure; this has a positive effect on the impedance of the cathode half-cell which turns out to be only a little higher as compared with $LiPF_6$ solutions [2, 52]. The electrode based on $LiMn_2O_4$ can be cycled sufficiently stably in electrolytes with LiBOB even at enhanced temperatures (up to 65°C) because the main reason for the capacity loss in such LIB, namely, the appearance of manganese ions in electrolyte solutions, is removed [2, 118–121]. This positive effect is usually associated with the absence of HF. Electrodes based on thermally stable $LiFePO_4$ can be cycled in LiBOB solutions in individual PC or EC up to record-breaking 100–120°C [24, 120]. This opens up the possibilities of creating middle-temperature high-power LIB to be used in electric vehicle or measurement tools in oil well drilling [24]. The literature contains also information on the possibility of improving cyclability of electrodes based on layered lithium transition metal oxides with the general composition $LiMO_2$ (M = Co, Mn, Ni, Al) at elevated temperatures in electrolytes with LiBOB [92, 120, 121]; however, the latter results are contradictory. It was stated [121] that LIB models with positive electrodes based on $LiNi_{1/3}Co_{1/3}Mn_{1/3}$ demonstrated stable (albeit lower) capacity when cycled in LiBOB at 55°C, whereas according to data of [120], after 12 cycles at 60°C such cells demonstrated capacity fade. Under the same conditions, the electrodes based on $LiCoO_2$ began immediately to lose their capacity [120]. According to authors of [120] who studied the behavior of cathode half-cells based on commercialized materials, the necessary condition of stable cycling of electrochemical cells with LiBOB-based electrolyte is the absence of cobalt in the positive electrode composition, because this element can supposedly catalyze the decomposition of the BOB^- anion during the anodic polarization. This is why the LiBOB-based electrolytes can be used at enhanced temperatures in combination with $LiFePO_4$, $LiMn_2O_4$, and $LiNi_{0.85}Co_{0.10}Al_{0.05}O_2$ but are inefficient in combination with $LiCoO_2$ and $LiNi_{1/3}Co_{1/3}Mn_{1/3}$ [120].

On the whole, despite the fact that LiBOB ranks below all lithium salts under consideration (Tables 4 and 6) as regards solubility in carbonate solutions, this salt exhibits quite a number of advantages which make it a worthy competitor to $LiPF_6$. Besides environmental compatibility, acceptable cost, and a considerable increase in thermal stability of the cell, the advantages include the mechanism of SEI formation on the surface of the carbon negative electrode, which allows PC to be involved in the electrolyte, and also the high thermal stability of SEI and its ability to efficiently passivate the surface of certain materials of positive electrode even at elevated temperatures. However, the low solubility of LiBOB in carbonate solvents limits the use of such electrolytes at low temperatures due to salt crystallization [9]. Yet another substantial disadvantage of LiBOB is the high resistance of SEI on the graphite electrode surface (several times higher as compared with $LiPF_6$ [52, 120]); this has an adverse effect on the power and discharge characteristics of LIB, especially at low temperatures. Hence, the successful practical use of LiBOB can so far be prognosticated only for middle-temperature LIBs and also for rechargeable batteries with the power from low to moderate [9].

In connection with the aforesaid, multiple attempts were undertaken to prepare new salts based on complex lithium borates (see review [24]). The most successful example of such structural modification is difluoro(oxalato)borate $LiBF_2C_2O_4$ (LiDFOB):



LiDFOB

This salt with asymmetrical anion representing a sort of "hybrid" between LiBOB and $LiBF_4$ was proposed for the first time in [78]. It was shown that substitution of two F for one oxalic-acid residue substantially improves the solubility in linear carbonates [62, 78, 94]. Thus, solubility in the mixture EC/DEC (3 : 7 (mass)) for LiBOB is only 0.65 mol/kg, whereas for LiDFOB it is already 1.4 mol/kg (compare with 1.75 mol/kg for $LiBF_4$) [62]. It is interesting to compare the conductivity of LiDFOB solutions with that of two related salts LiBOB and $LiBF_4$ in the same mixed carbonate solvent based on carbonates [78] (Fig. 6). As follows from the figure, the conductivities of 1.0 M solutions of LiDFOB, $LiBF_4$, and 0.8 M solution of LiBOB (its limiting solubility) in the mixture EC/PC/EMC (1 : 1 : 3 (mass)) above 10°C are related as LiBOB > LiDFOB > $LiBF_4$; however, at negative temperatures, the relationship changes: $LiBF_4 \approx$ LiDFOB > LiBOB. This is explained by the simultaneous influence of the salt dissociation degree and the solution viscosity, which act in opposition as the anion size increases. On the whole, the conductivity of electrolytes with LiDFOB is intermediate between the conductivities of electrolytes with LiBOB and $LiBF_4$; from the standpoint of transport properties, this salt combines the advantages of the both parent lithium salts [78] and provides conductivity at room temperature at a level of 10^{-3} S cm^{-1} [62, 78, 93, 94].

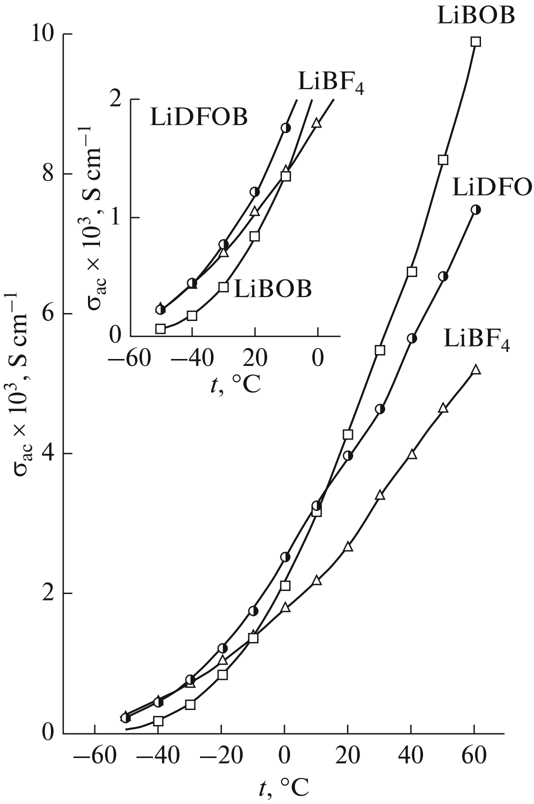


Fig. 6. Temperature dependence of conductivity of 1.0 M solutions of LiDFOB, $LiBF_4$, and 0.8 M solution of LiBOB in mixed solvent EC/PC/EMC (1 : 1 : 3 (mass)) (according to [78]).

The data on the thermal stability of LiDFOB shown in Table 6 differ considerably; apparently, this is associated with the different degree of purity of salts synthesized in the cited studies. Nonetheless, it follows from these data that as regards its thermal stability, LiDFOB considerably surpasses $LiPF_6$. This was also confirmed by the studies on thermal stability under conditions of long-term (170 days) isothermal exposure at 60°C, which revealed no indication of decomposition for this salt [62].

As regards the anion stability against oxidative decomposition at the positive electrode, LiDFOB compares well with LiBOB and $LiPF_6$ (Table 6). According to certain data, LiDFOB is even better than $LiPF_6$ [72, 74].

A comparative study of susceptibility of lithium borates to hydrolysis [62] has shown that the latter depends inversely on the number of fluorine atoms in anions, being expressed by the relationship $BOB^- >$ $DFOB^- > BF_4^-$. However, it deserves mention that HF is not among the hydrolysis products of LiDFOB because this process proceeds by the pathway different from that of $LiBF_4$ hydrolysis [62].

Electrolyte solutions based on LiDFOB, like other borates, can efficiently passivate the Al foil surface: anodic current is absent up to 6.0 V [78].

On the graphite surface, LiDFOB forms a solid-electrolyte layer with the strength the same as for LiBOB. The SEI formation with participation of LiDFOB as a result of oxalate ligand reduction begins at 1.5–1.7 V [6, 52, 54, 87, 93, 94, 122, 123] (these values are 0.04–0.12 V lower than for LiBOB [52, 54]); this process of formation of the primary SEI precedes the reduction of carbonate solvents at 0.6–0.7 V [6, 54, 87, 123] (as for LiBOB) (Fig. 5). The presence of primary SEI makes possible the addition of PC to the mixed solvent composition for LiDFOB too [78, 93]. It should be mentioned that the irreversible capacity for electrolytes with LiDFOB is lower as compared with LiBOB due to the lower content of oxalate ligands [123]. It is interesting that as regards morphology, the SEI formed in electrolytes with LiDFOB differ from those with LiBOB by their granular structure, resembling more the SEI for $LiBF_4$ due to the presence of a large amount of LiF in these layers [87]. Apparently, the thermal stability of SEI formed by LiDFOB is sufficiently high, because provides good cycle performance of lithium-ion cells at 60°C [92]. As regards this parameter, LiDFOB obviously surpasses $LiBF_4$ [24, 49]. There are polar opinions on the impedance of graphitic electrode. According to [6], the impedance is much lower for LiDFOB as compared with LiBOB and the gain in resistance is only 15% as compared with SEI formed in $LiPF_6$ solution. The authors of [52, 94] also pointed to the low resistance of SEI, comparable with $LiPF_6$. However, the authors of [93] showed the data on the increase of the SEI resistance by an order of magnitude.

There are many studies devoted to characteristics of electrochemical cells with electrolytes based on LiDFOB. The cell graphite|LiDFOB (sol)|$LiNi_{0.85}Co_{0.10}Al_{0.05}O_2$ was shown to demonstrate the stable discharge capacity in the wide interval of normalized discharge current and the temperature from –40 to 60°C (67.4% of the capacity at –30°C) [78]. The studies have shown that the total resistance of such cell is only slightly higher as compared with the case of electrolyte containing $LiPF_6$ [52]. For the cathode half-cell based on $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$, there are data on its cycling at room temperature with different rates [62]: the test cells could adequately retain the capacity and demonstrated high characteristics even at relatively high values of normalized discharge current. When cycled in electrolytes based on LiDFOB, both cathode and anode half-cells were characterized by exclusively stable discharge capacity values close to theoretical ones [6, 62]. The full cell graphite|LiDFOB (sol)|$LiNi_{1/3}Co_{1/3}Mn_{1/3}$ demonstrated the more stable characteristics on long-term cycling at 55°C as compared with the cell with $LiPF_6$-based electrolyte, which was attributed [122] to the formation of the higher-quality SEI on the negative electrode and the decrease in the resistance of this layer with the temperature. Among the authors of all cited studies there is consensus that the presence of LiDFOB in electrolyte favors retention of the cell capacity and simultaneously provides the high rates of electrode processes, i.e., favors the retention of power too.

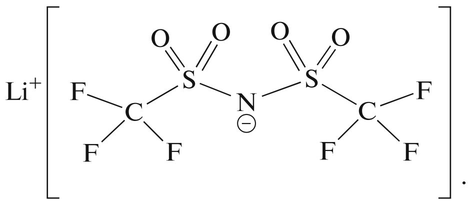
Electrolytes with LiDFOB are characterized by good electrochemical compatibility with $LiMn_2O_4$ [74]: no anion oxidation is observed on the surface of this material; at 4.9 V the oxidation of solvent components starts. The positive effect of LiDFOB (as compared with $LiPF_6$) on the impedance of the cathodic half-cell is manifested at elevated temperatures (60°C); studying the electrode surface morphology has shown that in contrast to $LiPF_6$, LiDFOB forms a smooth and dense passivating layer which is also retained at 60°C [74]. This layer prevents the appearance of Mn^{2+} ions in the electrolyte, whereas in the case of $LiPF_6$ considerable dissolution of manganese in the electrolyte is observed (this very process is considered responsible for the fast degradation of LIB with lithium-manganese spinel at elevated temperatures [3, 24]). Although the stability of such cells with respect to cycling cannot not be called ideal, the substitution of LiDFOB for $LiPF_6$ does has the positive effect both at room temperature and at 60°C [74].

Electrodes based on graphitic carbon and $LiFePO_4$ in LiDFOB-based electrolytes demonstrate the much higher impedance values as compared with $LiPF_6$ solutions; however, the discharge capacity of cells graphite|LiDFOB (sol)|$LiFePO_4$ is virtually independent of the number of cycles even at 65°C (in contrast to $LiPF_6$) [93]. Generally, such cells in LiDFOB solutions are cycled equally well as in $LiPF_6$-based solutions (room temperature) or much better (–10 and +65°C), at the normalized current up to 4 C (no data on the higher rates are given) [94]. LiDFOB forms a passivating layer on the surface of $LiFePO_4$ as a result of electrochemical processes in the first cycle (irreversible capacity in the cathode half-cell) [94]. It deserves mention that the impedance of the cathode and anode half-cells can be substantially reduced by varying the composition of the mixed carbonate solvent [94]. Moreover, the introduction of PC plays the positive role; this not only decreases the impedance but also provides cell performance at –10°C [94].

Summarizing the available data, it can be said that LiDFOB combines the advantages of $LiBF_4$ and LiBOB [10, 76, 123] but surpasses them as regards the SEI conductivity, approaching $LiPF_6$. As a result, it provides the higher power characteristics and the enhanced stability of cycling at low temperatures [123]. All borates including LiDFOB are close to $LiPF_6$ or surpass it as regards the electrochemical stability. However, LiDFOB is too sensitive with respect to the presence of water and oxalates in the electrolytes, which adversely affects the characteristics of rechargeable batteries [123]. Nonetheless, LiDFOB can surely compete with $LiPF_6$ in high-power batteries, because provides the capacity and power retentions [6, 76, 78, 94]. Particularly, this salt demonstrates much higher characteristics in the temperature range from –10 to +65°C as compared with $LiPF_6$ in the electrochemical system graphitic carbon–$LiFePO_4$ which forms the basis of high-power batteries of mass production.

Lithium Imide

The progenitor of this family of lithium salts is lithium *bis*(trifluoromethyl sulfonyl)imide $LiN(CF_3SO_2)_2$ (LiTFSI) (trivial name—lithium imide):



LiTFSI

LiTFSI is among the first thermally stable salts with organic anions; it was synthesized in the beginning of 1980s even before the appearance of lithium-ion batteries. LiTFSI well dissolves in dipolar aprotic solvents and is characterized by the enhanced stability against hydrolysis [2, 61, 97]. The conductivity of LiTFSI solutions in mixed carbonates is close to that of $LiPF_6$ solutions [98, 100] (Fig. 7); in a mixture of specially selected solvents, the conductivity of LiTFSI solutions is ~10^{-3} S cm^{-1} even at –25°C [58].

Crystalline salt LiTFSI is thermally stable; it melts without decomposition (which is rare for lithium salts, see Tables 4 and 6) and does not undergo destruction up to >360°C [2, 66, 68, 96] (Table 6). As a result of this, the thermal stability of electrolyte solutions containing LiTFSI is also considerably enhanced. SEI layers formed on the graphite electrode in solutions of this salt are thermally stable; exothermic processes above 125°C are determined by reactions of organic solvents rather than by SEI decomposition [49]. Thus, the substitution of lithium *bis*(trifluoromethyl sulfonyl)imide for $LiPF_6$ provides noticeable advantages as regards the higher safety and the working range of temperatures extended in both directions. Anion $TFSI^-$ is very stable towards electrochemical oxidation (Table 6). However, LiTFSI ranks below $LiPF_6$ and lithium borates as regards its ability to passivate the surface of Al foil: according to different sources, the critical corrosion potential of Al electrode in LiTFSI solutions based on cyclic and linear carbonates is from 3.6 to 4.5 V (Table 6). This is insufficient for the use of such electrolytes in mass-production LIB. However, the recent studies have shown that the corrosion activity with respect to Al is inhibited as the LiTFSI concentration in electrolyte increases up to 1.8 M due to the formation of a passivating layer of LiF [124].

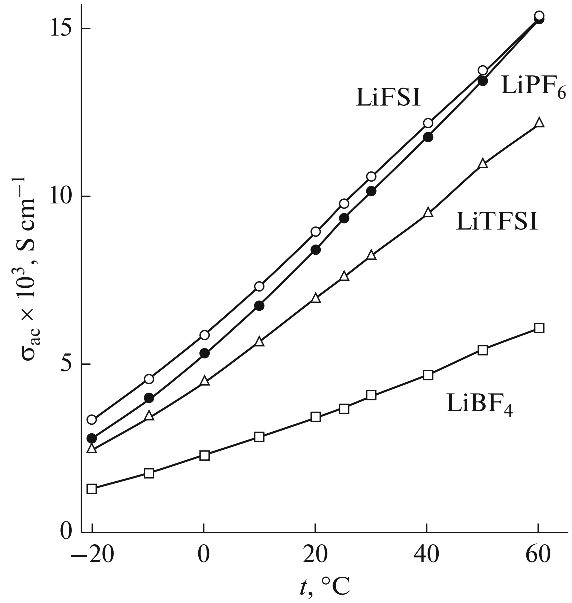
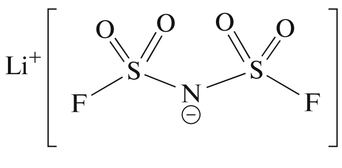
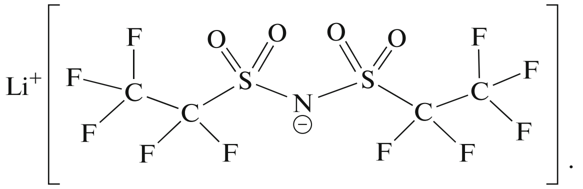


Fig. 7. Temperature dependence of conductivity of 1.0 M solutions of LiTFSI, LiFSI, $LiBF_4$, and $LiPF_6$ in mixed solvent EC/EMC (3 : 7 (mass)) (according to [99]).

It was shown that the corrosion activity of Al in lithium imide solution can be changed by modifying the nature of anion. This approach made it possible to synthesize several tens of salts in the lithium imide family many of which are of high practical interest. Among the latter, only two are commercially available so far. These are lithium *bis*(perfluoroethyl sulfonyl) imide $LiN(SO_2CF_2CF_3)_2$ or LiBETI and lithium *bis*-(fluorosulfonyl)imide $LiN(SO_2F)_2$ or LiFSI (Table 5):



LiFSI



LiBETI

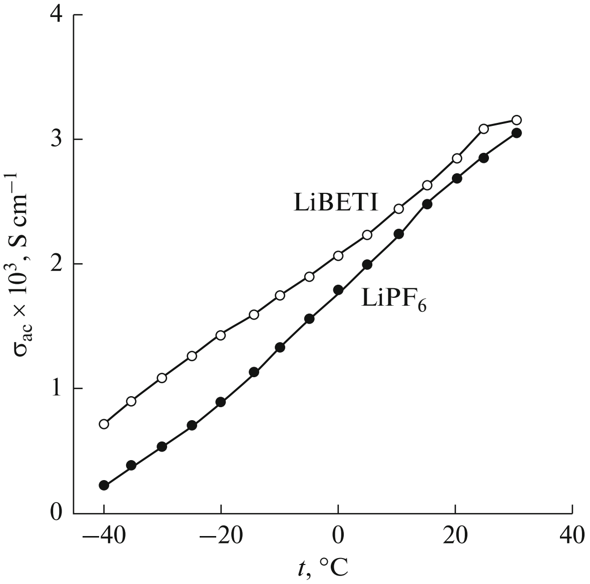


Fig. 8. Temperature dependence of conductivity of 1.0 M solutions of LiBETI and $LiPF_6$ in mixed solvent EC/EMC (3 : 7 (mass)) (according to [102]).

Like the progenitor of their family, LiTFSI, the salts LiBETI and LiFSI have anions the charge on which is considerably delocalized due to the presence of several heteroatoms and electro-withdrawing terminal $-CF_3$ groups [55, 58]. This is why all imides are well soluble in dialkyl and alkylene carbonates and their mixtures. For example, the solubility of LiFSI reaches 5 M even in DMC and EMC [81] with very low values of dielectric permittivity (Table 1). Conductivity of LiBETI solutions [60, 98, 102] and, especially, LiFSI [81] near room temperature is close to conductivity of $LiPF_6$ solutions in the same mixed solvent; below room temperature, LiBETI and LiFSI surpass $LiPF_6$ in conductivity (Figs. 7 and 8). Electrolytes with LiFSI demonstrate record-breaking conductivity at negative temperatures: 0.9×10^{-4} S cm^{-1} for LiFSI in DMC/EMC (3 : 7 (vol)) at –50°C [81]. Both salts are stable against hydrolysis [41, 97, 99].

Comparing the data on thermal stability of individual lithium imides (Table 6) shows that LiBETI has the highest onset temperature of thermal decomposition (≥400°C), whereas LiFSI that contains the inorganic fluorosulfonyl group $-SO_2F$ has the lowest thermal stability (its decomposition begins at >180–200°C). Nonetheless, even LiFSI is far more stable than $LiPF_6$ and decomposes at temperatures above its melting point. As regards the anion stability against electrochemical oxidation, the advantage belongs to BETI$^-$ (Table 6).

Insofar as LiBETI is the most thermally stable salt (Table 6), the electrolyte solutions on its basis are also the most resistant to enhanced temperatures: for LiBETI no changes in the electrolyte composition were observed during its isothermal exposure at 120°C [43, 102] and during its heating up to 340–350°C [43, 55]. In contrast to LiBETI, the introduction of LiFSI has no substantial effect on the thermal stability of electrolytes. Studies on combustion behavior [50] have shown that LiFSI provides no advantage over $LiPF_6$ as regards safety.

The graphitic electrode can be cycled fairly well in solutions of all lithium imides due to the formation of SEI with the high protective properties and enhanced (as compared with $LiPF_6$) thermal stability. Moreover, for imide LiFSI with the simplest inorganic anion and also for LiTFSI, the SEI formation begins at the same potential of ~0.8 V (vs. Li^0/Li^+) as for $LiPF_6$ [87], i.e., proceeds preferentially due to reduction of mixed solvent components. However, for LiBETI that contains the more complex anion, the SEI formation begins at the higher potential of 0.9–1.0 V, which suggests the involvement of this anion in the mentioned process [44, 125].

As was shown in [60], the complication of the imide anion structure leads to the higher corrosion stability of Al in the solution of this salt. In electrolytes with LiBETI, the corrosion of aluminum electrode does not begin below 4.5–4.6 V [41, 42, 60, 61]. The lowest corrosion stability of aluminum was observed in solutions of LiFSI salt that has the simplest symmetrical inorganic anion. Thus, it was found [103] that the electrolyte containing LiFSI without additional purification could induce the Al corrosion already at 3.3 V (according to other sources, at 3.7 V [99]). The more detailed studies have shown that such high corrosion activity of LiFSI, exceeding even the activity of LiTFSI, was associated with the presence of LiCl traces and, probably, other uncontrolled impurities [99]; if LiCl impurity is strictly excluded from the salt (<50 ppm), the electrolytes with LiFSI induced no corrosion of Al up to 4.2 V; according to other data, up to 4 V [81, 126]. Thus, it can be concluded that electrolytes with LiBETI and LiFSI can be used in LIBs.

The major merits of LiBETI that allow considering it as an acceptable alternative to $LiPF_6$ in a particular niche of electrochemical systems concern the higher thermal stability of this electrolyte and its acceptable cost (LiBETI is cheaper than $LiPF_6$ so that its higher molecular mass (Tables 4 and 6) is of no particular importance). Testing electrochemical cells with the carbonaceous negative electrode and the positive electrode based on $LiCoO_2$ at aluminum current collector has shown [60] that the LiBETI electrolytes provide even a small increase in cell characteristics as compared with $LiPF_6$. Cells with another positive electrode material, $LiNi_{0.80}Co_{0.15}Al_{0.05}O_2$, and the negative electrode based of a graphitic carbon were cycled in LiBETI solutions much better as compared with $LiPF_6$ solutions, due to the lower impedance of their cathode half-cell [102].

Taking into account the limitations imposed by the corrosion stability of aluminum, the electrolyte solu-

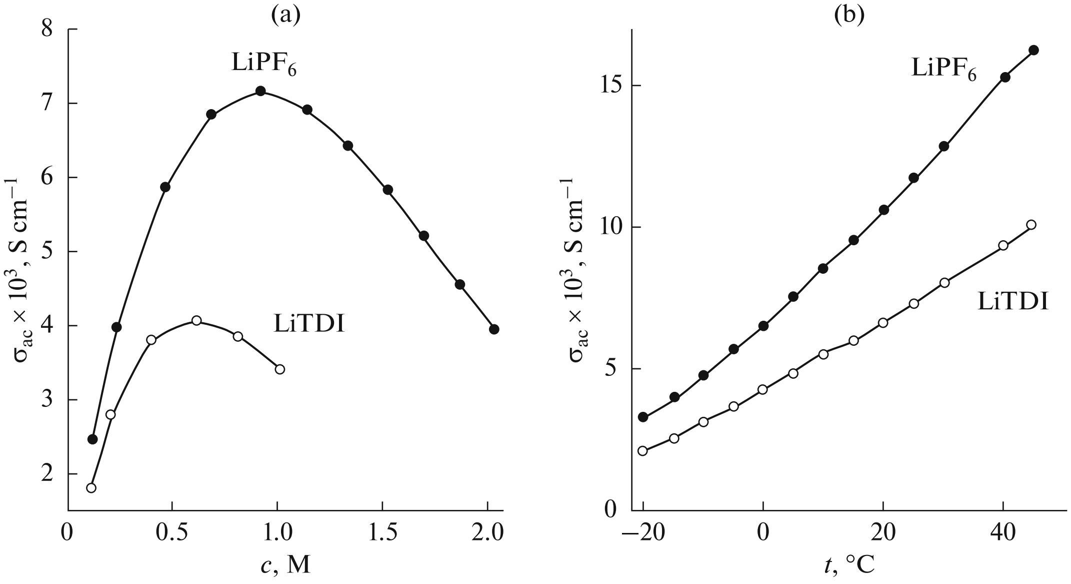
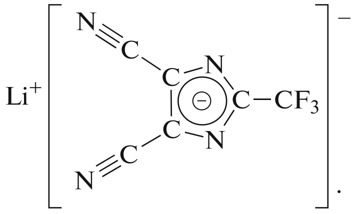


Fig. 9. (a) Dependence of conductivity of solutions of LiTDI and LiPF$_6$ in mixed solvent EC/DEC (3 : 7 (mass)) on concentration at 20°C; (b) temperature dependence of conductivity of 1.0 M solutions of LiTDI and LiPF$_6$ in mixed solvent EC/DMC (1 : 1 (mass)) (according to [104] and [40], respectively).

tions with LiFSI can be used only in lithium-ion batteries with the positive electrode based on LiFePO$_4$ [10]. Studying the test cells has shown that both graphitic carbon and LiFePO$_4$ are adequately cycled in these electrolytes [81, 103, 127].

Lithium Imidazolide

Yet another group is formed by salts with anions based on the substituted heterocycles specially “tailored” for LIB. The stable structures of these anions were, first of all, calculated by quantum-chemical methods and only then some of them were synthesized [53, 128, 129]. The high stability of these anions is associated with the covalent nature of all bonds and the conjugation of multiple bonds. In certain aspects, the heterocyclic anions can be considered as a version of imides but with conjugated and delocalized bonds [10]. The keenest practical attention is drawn to imidazol derivatives which can be synthesized sufficiently easily from low-cost precursors. Recently, one of these salts became commercially available; this is lithium 4,5-dicyano-2-trifluoromethylimidazolide (LiTDI) (Table 5):



LiTDI

LiTDI is well dissolved in carbonate solvents. In contrast to the other salts under consideration, the maximum of LiTDI conductivity falls on relatively low salt concentrations (~0.3–0.6 mol/kg) [21, 104, 130] (Fig. 9a). Taking into account that for these solutions σ_{ac} ~5 × 10^{-3} S cm^{-1} is combined with the cation transference number ($t_+ \approx 0.5$–0.6) higher as compared with LiPF$_6$ ($t_+ \approx 0.3$–0.4), the lithium-ion conductivity of electrolytes with LiTDI exceeds such in LiPF$_6$ electrolytes [21, 40, 105, 130]. Figure 9b shows the temperature dependence of conductivity of electrolytes based on LiTDI as compared with LiPF$_6$ solutions in the same mixed solvent.

Crystalline LiTDI salt is thermally stable up to >250°C [40, 104]. This is more than sufficient for its use in LIB electrolyte systems. The stability limit of TDI$^-$ anion as regards oxidation on the Pt surface reaches 4.8 V [40]. Electrolytes with LiTDI do not induce corrosion of the aluminum electrode up to 4.75 V presumably because they fail to destroy the protective oxide layer on the aluminum surface [40].

The formation of a SEI on the graphitic electrode during its cathodic polarization in electrolyte solutions with LiTDI begins at <1.0 V [51], much resembling the LiBETI solutions. Such SEI prevents graphite exfoliation [51].

Studying the behavior of the anode half-cell has shown [51] that at the small values of normalized current, the discharge capacity of the graphitic electrode in electrolyte based on individual LiTDI does not differ from that observed in LiPF$_6$ solutions containing a standard additive, 2% vinylene carbonate (VC) often used for stabilizing SEI; however, for the normalized current above 0.2 C the deviations against LiTDI become noticeable, increasing for 2 C and higher. However, this difference is easily leveled after the introduction of the same amount of VC or fluoroethylene carbonate (FEC) into the LiTDI-based electrolyte [51]. For another commercialized negative-electrode material, $Li_4Ti_5O_{12}$, no difference was observed during its cycling with different rates (from 0.1 to 4 C) in LiTDI-based electrolytes even containing no VC and FEC additives [51].

Cycling the cathode half-cells containing $LiCoO_2$, $LiMn_2O_4$, $LiFePO_4$, and $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ in the LiTDI-based electrolyte over a wide range of discharge rates has shown that the latter provides characteristics no lower than those typical of $LiPF_6$ and for $LiCoO_2$, even higher [104]. The latter results well agree with the data of other studies. According to [51], LiTDI-based electrolyte demonstrated adequate compatibility with $LiFePO_4$ and $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$; these positive-electrode materials could be cycled in this electrolyte equally successfully as in the $LiPF_6$ solution containing 2% VC [51]. Cycling of cells graphite|1 M LiTDI|$LiMn_2O_4$ at room temperature demonstrated that after 25 cycles the discharge capacity was stabilized at a value slightly lower than theoretical (its loss was only 3%) at adequate values of power [40].

Despite being obviously insufficiently well explored, LiTDI seems to be a quite reasonable alternative to $LiPF_6$ in electrolytes used in LIB. It is thermally and hydrolytically stable, not too hydroscopic (can be stored in air), passivates the surface of Al collector, and exhibits sufficiently high stability against electrochemical oxidation. Everything mentioned above makes it possible to combine the LiTDI-based electrolytes with positive electrode materials used at present in the mass production of LIBs.

CONSLUSIONS

The information presented in this review attests that electrolytes based on the standard nonaqueous solvents (mixtures of dialkyl and alkylene carbonates) and the commercially available alternative lithium salts may enhance the safety, extend the range of working temperatures, and prolong the service life of lithium-ion rechargeable batteries. Lithium imides LiFSI, LiTFSI, and LiBETI allow the electrolyte conductivity at negative temperatures to be substantially increased, lithium borates LiBOB and LiDFOB make it possible to prepare middle-temperature electrolyte systems based on individual high-boiling cyclic carbonates PC and EC in which the graphitic electrode can be steadily cycled up to temperatures of 100–120°C. The substitution of $LiPF_6$ for any of new salts described in this review improves the electrochemical behavior of the anode half-cell based on carbonaceous materials at the high temperature (>50°C); however, at room temperature and lower, this is accompanied by a certain increase in its impedance, especially noticeable for LiBOB. Taking into account the limitations imposed by the corrosion stability of aluminum, the electrolyte solutions with LiFSI can be used only in lithium-ion batteries with the positive electrode based on olivine ($LiFePO_4$). This material demonstrates very good capacity and discharge characteristics in combination with virtually all alternative versions of lithium salts; hence, for the electrochemical system graphitic carbon–$LiFePO_4$ there is real possibility to extend the range of working temperatures and improve some other parameters. For lithium-manganese spinel, a considerable effect is provided by changing $LiPF_6$ for lithium borates, particularly, LiDFOB, which allows the problem of stable cycling at 60°C to be solved. The positive electrodes based on a mixed layered oxide NCA demonstrate good characteristics when cycled with electrolytes containing LiBETI, LiBOB (up to 55°C), and LiDFOB (even at −30°C), while electrodes based on NCM are well compatible with LiDFOB (up to 60°C); the behavior of lithium cobaltate is benefited by LiBETI. All commercialized positive-electrode materials are electrochemically compatible with LiTDI at room temperature (the wider temperature interval was not studied so far). Thus, the possible correct strategy is to use the new lithium salts in place of $LiPF_6$ each in its own niche by fitting them individually to the particular electrode material in view of the problem that confronts the developer. It is quite evident that neither of salts described in this review can be considered as the universal version suitable for all active materials of positive electrodes and for batteries of all purposes.

The studies on selecting the alternative solvents (individual or mixed) for new lithium salts are beyond the scope of this review. For LiBOB, such studies allow the problem of limited solubility to be solved. In many cases, such electrolytes prove to be more efficient as compared with electrolytes based on conventional mixtures of carbonate solvents and are also of considerable interest. Furthermore, this review does not also consider the numerous studies of electrolytes with mixed lithium salts and also the studies on the use of new lithium salts as the additives to the standard electrolyte based on $LiPF_6$. Each of these individual directions in the development of improved electrolyte systems for LIBs deserves separate discussion.

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