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Review

A critical review of electrode materials and electrolytes for Low-Temperature Lithium-Ion Batteries

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The critical analysis of literature of last 15 years, concerning features of low-temperature behavior of lithium-ion batteries is presented. Certain approaches to the problem; the role of different constituents of electrode polarization at low temperatures; features of functioning of negative and positive electrodes are reviewed. Low-temperature electrolytes are reviewed as well.

Keywords: lithium-ion batteries, low temperatures, electrode polarization, low-temperature electrolytes.

1. INTRODUCTION

Most modern lithium-ion batteries are designed to power portable electronic equipment (cell phones, laptop computers, portable cordless power tools, etc.). The range of operating temperatures of such devices most often falls within the range from −20 to +35 °C. Most manufacturers guarantee that at a temperature of −20 °C the discharge capacity of the battery at C/5 rate will be 80% of the nominal capacity. However, there are ever new areas of the possible use of lithium-ion batteries, where operating temperatures can drop to −40 and even −50 °C (weapons and military equipment, aviation and space technology, transport devices, etc.). For instance, battery of typical hybrid electric vehicle should be able to deliver up to 5 kW cold-cranking power at the temperature as low as −30 °C. A decrease in temperature leads to fundamental problems in the functioning of a lithium-ion battery, since the rates of all activation processes decrease. In particular, the electrolyte conductivity, the diffusion rate in the solid and liquid phases, and the charge transfer rate in electrochemical processes decrease [1−12]. Since the temperature dependence of the rates of all these processes is usually described by the Arrhenius equation (or close to it), the inhibition greatly increases with decreasing temperature. As far back as 2001, it was shown [13] that a decrease in temperature from room temperature to −40 °C leads to a decrease in the energy density of commercial batteries of type 18650 manufactured by Panasonic from 100 to 5 Wh/l and a decrease in their maximum specific power from 800 to 10 W/l.

It is important to note that all the above factors are interrelated [14]. For example, the replacement of one electrolyte with another while keeping the composition and structure of the electrodes unchanged is accompanied not only by a change in the internal ohmic resistance, but also by the rate of charge transfer at the interface, the composition and structure of passive layers (SEI – solid electrolyte interphase), the rate of ion transfer through these layers, etc. In certain cases, one stage can be distinguished that limits the behavior of the entire battery at low temperatures. For example, in [15], based on an analysis of the data of electrochemical impedance spectroscopy of disk batteries with a graphite negative electrode and a positive electrode based on lithium nickelate, it was shown that the charge transfer resistance R_{ct} increases with decreasing temperature much faster than the ion transfer through SEI resistance (R_{SEI}) and the total ohmic resistance R_b. As a result, at a temperature of +20 °C the fraction of R_{ct} is about 30% of the total internal resistance ($R_{ct} + R_{SEI} + R_b$), and at temperatures from −20 to −60 °C this fraction is very close to 100%. The described result does not allow us to distinguish the contribution of individual electrodes to the total value of R_{ct}, especially since such an analysis does not show resistance of solid-phase diffusion, however, it clearly shows the complexity of the relationship of individual factors affecting the low-temperature behavior of a lithium-ion battery.

A characteristic feature of the functioning of lithium-ion batteries at low temperatures (approximately −20 °C and below) is that the polarization during the charge usually exceeds the polarization during the discharge [1, 2, 16, 17]. As a result, the discharge capacity at the same negative temperature turns out to be the greater, the higher was the temperature of the charge.

2. PROBLEMS OF NEGATIVE ELECTRODES

In early works, the deterioration of the performances of lithium-ion batteries with a temperature lowering was attributed mainly to the deterioration of the performances of negative electrodes made of carbon materials [2]. As already mentioned in the introduction, a decrease in temperature results in an increase in ohmic polarization due to a decrease in the electrolyte conductivity, to a decrease in the rate of transfer of lithium ions through the SEI layer (both due to an increase in the SEI thickness and due to a decrease in the diffusion coefficient of lithium in the SEI material), decrease in charge transfer rate, i.e. the true electrochemical stage of the process, as well as a decrease in the diffusion rate of lithium in carbon. In 1999 [17, 18], it was noted that when using $LiPF_6$ solutions in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) as an electrolyte, the ohmic drop in the electrolyte at temperatures below −20° C can play a noticeable role, but in going to more complex solvents, in particular to the mixture EC – DMC – diethyl carbonate (DEC), the role of this factor becomes insignificant. The question of the relative contribution of other polarization components to the total polarization does not yet have a clear answer. So, according to [19], a decrease in temperature from +25 to −30 °C led to an increase in the electrolyte resistance by 10–12 times, an increase in SEI resistance by 28–32 times, and an increase in charge transfer resistance by 28–41 times, therefore the contributions of various polarization components were comparable. At the same time, according to the data of [20], when the temperature decreases from +60 to −40 °C, the electrolyte resistance in the cell with a graphite electrode increased from 3.3 to 39 Ohms, SEI resistance from 10 to 1000 Ohms and charge transfer resistance from 15 to 35000 Ohms (the results were obtained by electrochemical impedance spectroscopy). Note that such a strong temperature dependence of the charge transfer rate corresponds to a rather large value of the activation energy, 97.4 kJ/mol. According to the same work, the diffusion coefficient of lithium in graphite upon transition from 30 to −40 °C decreases 12 times in the fully lithiated state and 25 times in the delitated state.

The conclusion about the slow diffusion of lithium in graphite as a determining factor in the deterioration of performances at temperatures of −20 °C and below was made in [1, 2]. The effect of graphite particle size on the electrode capacity described in [21] at a temperature of –40 °C is also explained by the diffusion nature of the slow stage of electrode discharge. It is characteristic that the concentration polarization caused by the diffusion of lithium in graphite during the deintercalation process turns out to be smaller than during graphite intercalation, and this difference, which is not significant at room temperature, noticeably increases with decreasing temperature [1, 2]. At the same time, the data [3, 19] show a strong influence of the nature of the electrolyte on the polarization of graphite electrodes, which refutes the conclusions of [1, 2] and explains the polarization asymmetry during lithiation and delithiation by the effect of the charge transfer rate.

In [22], the data of a thorough study of the kinetics of electrode processes by the method of electrochemical impedance spectroscopy (EIS) are presented. In this work, negative electrodes from graphite (MCMB) and positive electrodes from $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ in three different electrolytes ($LiPF_6$ solutions in mixtures of EC with ethyl methyl carbonate (EMC) of several compositions) were studied. The charge transfer resistance on the MCMB was independent of the electrolyte composition and increased with decreasing temperature according to the Arrhenius law with an activation energy of 41.6 kJ/mol. In [23], a charge transfer activation energy of 58 kJ/mol was obtained for a graphite electrode. In [24], an activation energy of 61 kJ/mol was reported for the charge transfer process on a graphite electrode. In [25], it was noted that the activation energy of charge transfer on the MCMB electrodes, measured in the range from –20 to 40 °C, significantly depends on the electrolyte composition: in $LiPF_6$ and $LiBF_4$ solutions in the EC−DMC mixture, it increased from 58 to 66 kJ/mol with increasing EC content from 0 to 40%. Close results are given in [26].

In some cases, lowering the operating temperature of the lithium-ion battery leads to unexpected consequences. For example, a situation was described in [27] when, in the temperature range from 25 to 70 °C, an increase in temperature is accompanied by an acceleration of degradation of characteristics during cycling due to the natural acceleration of self-discharge processes. At the same time, in the temperature range from 25 to −20 °C, the degradation rate during cycling increases with decreasing temperature. (In both cases, the temperature dependence of the rate of degradation is described by the Arrhenius equation, but the activation energy is positive in the temperature range from 25 to 70 °C, and the effective activation energy is negative in the temperature range from −20 to +20 °C). The acceleration of degradation with decreasing temperature was explained by the possible deposition of lithium metal on the negative electrode when the battery is charged at low temperature [28]. The well-known phenomenon of encapsulation of freshly precipitated lithium leads to an acceleration of the decrease in capacity during cycling [29−33]. To eliminate risk of lithium deposition onto surface of graphite various approaches were used. For instance, work [34] describes a surface modification by uniform carbon coating via chemical vapor deposition (CVD). It was found that thin carbon coating not only suppresses the dendrite forming but enhances the formation of LiC_6 at low temperatures as well. The authors of [35] suggest alumina coating instead of carbon for the same aim. To diminish activation polarization, and therefore to decrease a tendency to dendrite formation it was suggested to use certain composite of porous graphite nanosheets and carbon nanotubes [36]. Low-temperature performance of lithium-ion battery could be improved at change of core-shelled silicon–carbon composites for plain graphite in negative electrodes [37].

In [21], lithium-ion batteries were tested, in which a large amount of silver powder was introduced into the negative electrodes along with MCMB. This approach made it possible to triple the discharge capacity at a temperature of −40° C at the 1C-rate, but the mechanism of such an effect is not discussed in the article. Later, the beneficial effect of the addition of metal nanopowders to a graphite electrode was confirmed in [38], and a strong influence of the nature of the metal on the decrease in polarization was noted (the best results were achieved with the addition of copper, aluminum, and tin). In addition, a decrease in polarization at low temperatures was observed with mild oxidation of graphite surface. In later works of the same group of researchers [39−42], the behavior of graphite composites with nano-tin at low temperatures was studied in detail, and tin was introduced either as a vacuum coating about 5 nm thick on individual graphite particles or as an additive of nanopowder (with a particle size of less than 100 nm). The best results were achieved with vacuum deposition of tin. So, if electrodes from pure weakly oxidized graphite had a capacity of 365 and 1 mAh/g at room temperature and a temperature of –30 °C, then electrodes from a mixture of graphite with tin nanopowder at the same temperatures showed a capacity of 370 and 94 mAh/g, and electrodes made of graphite with tin nanocoating, correspondingly 377 and 152 mAh/g, respectively. The mechanism of tin effect was manifested both in a change in the properties of SEI and in a change in the kinetics of charge transfer itself. At room temperature, the SEI resistance on graphite electrodes ranged from 20 to 35 Ohms (depending on the degree of lithiation), and the SEI resistance on tin composites ranged from 5 to 10 Ohms. A much greater contribution to polarization was made by the charge transfer resistance, which at room temperature was more than 200 Ohm on pure graphite electrodes and about 25 Ohm on composites. A decrease in temperature led to a significant increase in charge transfer resistance in accordance with the Arrhenius equation, and the activation energy was 55 to 60 kJ/mol for electrodes of pure graphite and a mixture of graphite with tin nanopowder and 50 to 55 kJ/mol for electrodes with tin nanocoating.

It is worth noting that an increase in the tin coating thickness from 5 to 50 nm contributed to a decrease in both SEI resistance (especially at low temperatures) and a decrease in charge transfer resistance, and even the activation energy of this latter process, to 35 kJ/mol [42].

In [43, 44], similar electrodes with a coating of copper or with the addition of copper nanopowder were described, on which qualitatively the same results were obtained as on graphite and tin composites.

A Sn/C composite with nano-tin particles embedded into expanded graphite is described. These nano-particles are uniformly distributed in the graphite interlayers to create a tightly stacked layered structure [45]. The composite demonstrated discharge capacities of 200 mAh/g at 0.1C and 130 mAh/g at 0.2C, at the temperature −20 °C.

The authors of [46] reported on unexpected feature of core-shell silicon-carbon nanocomposites with silicon content from 2 to 14.5%. The laboratory soft-packed full cells with positive electrodes made from $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$ and negative electrodes from above composites demonstrated identical discharge curves at room temperature irrespective on silicon content. At the same time at the temperature −20 °C the capacity of cell with nanocomposite with 14.5% Si was by 25% higher than that of cell with nanocomposite with 2% Si.

Of non-carbon materials, the low-temperature behavior has been most thoroughly studied on lithium titanate $Li_4Ti_5O_{12}$ [47−49]. Even in the very first work of 2006 [50], it was found that a decrease in temperature from +20 to –30 °C leads to a regular increase in the total polarization and a decrease in discharge capacity. When cycling with low currents (C/8), the discharge capacity on the sample with larger particles (700 nm) at all temperatures was lower than on the sample with smaller particles (350 nm), which was explained by the difficulties of solid-state diffusion. However, with increasing cycling currents, the capacitances recorded on the sample with smaller particles at low temperatures turned out to be less than on the sample with larger particles, which the authors explained by increased contact (interparticle) resistance. At the same time, in [51] it was shown that electrodes made of lithium titanate obtained by cellulose-assisted glycine-nitrate combustion (cellulose-GN) process [52], and having smaller particles, do not differ in their characteristics from ordinary electrodes at room temperature, but have much lower polarization resistance and a much larger capacitance at a temperature of –20 °C.

The contribution of different polarization components of lithium titanate electrodes to the total polarization was determined in the work of the same research group [53] with using electrochemical impedance spectroscopy. It is noted that as the temperature decreases, the role of charge transfer resistance noticeably increases. So, for a material without a carbon coating, the charge transfer resistance at temperatures of 25, 0, –10, and –20 °C was 45.3, 358.6, 1208.0, and 2943.0 Ohms, respectively. (Such a temperature dependence of the charge transfer resistance corresponds to an activation energy of 58 kJ/mol). The resistance of the surface film in this case was 2.0, 10.9, 4.1, and 2.3 Ohms, i.e. SEI on pure lithium titanate is practically not formed. For the same material with a carbon coating (common for lithium titanate), the charge transfer resistance at the same temperatures was less and increased less with decreasing temperature (50.9, 144.9, 347.9, and 993.4 Ohms, respectively). But in this case, the influence of SEI was already affecting: the resistance of the surface film at the indicated temperatures was 4.5, 12.6, 20.5, and 39.2 Ohms. (In [54], the value of the activation energy of charge transfer on the electrode of lithium titanate 52.75 kJ/mol is given).

Qualitatively, the same conclusions about the effect of the particle size of lithium titanate and the carbon shell on the functioning of electrodes at low temperatures were made by Finnish researchers [55, 56].

In [57], data were presented on the kinetics of an electrode based on $Li_4Ti_5O_{12}$ in the temperature range from 10 to 70 °C. The activation energy of the limiting stage of the process calculated from these data is only 22.3 kJ/mol.

The paper [58] describes the synthesis of lithium nanotitanate in supercritical methanol using oleylamine as a surface modifier and carbon source. The synthesis is carried out in a short time (15 min.) and the result is a material with a core – shell structure, where a core with a size of 5–15 nm consisted of highly crystalline $Li_4Ti_5O_{12}$, and a shell with a thickness of 0.7–2.3 nm was well graphitized carbon.

Electrodes made of such a material were characterized by lower values of all resistance components, and at a temperature of –20 °C they had a capacity of about 150 mAh/g, which is only 10% less than that at room temperature. Similar structures were synthesized by other methods [59, 60]. An original version of the “core – shell” structure, in which several titanate nuclei (a “pod-like structure”) is contained in a single cylindrical carbon shell, is described in [61].

One of the varieties of nanomaterial based on $Li_4Ti_5O_{12}$ is described in [62]. In this work, $Li_4Ti_5O_{12}$ corrugated plates with a thickness of about 10 nm and a size of from 0.4 to 1 μm were synthesized. Such a material has a specific surface area of 206 m^2/g with a true density of 6 g/cm^3 (!). Doping such a material with a small amount of carbon (0.6%) and nitrogen (0.1%) ensures its high conductivity. Even at a rate of 10 C, the electrodes of this material had a capacity of 180 and 135 mAh/g at temperatures of +20 and –20 °C.

A noticeable improvement in the low-temperature behavior of lithium titanate electrodes was achieved by replacing the usual carbon coating of individual material particles with a carbon coating (Super-P) with 30–50 nm copper nanoparticles deposited on it [63]. The amount of copper was only 8.7% of the mass of carbon. The effect of copper nanoparticles was manifested in a marked decrease in the polarization of charge transfer, moreover, for the lithiation process, this effect was more pronounced than for delithiation. As a result, the decrease in capacity with increasing current and lowering the temperature for the sample with copper nanoparticles was much smaller. So, at a current of C/5, the capacity of the electrode without copper additives was 160 and 100 mAh/g at temperatures of +20 and –30 °C, whereas for the electrode with copper addition these capacities were 165 and 130 mAh/g. This effect was even more pronounced at 5C, namely, for an electrode without copper additives, the corresponding capacities were 120 and 5 mAh/g, and for an electrode with copper additives 140 and 80 mAh/g.

Another version of improvement in the low-temperature behavior of lithium titanate electrodes is synthesis of homogeneous $Li_4Ti_5O_{12}$/graphene composite [64].

The paper [65] describes a binder-free flexible electrode in which $Li_4Ti_5O_{12}$ nanosheets decorated with silver nanoparticles are located in between aligned carbon nanotubes nanosheets. Such an electrode revealed the capacity more than 140 mAh/g at the temperature as low as −60 °C (at the current rate 0.2 C).

In the work [66], it was found that fluoride treatment of the surface of lithium titanate particles significantly improves its performances at low temperatures. The fluoride coating was applied by solid-phase synthesis, namely heat treatment of lithium titanate with the addition of 1% ammonium fluoride at a temperature of 300 °C for 2 hours. The resulting coating had a thickness of about 50 nm and increased roughness (the specific surface area of the initial lithium titanate was 3.86 m^2/g, and after surface fluorination it increased to 4.20 m^2/g). Surface fluorination led to a noticeable decrease in charge transfer resistance during lithiation and delithiation, and a corresponding increase in capacity at elevated current rates and low temperatures. In this work, it was convincingly shown that the cycling of titanate electrodes at a temperature of –20 °C is accompanied by the formation of SEI, and the passive film on the fluorinated sample is thinner and denser.

The doping of lithium titanate with foreign ions is known to increase its electronic conductivity. In [67], lithium titanate doped with lanthanum having the formula $La_{0.06}Li_{3.94}Ti_5O_{12}$ is described.

Electrodes with such a material demonstrated a capacity of 118 mAh/g at a temperature of –40 °C and current rate C/10. In [68], characteristics of nanofibers of lithium titanate doped with chromium and having the composition $Li_{3.9}Cr_{0.3}Ti_{4.8}O_{12}$ are presented. The combination of a one-dimensional nanostructure and heterovalent doping (in this case, chromium is integrated into the positions of both titanium and lithium) ensured rather high electrical characteristics of the electrodes: a capacity of 100 mAh/g at a temperature of –20 °C and a current rate of 1 C.

Although TiO_2 is inferior to lithium titanate in its anode performances (mainly due to a large change in potential during discharge), it is still considered as one of the possible materials of the negative electrode of a lithium-ion battery. In [69], the characteristics of a rutile electrode in the temperature range from –40 to +20 °C were described. In all cases, such an electrode turned out to be operable, and when cycling in the range of potentials from 1 to 3 V, its discharge capacity was 183 and 34 mAh/g at temperatures of 20 and –40 °C. Similar electrodes based on anatase modification of TiO_2 are described in [70]. Recently, rather sophisticated version of TiO_2-based composite, having attractive low-temperature performances was presented [71]. The multiphase composite consists of TiO_2/TiN nanotubes and graphene. At the temperature of −20 °C, the composite has specific capacity 211 mAh/g at 0.1 A/g and 150 mAh/g at 1 A/g.

Other materials of negative electrode studied at low temperatures represent a certain exotic. In [72], a composite of carbon nanofibers, Fe_2O_3, and silver nanoparticles was described, the electrodes of which were tested at a temperature of –5 °C, and in [73], a similar composite of carbon nanofibers and α-iron and Fe_3C nanoparticles was described. The work [74] devotes to Co-doped Zn_2SnO_4–graphene–carbon nanocomposite, whereas [75] has deal with electrodes with $Fe_2(MoO_4)_3$ hollow hierarchical microspheres.

3. PROBLEMS OF POSITIVE ELECTRODES

Most studies related to the operation of positive electrodes of lithium-ion batteries at low temperatures relate to electrodes based on lithium iron phosphate $LiFePO_4$, which is considered as the main material for lithium-ion batteries intended for electric transport, since it has a sufficient specific capacity, excellent cyclability, thermal stability, low self-discharge, and other advantages [76−78]. The main disadvantage of $LiFePO_4$ is its extremely low electronic and ionic conductivity [79−81]. To overcome this drawback, it has become generally accepted to apply a conductive coating (usually carbon) to $LiFePO_4$ particles, to minimize the size of $LiFePO_4$ particles, and to dope $LiFePO_4$ with foreign ions. As far back as 2000, it was experimentally shown that the activation processes that determine the kinetics of the $LiFePO_4$-based electrode are significantly accelerated with increasing temperature [82]. So, when the electrode was cycled with a current of 23 mA/g at temperatures of 23, 40, and 60 °C, the difference in median potentials (potentials at a lithiation degree of 50%) during charge and discharge was, respectively, 0.15, 0.10, and 0.05 V. Accordingly, the discharge capacity at these temperatures were 60, 95 and 120 mAh/g. It was natural to expect significant deceleration of the processes at the $LiFePO_4$ electrode with decreasing temperature. This fact was experimentally confirmed in [76], where an electrode of $LiFePO_4$ nanopowder with a continuous carbon coating 1–2 nm thick without conductive additives was studied. At room temperature and a current of 100 mA/g, the capacity of such an electrode was 160 mAh/g (close to theoretical). At a temperature of –20 °C, the capacity at currents of 100 and 10 mA/g was 60 and 125 mAh/g, and at a temperature of –35 °C, the capacity at a current of 10 mA/g decreased to 80 mAh/g.

It was found in [83] that slow solid-state diffusion is the main contribution into electrode polarization at low temperatures. The Li^+ ion diffusion coefficient was shown to be $2.7*10^{-12}$ cm^2/s at +60 ^oC, and $1.01*10^{-14}$ cm^2/s at −20 ^oC.

The kinetics of processes at $LiFePO_4$-based electrodes is determined, however, not only by ohmic and diffusion factors, but also by the rate of surface reaction, which follows, in particular, from the noticeable effect of the electrolyte composition on the characteristics of such electrodes. Most of the work performed in the last 10−15 years was aimed specifically at optimizing the composition and structure of the active material and at optimizing the electrolyte. In [84], a systematic study was made of the effect of $LiFePO_4$ particle size and its purity on the characteristics of electrodes at different temperatures. It turned out that a decrease in particle size even from 1.5 to 1.0 μm leads to a certain increase in capacity, and this effect becomes more significant with decreasing temperature. So, at a current of C/5 and a temperature of 25 °C, the capacity of the material synthesized from industrial grade raw materials with particle sizes of 1.5 and 1.0 μm was 151 and 158 mAh/g (5% increase). At a temperature of –20 °C the same indicator was 43.5 and 75.5 mAh/g (an increase of 74%). When the same electrodes were made of material of reactive purity, the capacity at a temperature of 25 °C remained at the same level (151 and 158 mAh/g), and at a temperature of –20 °C it amounted to 78 and 113 mAh/g. The influence of the particle size of $LiFePO_4$ on the capacity at a reduced temperature was also noted in [85]. In [23], data on the activation energy of the charge transfer process on electrodes of lithium iron phosphate, which turned out to be equal to 31 kJ/mol, are presented. At the same time, another value of this activation energy, 40.9 kJ/mol, is given in [86].

It is not surprisingly that the morphology and thickness of the carbon coating exert a large influence on the low temperature behavior of $LiFePO_4$ [87]. In this work, the active material was obtained by solid-state synthesis from a mixture of FeC_2O_4, Li_2CO_3 and $NH_4H_2PO_4$ with the addition of polystyrene in the form of spherical particles with a diameter of 150-300 nm. Depending on the polystyrene content in the initial mixture, particles of lithium iron phosphate of different sizes and different thicknesses of the carbon coating were obtained: with an increase in the polystyrene content (from 3 to 8%), the size of the particles of iron phosphate decreased from 1 to 0.2 μm, the amount of carbon in the final material increased from 1.4 up to 3.7%, and the thickness of the carbon coating increased from 1 to 5 nm. An increase in the thickness of the carbon coating led to a decrease in polarization during discharge at a temperature of –20 °C, especially at high currents. So, when discharging in the C/10 rate, the median potential of the samples with the minimum and maximum carbon contents was 3.27 and 3.35 V, while when discharging in the 5 C rate, it was 2.53 and 2.75 V, respectively. In terms of capacity, there was a certain optimum carbon content, specifically 3.0%. At a temperature of –20 °C at the C/10 rate, the capacity of the samples with a carbon content of 1.4 and 3.0% was 87 and 147 mAh/g, and at the 5 C, 3 and 32 mAh/g, respectively.

The paper [88] describes electrodes made of carbon-coated lithium iron phosphate synthesized by the polyol method [89] from $Fe_3(PO_4)_2 \cdot 8H_2O$, H_3PO_4, LiOH, citric acid, and triethylene glycol. The resulting material consists of nanorods with a length of about 160 nm and a diameter of 80 nm with a thin coating of amorphous carbon. At a current rate of C/10, such electrodes had a capacity of 160 and 110 mAh/g at temperatures of 25 and −20 °C, and at a current of 1C these values decreased to 150 and 65 mAh/g. A porous nanocomposite made of lithium iron phosphate with a thin carbon coating synthesized by a method like that described in [58] is described in [90]. The electrodes of this material had a capacity of 117 mAh/g at a temperature of –20 °C at 5C rate.

Instead of applying a thin carbon coating to each $LiFePO_4$ particle, the authors of [91] created a structure where $LiFePO_4$ nanoparticles 50–100 nm in size are placed in a sponge made of well-graphitized carbon. The wall thickness of this sponge was about 10 nm. Such a structure was synthesized by pyrolysis of polyferrocene. The presence of a graphite sponge ensured high electronic conductivity of the material up to 0.2 S/cm. Electrodes with such a composite at a temperature of –40 °C and discharge at C/5 rate had a capacity of about 80 mAh/g, while the capacity of electrodes from ordinary $LiFePO_4$ did not exceed 20 mAh/g. The median potential for the discharge of the described composite at a temperature of –40 °C and current rate C/5 was close to 3.0 V, whereas for a comparative electrode this potential was about 2.2 V. A similar approach with a 3D carbon structure was also described in [92], where the carbon structure more like a web than a sponge.

In [93], attention is drawn to the role of the conductive additive, which is introduced into the active mass of positive electrodes based on $LiFePO_4$, regardless of the presence of a thin carbon coating on individual particles, on the low-temperature behavior of the electrodes. Typically, carbon black is used as a conductive additive, but carbon nanotubes are also noted in many papers. It was shown in [93] that even when cycling in a rather mild C/5 mode, $LiFePO_4$ electrodes without carbon coating and without conductive additives at a temperature of 25 °C reveal a capacity of 53.4% of the capacity at a temperature of +25 °C. For electrodes with a carbon coating with a thickness of 2−3 nm, but without a conductive additive, this value increases to 66.1%, and for an electrode with a coating and with the addition of carbon nanotubes with a total carbon content of 5.7%, the fraction of capacity at a temperature of –25 °C was 71.4% of capacity at a temperature of +25 °C.

In [94], Ti_3SiC_2 was proposed to be used as an electrically conductive component. The composite in this case is a tight mixture of granular particles of thin carbon coated $LiFePO_4$ and lamellar particles of Ti_3SiC_2. Such a composite with a content of 4% Ti_3SiC_2 had a conductivity of only 3.4 μS/cm, but its low-temperature characteristics turned out to be quite acceptable. At a temperature of –20 °C and discharge rates C/10 and 1 C, the electrodes from this composite had a capacity of 120 and 100 mAh/g, and the difference in median potentials for charge and discharge, respectively, was 0.13 and 0.38 V.

In [95], it was proposed to use multi-walled carbon nanotubes coated with a thin (6–7 nm) layer of a polymer electrolyte based on polyethylene glycol and $LiClO_4$ as an electrically conductive (electron-conductive and ion-conductive) agent. The electrodes contained commercial $LiFePO_4$ with thin carbon coating and 10% addition of such a conductive agent demonstrated capacity of 160, 138 and 90 mAh/g, respectively, at temperatures of 25, 8 and –20 ° C, at C/10 rate.

An alternative to a carbon coating may be a coating of conductive polymers. [96] described a composite of $LiFePO_4$ coated with polyacene (a polymer consisting of a linear chain of benzene rings) obtained by pyrolysis of phenol-formaldehyde resin. By itself, the application of such a coating led to an increase in the electron conductivity at room temperature from 10^{-9} to 10 S/cm. When the electrodes from such a composite were cycled at 1 C rate at temperatures of 60, 40, 20, 0, –10, and –20 °C, a capacity of 145, 140, 130, 112, 100, and 88 mAh/g was recorded.

An interesting feature of the low temperature behavior of $LiFePO_4$-based electrodes is described in [97]. A decrease in temperature slows down not only current-producing processes, but also slows down the degradation processes. In this work, it was found that when cycling at a temperature of 25 °C, the electrode degradation rate is 2.25 mAh/g per cycle, while at a temperature of –20 °C it decreases to 0.5 mAh/g per cycle. As a result, in the initial period of cycling, the capacity at room temperature noticeably exceeds the capacity at a temperature of –20 °C, and after the 20th cycle, inversion occurs and at the 40th cycle, the capacity at a temperature of –20 °C is almost one and a half times higher than the capacity at room temperature.

In the literature, one can find many works devoted to doping of $LiFePO_4$ to increase its conductivity. Regarding the low-temperature functioning of such electrodes, doping with manganese has been most studied [98−101]. In the paper [98], it was found that of the three materials studied, namely $LiFePO_4$, $LiFe_{0.95}Mn_{0.05}PO_4$, and $LiFe_{0.9}Mn_{0.1}PO_4$ at elevated discharge currents and at lower temperatures, the average doped material $LiFe_{0.95}Mn_{0.05}PO_4$ has an advantage. From impedance measurements, it was found that with decreasing temperature, the charge transfer resistance increases most of all. Upon transition from a temperature of +25 °C to –40 °C, this resistance increases by a factor of 280, whereas the resistance of the passive film increases 136 times only. In [99], materials of the compositions $LiFePO_4$, $LiFe_{0.8}Mn_{0.2}PO_4$, $LiFe_{0.5}Mn_{0.5}PO_4$, and $LiMnPO_4$ are compared. In this series, all manganese-containing materials are inferior to simple $LiFePO_4$, both at room and at low temperatures.

In [100], the behavior of a material consisting of $Li_{0.99}La_{0.01}Fe_{0.9}Mg_{0.1}PO_4$ nanoparticles enclosed in a matrix of carbon airgel (i.e., a structure like that described in [91]) was studied. Such a material has distinct advantages over similar non-doped lithium iron phosphate, especially at low temperatures. So, at room temperature, the charge transfer resistance for undoped and doped materials was 79 and 65 Ohms, and at a temperature of –20 °C these values were equal, respectively, to 780 and 391 Ohms.

In the practice of lithium-ion batteries, it is common to apply thin layers of oxide coatings on the active materials of the positive electrode to reduce contact (interparticle) resistances and change the nature of surface films. In particular, coatings of lithium iron phosphate by nanoparticles of zirconium, silicon, copper, zinc, and titanium oxides are described. In [102], data are presented on the low-temperature behavior of $LiFePO_4$ electrodes coated with ceria particles with a size of about 50 nm. This coating provided improved electrode performance, especially at elevated currents and lower temperatures. So, even at the mild rate (C/10), the capacity of the electrode without coating was 150.0 and 87.0 mAh/g at temperatures of +20 and –20 °C, while the capacity of the electrode with a coating of CeO_2 at the same temperatures was 153.8 and 99.7 mAh/g, respectively. An increase in capacity correlated with a decrease in polarization. At a temperature of +20 °C, the difference in median potentials during charge and discharge was 0.07 V for an electrode without coating and 0.05 V for an electrode with a coating of CeO_2. At a temperature of –20 °C, this difference was 0.26 V for an uncoated electrode and 0.20 V for a coated electrode. On the basis of impedance measurements, it was concluded that a CeO_2 coating leads not only to a decrease in interparticle resistances, but also to a decrease in charge transfer resistance, although the mechanism of this last effect was not discussed by the authors of [102].

Recently, special attention of researchers has been attracted to lithium vanadium phosphate $Li_3V_2(PO_4)_3$ as a certain alternative to lithium iron phosphate [103−105]. In the potential range from 3.0 to 4.3, reversible extraction and insertion of two lithium ions is possible for this material (which corresponds to the $V3^+/V4^+$ redox pair), and three plateaus are recorded on the charging curves at potentials of 3.65, 3.70, and 4.10 V corresponding to two-phase transitions $Li_3V_2(PO_4)_3 \leftrightarrow Li_{2.5}V_2(PO_4)_3$, $Li_{2.5}V_2(PO_4)_3 \leftrightarrow Li_2V_2(PO_4)_3$ and $Li_2V_2(PO_4)_3 \leftrightarrow LiV_2(PO_4)_3$. The advantages of $Li_3V_2(PO_4)_3$ over $LiFePO_4$ are shown in [106]. In this work, a capacity of 141.8, 92.7, 57.9, and 46.7 mAh/g was obtained on $LiFePO_4$ electrodes at temperatures of 23, 0, –10, and –20 °C at the 0.3C current rate. And on $Li_3V_2(PO_4)_3$ electrodes under the same conditions, a capacity of 127.0, 109.9, 108.6 and 103.8 mAh/g is realized. Measurements of electrochemical impedance showed that lithium vanadium phosphate has advantages over lithium iron phosphate at low temperatures both in the kinetics of the surface reaction (charge transfer) and in the solid-state diffusion of lithium. At a temperature of –20 °C, the charge transfer resistance on the electrode of lithium iron phosphate was 781 Ohms, and on the electrode of lithium vanadium phosphate 505 Ohms. The diffusion coefficient of lithium in lithium vanadium phosphate was larger in absolute value and varied less with temperature than in lithium iron phosphate. At temperatures of 23, 0, –10, and –20 °C, the diffusion coefficient of lithium in lithium iron phosphate was $8.63{*}10^{-11}$, $2.16{*}10^{-11}$, $1.64{*}10^{-11}$, and $0.25{*}10^{-11}$ cm^2/s, and in lithium vanadium phosphate, respectively, $8.66{*}10^{-10}$, $8.02{*}10^{-10}$, $7.41{*}10^{-10}$ and $5.22{*}10^{-10}$ cm^2/s. The temperature dependence of the rate of lithium diffusion in lithium iron phosphate and lithium vanadium phosphate corresponded, therefore, to the diffusion activation energy of 47.48 and 6.57 kJ/mol. A weak temperature dependence of the characteristics of the electrode from lithium vanadium phosphate nanoplates was also noted in [107]. When cycling at C/10 rate at temperatures of 25, 0, –10, and –20 °C, a discharge capacity of 126.6, 125.8, 122.5, and 120.7 mAh/g was recorded. More modest results for lithium vanadium phosphate electrodes were reported in [108]. In this work, at C/10 rate at temperatures of 65, 40, 25, 0, and –20 °C, the capacity was 132.1, 129.2, 128.7, 111.1, and 84.3 mAh/g. The activation energy of lithium diffusion in this work was equal to 44.61 kJ/mol. The value of 65.15 kJ/mol was obtained in [109] for the activation energy of lithium diffusion in $Li_3V_2(PO_4)_3$ (in the temperature range from –40 to +40 °C), and 55.4 kJ/mol for the activation energy of the charge transfer process. Since articles [107] and [109] were published at the same time, they did not discuss the significant difference in the results obtained.

Remarkable characteristics of the electrode of the $Li_3V_2(PO_4)_3$ composite with carbon nanotubes were noted in [110]. Such electrodes at a temperature of –20 °C at C/2, 1C, 2C, 5C and 10C (!) rates showed a discharge capacity of 116.2, 108.2, 103.7, 96.3, and 86.1 mAh/g. In [111], the beneficial effect of applying coatings of CeO_2 nanoparticles to lithium vanadium phosphate was shown (similar to the effect described in [102]), and a clear extremal dependence of the characteristics on the amount of deposited CeO_2 was established. So, at a temperature of 0 °C, the resistance of the surface film on samples without coating and with coating in the amount of 1%, 2% and 3% was 43.92, 24.62, 12.45 and 18.91 Ohms. At a temperature of –20 °C the same resistances were 83.10, 61.47, 22.90, and 56.59 Ohms. The charge transfer resistance at 0 °C for the same samples was 56.98, 35.19, 25.89, and 31.72 Ohms, and at –20 °C, respectively, 491.80, 129.90, 119.50, and 198.90 Ohms. In [112], lithium vanadium phosphate electrodes coated with Ti_3SiC_2 nanoparticles were described. Such a coating also leads to an improvement in characteristics at a reduced temperature, and this effect also extremally depends on the amount of Ti_3SiC_2 on the surface of the vanadate particles. The optimal coating was 4% Ti_3SiC_2.

Of the traditional oxide materials of the positive electrodes of lithium-ion batteries, when applied to operation at low temperatures, layered compounds with an excess of lithium of the general formula $Li_{1+x}Mn_yM_{1-x-y}O_2$ deserve special attention. Such compounds can be considered as solid solutions of Li_2MnO_3 and $LiMO_2$ (here M = $Ni_{1/3}Co_{1/3}Mn_{1/3}$, $Ni_{1/2}Mn_{1/2}$, etc.) [113, 114]. Upon the first charge of such electrodes, anodic extraction of lithium ion occurs, as well as the loss of a certain amount of oxygen involving manganese in the subsequent redox process. Thus, the specific reversible capacity of the material is increased. The rates of the indicated anode processes depend on temperature differently. A related feature of the compound $Li[Li_{0.2}Co_{0.4}Mn_{0.4}]O_2$ (which can be represented as a solid solution of $Li[Li_{0.2}Co_{0.4}Mn_{0.4}]O_2$ and $LiCoO_2$) was noted in [115]. At room temperature, the electrodes from this compound had a discharge capacity of 246 mAh/g in the first cycles at C/10 rate, but by the 30th cycle this value decreased to 180 mAh/g. At a temperature of –20 °C, the capacity for 35 cycles remained almost constant at about 150 mAh/g. An increase in the initial capacity and a simultaneous increase in the degradation rate during cycling with increasing temperature (in the range from 0 to 50 °C) were also noted in [116] using $Li[Li_{0.144}Ni_{0.136}Co_{0.136}Mn_{0.544}]O_2$ as an example. The same effect was described in [117] as applied to $0.6Li_2MnO_3{\bullet}0.4LiMn_{1/3}Co_{1/3}Ni_{1/3}O_2$. The mechanism of this effect is discussed in detail in [118]. In [119, 120], it was noted that in the series of compounds $xLi_2MnO_3{\bullet}(1-x)$ $LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$ (where x = 0.1, 0.2, 0.3, 0.4) the temperature dependence of the kinetics of lithium incorporation and extraction, and, accordingly, discharge capacity (in the temperature range from −10 to 45 °C) correlates with the conductivity of the compounds. The best characteristics were noted for the compound with x = 0.3: at a temperature of –10 °C, its discharge capacity was 114.5 mAh/g. A close conclusion was made in [121] when studying the electrochemical behavior of $Li_{1.2}Ni_{0.2-x}Co_{2x}Mn_{0.6-x}O_2$ (x = 0, 0.01, 0.02, 0.03, 0.04, and 0.05) at temperatures from 30 to –20 °C. It is shown here that doping of $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$ with small amounts of cobalt helps to reduce the charge transfer resistance, as well as to reduce the activation energy of the discharge in the first stage (to a potential of 3.85 V). For the $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$ compound, this value was 34.2 kJ/mol, and for $Li_{1.2}Ni_{0.1}Co_{0.1}Mn_{0.5}O_2$, it was 25.1 kJ/mol. The capacity of the electrode of $Li_{1.2}Ni_{0.1}Co_{0.1}Mn_{0.5}O_2$ during cycling at a temperature of –20 °C at C/10 rate decreased over 40 cycles from 113 to 58 mAh/g (i.e., less than half), while the capacity of the electrode of $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$ under the same conditions decreased from 60 to 15 mAh /g, i.e. fourfold.

The experiments at the lowest temperature at which the electrochemical behavior of $Li_{1.1}(Co_{1/3}Ni_{1/3}Mn_{1/3})_{0.9}O_2$ was studied are described in the above cited work [22]. At a temperature of –40 °C at C/20, C/10, C/5 and 1C rates, a capacity of 83.4, 78.9, 70.9 and 13.9 mAh/g was obtained. At a temperature of –50 °C (!) at C/20, C/10 and C/5 rates, a capacity of 50.9, 26.1 and 11.9 mAh/g was obtained.

It was shown in [122] that the deposition of lithium borate (Li_3BO_3) onto $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$ particles improves the low-temperature performance, and the dependence of this effect on the amount of coating is extremal. The best characteristics were possessed by a material with a 3% coating 5–8 nm thick. The discharge capacity of an electrode made of a material without a borate coating was 256.0 and

54.9 mAh/g at temperatures of 30 and –30 °C, and for a material with a 3% coating, respectively, 288.0 and 87.6 mAh/g.

From studies on the low-temperature behavior of layered oxides that do not contain excess lithium, it should be noted [123−126]. In [123], it was shown that the deposition of a thin AlF_3 surface layer on $Li[Ni_{0.8}Co_{0.15}Al_{0.05}]O_2$ helps to improve the cyclability at a temperature of –10 °C, which is explained by the stabilization of the passive layer (SEI) formed on the surface during cycling. (The beneficial effects of AlF_3 coatings on $Li_{1.2}Ni_{0.13}Co_{0.13}Mn_{0.54}O_2$ particles are described in [124]).

A similar effect was described in [125] when a glassy lithium borate coating with a thickness of about 8 nm was deposited on $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$. When cycling at C/5 rate on an electrode without a lithium borate coating at temperatures of 20, 0, –20, –30, and –40 °C, a capacity of 165, 147, 120, 82, and 38 mAh/g, respectively, was recorded, whereas on the coated electrode, the corresponding capacitance values were 176, 154, 133, 117, and 103 mAh/g.

The low-temperature behavior of such an exotic compound as $Li_2Cr_{0.2}V_{0.8}O_2F$ was described in [127]. At a temperature of –10 °C at C/10 rate, a capacity of 250 mAh/g was reached on it for 60 cycles, and at a temperature of –20 °C, at C/2 rate, 160 mAh/g was obtained for 100 cycles.

Although vanadium oxides, due to their high theoretical specific capacity (associated with the fundamental possibility of changing the vanadium valence by 3 units), attract very much attention as a potential material for positive electrodes of lithium-ion batteries, their low-temperature behavior has been studied very poorly. Back in 2005, it was noted that when using V_2O_5 in a nanostructured form (fibers with a diameter of less than 100 nm), it is possible to obtain quite acceptable results at low temperatures [128]. In [129], data are presented on a thorough study of the positive electrodes of vanadium bronze β-$Li_xV_2O_5$ in the form of rods with a diameter of about 0.5 μm. With a decrease in temperature from +25 to –40 °C, the discharge capacity in the first cycle decreased from 206 to 124 mAh/g. Such a high capacity at a temperature of –40 ºC points to good prospects for the development of electrodes based on vanadium bronzes. It is important to note that in [129] the same result was recorded as in [97]: the degradation of electrodes made of vanadium bronze during cycling at room temperature was much greater than during cycling at low temperatures; as a result, already at the hundredth cycle, the capacity at a temperature of –40 °C did not differ from the capacity at a temperature of 25 °C. A somewhat unusual conclusion was made in [129] that the activation energy of solid-state diffusion slightly exceeds the activation energy of the charge transfer process, so that the role of concentration polarization increases with decreasing temperature.

In many works, a noticeable effect of the electrolyte on the low-temperature behavior of positive electrodes is noted, both the nature of the solvent and the nature of the salt being of importance. So, when using $LiPF_6$ as the main electrolyte salt, the advantage of the four-component carbonate solvent EC–DMC–DEC–EMC was noted when both $LiFePO_4$ [130] and $LiNi_{0.8}Co_{0.2}O_2$ [131] were used. In an early work [132], for low-temperature operation of lithium iron phosphate electrodes, a solution of lithium tetrafluoroborate and lithium bisoxalate borate (90% $LiBF_4$ + 10% $LiB(C_2O_4)_2$) in a mixture of PC (propylene carbonate) – EC – EMC is proposed. In such an electrolyte during cycling at 1C rate at temperatures of 20, 10, 0, –10, –20, –30, –40 and –50 °C, a discharge capacity of 131, 122, 110, 98, 87, 77, 63 and 43 mAh/g was recorded. An electrolyte based on (80% $LiBF_4$ + 20% $LiB(C_2O_4)_2$) was also proposed in [133]. The solvent in this case was PC – EC – EMC (1: 1: 3) with the addition of methyl butyrate (MB), and the exact composition of the solvent significantly affects the kinetics of lithium insertion and extraction. The minimum charge transfer resistance at a temperature of –20 °C was noted for a solution of lithium salts in PC – EC – EMC – MB (1: 1: 1: 2).

The effect of the salt composition of the electrolyte on the low-temperature behavior of positive electrodes is clearly shown in [134]. In this work, it was shown that the activation energy of the electrode process on electrodes of lithium iron phosphate in an electrolyte containing 0.8 M $LiPF_6$ in an EC – PC – EMC mixture with the addition of 2% vinylene carbonate (VC) is 58.4 kJ/mol, and when replacing $LiPF_6$ with $LiBF_4$ it increases to 63.2 kJ/mol.

In [135], the well-known beneficial effect of the addition of FEC to the $LiPF_6$ solution in EC – PC – EMC (1: 1: 3) on the low-temperature behavior of $LiFePO_4$ was noted. Undoubtedly, this effect is associated with the modification of the passive film (SEI) on the positive electrode. The effect of FEC on the low temperature performances of lithium ion batteries was also noted in [136]. The same effect was described in [137] by the example of VK additives and some organic borates.

4. LOW TEMPERATURE ELECTROLYTES

Based on the most general considerations, it can be argued that the effect of an electrolyte on the low-temperature behavior of lithium-ion batteries can manifest itself through ohmic losses in the electrolyte (determined by its resistivity), through the properties of surface films on active electrode materials (SEI), and also through the charge transfer rate at the interface between the electrode and the electrolyte. (The diffusion resistance in the liquid phase is generally small compared with the resistance of solid-state diffusion). All these effects depend both on the composition of the solvent (usually mixed) and the nature of the electrolyte salt, and on various additives to the electrolyte, the content of which is small, and the effect is very significant [138−143]. In the literature, one can find several review articles devoted directly to low-temperature electrolytes (e.g., [144, 145]).

As early as 1997, an attempt was made to optimize the composition of an electrolyte intended for low temperatures (below 0 °C) [146]. It was assumed that methyl formate (MF) could be a suitable diluent for EC (having a melting point of 36 °C). A graphite electrode was then adopted as a limiting one and the composition of the electrolyte was optimized with respect to this very electrode. Lithium hexafluoroarsenate ($LiAsF_6$), hexafluorophosphate ($LiPF_6$), bis-trifluoromethanesulfonylimide (LiTFSI, imide, $LiN(SO_2CF_3)_2$) and tris-trifluoromethanesulfonylmethide (methide, $LiC(SO_2CF_3)_3$) were tested as electrolyte salts. The best electrolytes for operation at low temperatures were recognized as 1 M solutions of $LiAsF_6$ and $LiC(SO_2CF_3)_3$ in a mixture of MF-EC (3:1). Subsequently, however, electrolytes with MF did not receive dissemination, and the main attention was paid to ternary or four-component electrolytes with a minimum EC content [16, 17, 131, 147−149].

In [16], eloquent data were obtained on the strong influence of the composition of the solvent on the low-temperature behavior of batteries. In the study of commercial batteries with electrodes based on graphite and $LiCoO_2$ and 1 M $LiPF_6$ in mixtures of EC-DMC (3:7), EC-DEC (3:7) and EC-DEC-DMC (1:1:1) as an electrolyte at a temperature of –20 °C, a capacity of 0.105, 0.342, and 0.460 Ah was recorded. The difference in the capacities obtained was due to the difference in the total charge transfer resistance and SEI on the graphite electrode, as follows from the results of electrochemical impedance spectroscopy, and this factor is more important than the difference in the electrical conductivity of electrolytes. (See also [3, 19, 150−152]). 1 M $LiPF_6$ in EC-EMC-DMC (1:1:1) was also recommended in [153] for operation at temperatures up to –40 ºC. In [154], it was proposed to use ethyl acetate (EA) and methyl butyrate (MB) as a diluent in ternary electrolytes. Batteries with a graphite negative electrode and a positive electrode based on $LiCoO_2$, when discharged at a temperature of –40 °C at C/2 rate, had a capacity of 81% of the nominal if the electrolyte had a composition of 1 M $LiPF_6$ in an EC-DMC-EA mixture and 87% from the nominal if 1 M $LiPF_6$ in the mixture EC-DMC-MB was used as the electrolyte. The nominal capacity was taken to be the capacity when discharged at C/5 rate and at a temperature of +20 ° C. The positive effect of the use of MB was also noted in [155−159]. Similar results were reported in [160, 161] when methyl acetate (MA) and ethyl propionate (EP) were used as a diluent.

The advantages of the four-component carbonate solvent EC–DMC–DEC–EMC for the operation of positive electrodes have already been noted. It was shown in [162] that 0.75 M $LiPF_6$ in EC–DMC–DEC–EMC (1:1:1:1) provides the minimum charge transfer resistance on graphite. A detailed study [163] also concluded that it is advisable to use four-component solvents at low temperatures (below –40 °C) for lithium-ion batteries with different electrodes.

There are references in the literature that various fluorine-containing additives have a beneficial effect on the operation of lithium-ion batteries at low temperatures. Back in 1998, when studying the cycling of graphite electrodes in 1 M $LiClO_4$ in an EC-DEC mixture [164], the addition of 4.8% difluoromethyl acetate (CHF_2COOCH_3) to this electrolyte was found to result in a noticeable increase in capacity at temperatures of 0 and –4 ºC, although at room temperature this effect was not visible. Additives of higher molecular weight fluorinated esters did not affect the behavior of graphite under these conditions.

It was shown in [165] that the addition of 2% fluorosulfonyl isocyanate (FI) to a standard electrolyte (EC-DMC) leads to a significant improvement in the SEI on a graphite electrode, since FI is reduced at more positive potentials than EC. As a result, SEI is formed with a dense inorganic layer with high conductivity, which ensures a decrease in the polarization of the negative electrode at low temperatures.

The effects of fluorinated carbonate additives (methyl-2,2,2-trifluoroethyl carbonate (MTFEC), ethyl-2,2,2-trifluoroethyl carbonate (ETFEC), propyl-2,2,2-trifluoroethyl carbonate (PTFEC), methyl-2,2,2,2',2',2'-hexafluoroisopropyl carbonate (MHFPC), ethyl-2,2,2,2,2,2',2'-hexafluoroisopropyl carbonate (EHFPC) and di-2,2,2 trifluoroethyl carbonate (DTFEC)) into a $LiPF_6$ solution in a binary or ternary mixture of EC with other carbonates for the operation of a lithium-ion battery with a graphite electrode (MCMB) and an electrode of $LiNi_{0.8}Co_{0.2}O_2$ were studied in [148]. It was found that the polarization resistance of graphite in all the studied electrolytes at a temperature of 23 °C is almost the same (less than 1 kΩ), while at a temperature of –20 °C it varies very much: from 12 kΩ in an electrolyte without fluorinated additives (1 M $LiPF_6$ in EC- DEC-EMC (1:3:1)) up to 1.6 kOhm in 0.75 M $LiPF_6$ in EC-DEC-DMC-ETFEC (1:1:1:1). The discharge capacity of a graphite electrode at a temperature of –20 °C in an electrolyte without additives amounted to about 0.1 Ah, and in 0.75 M $LiPF_6$ in EC-DEC-DMC-ETFEC (1:1:1:1) almost 0.3 Ah. The beneficial effects of the addition of fluorinated esters, 2,2,2-trifluoroethyl butyrate (TFEB), 2,2,2-trifluoroethyl acetate (TFEA), ethyl trifluoroacetate (ETFA), and methyl pentafluoropropionate (MPFP) in the standard $LiPF_6$ solution in EC-EMC were noted in [166] in the study of the battery of the same electrochemical system. Good results were obtained when non-polar fluorinated solvents (tetrafluoro-1-(2,2,2-trifluoroethoxy) ethane or methoxyperfluorobutane) were introduced into the electrolyte [167].

The low-temperature behavior of electrolytes improves markedly with the addition of methyl trifluoroacetate [168]. Such an addition to a standard 1 M $LiPF_6$ solution in an EC-EMC mixture (1:4) contributes to a noticeable decrease in viscosity and a corresponding increase in the conductivity and diffusion coefficient of lithium ion at low temperatures (up to −35 °C).

Interesting examples of improving the low-temperature performances of lithium-ion batteries with additives such as polydimethylsiloxane-based copolymers (PDMS) are given in [169, 170]. The authors of [169] showed that the addition of a PDMS-phenylsiloxane copolymer (PDMS-P or phenylsilicone oil) and a PDMS-siloxane-g-ethylene oxide copolymer (PDMS-EO or ether-silicone oil) lead to a significant (more than twofold) increase in the conductivity of the standard electrolyte (1 M $LiPF_6$ in a mixture of EC-DMC (1:1)) at a temperature of –20 °C, without affecting conductivity at temperatures of 20 °C and above. At a temperature of –20 °C, the capacity of the battery with an ordinary electrolyte (1 M $LiPF_6$ in a mixture of EC-PC-EMC-DEC-VC-FEC (20:5:55:20:2:5)) was 86 and 56 mAh/g (in calculated on the mass of $LiCoO_2$) in the first and fiftieth cycles, and the capacity of the same battery with the addition of 1% PDMS copolymer with siloxane-g-acrylate (PDMS-A) in the electrolyte in the first cycle was 96, and in the fiftieth 88%. It was found that the positive effect of additives of PDMS copolymers manifests itself through a decrease in the resistance of the SEI on the negative electrode. In [170], a certain synergistic effect was described from the combined addition of PDMS-A and silica gel modified with $–SO_3Li$ surface groups (nanosol Li202). At the same time, it was pointed out in [170, 171 that additives of such a modified silica gel themselves also modify SEI and lead to some improvement in the operation of lithium-ion batteries at a temperature of –20 °C.

Recently, it was found that the introduction of sulfur into SEI leads to a noticeable decrease in the polarization of graphite electrodes, especially at low temperatures [172]. To create such SEI, it is recommended that small additives of allyl sulfide be introduced into the electrolyte [173]. The formation of good SEI with high conductivity is also facilitated by the addition of an ionic liquid (in particular, 1-ethyl-3-methylimidazolium tetrafluoroborate). Even 1% of such an additive noticeably improves the characteristics of both positive electrodes based on $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ and graphite negative electrodes at temperatures up to −30 °C [174].

[175] indicated that solutions of lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in ethyl acetate can ensure the functioning of a lithium-ion battery at temperatures up to −70 °C, and the best results were obtained with organic electrodes (polytriphenylamine (PTPAn) as cathode material, and 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTCDA)-derived polyimide (PNTCDA) as anode material, respectively.

Record-breaking low temperatures during operation of lithium-ion batteries were achieved using an electrolyte based on 1,3-dioxane, in particular, 0.75M LiTFSI in 1,3-dioxane [176]. So, electrodes based on $Li_4Ti_5O_{12}$ in such an electrolyte at a temperature of −80 °C had a discharge capacity of 130 and 90 mAh/g at current rates C/100 and C/10.

Important for the operation of lithium-ion batteries are additives not only solvents, but also certain salts. So, in [177, 178] it was shown that small additions of cesium salts to an electrolyte containing both EC and PC and, therefore, capable of working at low temperatures, upgrade SEI on graphite, providing good cycling. It was shown in [179] that when the battery was operated with a graphite electrode and a positive electrode of $LiNi_{0.80}Co_{0.15}Al_{0.05}O_2$ at a temperature of –40 °C, the capacity at C/5 rate was 33 and 116 mAh/g (calculated on the mass of $LiNi_{0.80}Co_{0.15}Al_{0.05}O_2$) when using 1.0 M $LiPF_6$ as an electrolyte in an EC – EMC mixture (3:7) and 1.0 M $LiPF_6$ in an EC–PC–EMC mixture (1:1:8) with the addition of 0.05 M $CsPF_6$. In [180], the beneficial effect of adding even 1% $LiPO_2F_2$ was reported.

The nature of the electrolyte salt generally has a significant effect on the low temperature characteristics of lithium-ion batteries. It has already been pointed out that the replacement of $LiPF_6$ with $LiBF_4$ leads to a decrease in activation polarization at a temperature of –20 °C [98, 155]. The same effect was noted in [181, 182]. It was shown in [183] that a certain addition of lithium bisoxalate borate (LiBOB) to $LiBF_4$ in PC-based electrolytes leads to a significant improvement in SEI and to a corresponding increase in the characteristics of the full battery. Even better SEIs on graphite at low temperatures are formed when instead of LiBOB, a structurally simpler compound of lithium oxalyl difluoroborate (LiODFB) is used [159, 184]. It was shown in [185] that the use of the already mentioned LiTFSI as an electrolyte salt allows one to reduce charge transfer resistance at low temperatures, which allows a battery with an electrolyte containing 0.9M LiTFSI in an EC-DMC-EMC (15:37:48) mixture at a temperature of –40 °C have a discharge capacity of more than 20% of the capacity at a temperature of 25 °C.

5. ALTERNATIVE APPROACH (PREHEATING)

Along with improvement of chemistry of lithium-ion batteries there is another approach to solving the problems of low-temperature operation, namely external or internal heating [6, 186]. Various heating strategy are described, including heating with alternating or direct current, mutual pulse heating, using of latent heat of phase change et so on [187−191].

As a rule, external heating is quite slow, is accompanied by energy loss to the environment, and results in temperature non-uniformity. That is why, the internal heating based on Joule heat generated on the battery internal resistance and having higher efficiency is more popular. In principle, both external power sources, and the battery itself can be the heating source. An alternating current generator is usually used as an external energy source [187−189, 192−197], since the use of direct current is associated with the risk of overcharging and lithium metal deposition on the negative electrode. In [190], it was proposed to use not a sinusoidal current, but rectangular current pulses. When using an internal source, it is necessary to include a DC/AC inverter in the load circuit [188].

Recently, a special attention is paid to internal heating (self-heating start) with using a nickel foil heating element embedded inside a battery [198−201]. This heating element is placed in vicinity to negative electrode. One tab of this element is welded to the negative terminal of the battery, whereas the other tab of the heating element forms so-called “activation terminal” (third terminal of the battery). A switch is placed between activation terminal and negative one. At the beginning of charging this switch is open, so the current flows through heating element. When the battery is warmed up to temperature sufficient for regular charging the switch closes, and the heating element becomes shunted. A similar device allows heating the battery from −20 °C to 0 °C for 12 seconds.

6. CONCLUSION

Most modern lithium-ion batteries are designed to power portable electronic equipment and are designed to operate at ambient temperatures. At the same time, new areas of the possible use of lithium-ion batteries are expanding, where operating temperatures can decrease to −40 and even −50 °C, including weapons and military equipment, aviation and space technology, transport, etc. With a decrease in temperature, the rates of all activation processes decrease (electrolyte conductivity, diffusion rate in solid and liquid phases, charge transfer rate in electrochemical processes). An analysis of the literature shows that the highest activation energy is usually inherent in charge transfer processes, i.e. the electrochemical stage itself, and it is it that determines the kinetics of electrode processes in lithium-ion batteries at low temperatures. The second important process that determines the operability of lithium-ion batteries at low temperatures is solid-state diffusion; therefore, the use of nanomaterials in the manufacture of electrodes is an important factor that ensures the operability of batteries at low temperatures. A separate problem is the development of electrolytes that provide high discharge rates and, especially, charge at low temperatures.

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