

## ELECTROCHEMICAL TECHNOLOGIES FOR LOW TEMPERATURES

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*This review is devoted to analysis of the possibility to use electrochemical energy systems at low temperatures. For northern and mountain regions environment friendly autonomous energy sources - chemical current sources capable of operating at temperatures up to  $-60$  °C which are under development now. Renewable energy systems combined with hydrogen fuel cells could also be used for this purpose, in particular with fuel cells with solid polymer electrolyte, which already can function normally in the temperature range from  $-20$  to  $+50$  °C and demonstrate some perspectives for a lower temperature storage and operation.*

**Keywords:** *fuel cell, solid polymer electrolyte, proton-exchange membrane, membrane-electrode block, cold start/stop of the fuel cell, chemical current sources, lithium-ion batteries, supercapacitors.*

### Introduction

The elimination of energy poverty is an urgent task not only for developing countries, but also for a number of regions of the Russian Federation [1]. In the energy balance of the North, for example, over 70% of the capacity is account for by environmentally "dirty" organic fuels - coal, fuel oil and firewood, the delivery of which is very expensive. Therefore, the problem of ecologization of the northern energy sector is becoming ever more acute [2-4].

The mountain and northern regions have a rich wind resources and a high level of solar radiation in the summer, so renewable energy can play a significant role in the energy supply of this region [5].

However, the development of autonomous and renewable energy in this region requires efficient electrochemical energy storage/conversion systems that are operational at low temperatures.

The progress in this field and some perspectives are analyzed in the present review.

#### 1. Chemical current sources

In case of "traditional" chemical current sources (CCS) one you can use primary lithium thionyl chloride and lithium sulfuryl chloride current sources here. The operating temperature range of lithium thionyl chloride current sources is  $-50$  -  $+70$  °C [6], and there is evidence that such elements can remain operational at  $-100$  °C [7]. However, they can only be used for solving particular problems.

A large number of modern commercial CCSs and, especially, rechargeable batteries (accumulators) are not designed to work in the Arctic region, since at low temperatures their capacity drops significantly and the possibility of freezing of aqueous electrolytes arises. The exception are nickel-cadmium batteries with an alkaline electrolyte containing special additives that serve to a lower freezing point of the electrolyte. For example, the company SAFT (France) produces highly compact nickel-cadmium rechargeable batteries of the MRX series, operating at temperatures down to  $-50$  °C and designed for electric vehicles. The disadvantage of nickel-

cadmium batteries is the need for their periodic maintenance, as well as low specific energy values [6].

In perspective, lithium-ion batteries (LIB) can also be considered as sources of energy for low temperatures use. Most companies producing lithium-ion batteries guarantee that at a temperature of  $-20\text{ }^{\circ}\text{C}$ , the discharge capacity of a battery with a five-hour charge-discharge mode will be 80% of the nominal capacity. However, for  $-40$  and even  $-60\text{ }^{\circ}\text{C}$  such batteries are not applicable. A decrease in temperature leads to a decrease in the electrical conductivity of the electrolyte, the rate of diffusion in the solid and liquid phases, and the rate of charge transfer in electrochemical processes [8–22]. A characteristic feature of the lithium-ion batteries at low temperatures (approximately  $-20\text{ }^{\circ}\text{C}$  and below) is that the polarization in the charge process usually exceeds the polarization during the discharge [9, 10, 17, 23]. As a result, manufacturers such batteries sources recommend charging batteries at a temperature not lower than  $-20\text{ }^{\circ}\text{C}$ .

One way to increase the discharge capacity of lithium-ion batteries at negative temperatures is to increase the electronic conductivity of the electrodes, for example, by introducing metallic nanopowders into the negative electrode [24, 25], which allows a thrice increase in capacity at  $-40\text{ }^{\circ}\text{C}$  in the 1C mode

Another way to increase the discharge capacity of lithium-ion batteries at low temperatures is to reduce the particle size of functional materials [26–28]. In addition, it is advisable to modify the surface of the electrodes. For example, fluoride treatment of the surface of particles of lithium titanate (material of the negative electrode) significantly improves its characteristics at low temperatures [29]. To increase the electronic conductivity and, as a consequence, to reduce the polarization at lower temperatures, it is proposed to use lithium titanate doped with trivalent metal as a negative electrode. For example, lithium titanate doped with lanthanum ( $\text{La}_{0.06}\text{Li}_{3.94}\text{Ti}_5\text{O}_{12}$ ) was described in [30]. Electrodes with such a material had a capacity of 118 mAh/g at a temperature of  $-40\text{ }^{\circ}\text{C}$  and a current of C/10, which is significantly higher than similar characteristics of undoped lithium titanate. The authors of [31] described an improvement in the characteristics of nanofibers of lithium titanate doped with chromium and having the composition  $\text{Li}_{3.9}\text{Cr}_{0.3}\text{Ti}_{4.8}\text{O}_{12}$  at  $-20\text{ }^{\circ}\text{C}$  and a current of 1C. A certain potential has doped lithium ferrophosphate [21, 32–34], especially with carbon coating [35].

Since 1997, work has continuously been carried out to optimize an electrolyte designed specifically for operation at low temperatures [36]. The electrolyte composition 1 M lithium hexafluorophosphate ( $\text{LiPF}_6$ ) in a solution of ethylene carbonate-ethyl methyl carbonate-dimethyl carbonate (1: 1: 1, vol.%) is recommended in [37] for operation at temperatures down to  $-40\text{ }^{\circ}\text{C}$ . In [22], it was proposed to use ethyl acetate and methyl butyrate as additives in ternary electrolytes. In this case, batteries with a graphite negative electrode and a positive electrode based on lithium cobalt oxide ( $\text{LiCoO}_2$ ). Such batteries when discharged at  $-40\text{ }^{\circ}\text{C}$  in C/2 mode, have a capacity of 81% of the nominal one if the electrolyte is a composition of 1 M  $\text{LiPF}_6$  in a mixture of ethylene carbonate- dimethyl carbonate- ethyl acetate, and 87% of the nominal, if the electrolyte was used 1 M  $\text{LiPF}_6$  in a mixture of ethylene carbonate-dimethyl carbonate-methyl butyrate. The positive effect of the use of methyl butyrate was also noted in [38–42]. Similar results were reported in [43] using methyl acetate and ethyl propionate as a diluent. Various fluorine-containing additives also contribute to the operation of lithium-ion batteries at low temperatures [44–46]. Important for the operation of lithium-ion batteries at low temperatures are different additives (not only solvents) including certain salts, for example, cesium salts ( $\text{CsPF}_6$ ) [47, 48].

It should be noted that lithium-ion batteries for low temperatures are already being produced, in particular, by SAFT. They are intended, among other things, for the individual provision of military personnel and the provision of energy for various weapons, in particular, naval torpedoes. Operating temperature ranges from  $-40\text{ }^{\circ}\text{C}$  to  $+60\text{ }^{\circ}\text{C}$  [49].

The use of low-temperature electrolyte (1 M lithium bis-trifluoromethanesulfonimide ( $\text{LiTFSI}$ ) in ethyl acetate) and electrode materials based on polytriphenylamine - and 1,4,5,8-naphthalenetetracarboxylic dianhydride -derived polyimide permit the batteries to operate at

record low temperatures ( $-70\text{ }^{\circ}\text{C}$ ). But commercial production of such batteries has not yet been established.

An alternative to lithium-ion batteries capable of operating at low temperatures may be sodium-ion batteries primarily due to the composition of the electrolyte (1 M sodium perchlorate ( $\text{NaClO}_4$ ) in propylene carbonate- ethylene carbonate mixture), the freezing point of which is about  $-80\text{ }^{\circ}\text{C}$  [51-53].

Certain prospects for low temperatures have supercapacitors, which have a higher power density, but also lower energy capacity. The operating temperature of commercial non-aqueous electrolyte supercapacitors is currently limited to the freezing point of acetonitrile  $-45\text{ }^{\circ}\text{C}$  [54]. The use of mixed solvent systems such as a mixture of acetonitrile, ethyl acetate, methyl formate, methyl acetate and 1,3-dioxolane, can reduce the freezing point of the electrolyte and increase the working temperature range to  $-70\text{ }^{\circ}\text{C}$  [55]. Another way to extend the low-temperature range may be the use of additives of various salts [56]. The use of ionic liquids as an electrolyte is another way for supercapacitors to function at lower temperatures [57-58].

Among commercial manufacturers of super capacitors, the company Eaton should be noted, producing supercapacitors of the XL60 series, whose working temperature ranges from  $-40\text{ }^{\circ}\text{C}$  to  $+65^{\circ}\text{C}$ . In Russia, the Partnership of Energy and Electro mobile Projects announced the release of supercapacitors with a useful specific power density of up to  $15.5\text{ kW/kg}$  (specific power in the mode of a pulse load of  $100\text{ kW/kg}$ ) and an operating temperature range from  $-55$  to  $+85\text{ }^{\circ}\text{C}$  [59]. Another Russian company, Titan Power Solutions, produces supercapacitor systems for starting internal combustion engines at  $-50\text{ }^{\circ}\text{C}$  to  $+65\text{ }^{\circ}\text{C}$  [60].

## **2. Electrochemical systems based on solid polymer electrolyte**

Despite the significant progress in the field of batteries and supercapacitors for low temperatures, they cannot provide long-term energy storage and hydrogen is very promising for this purpose in the conditions of northern and mountain regions [61].

Certainly, for a large number of practical problems, electrochemical systems based on solid polymer electrolyte are of considerable interest, but the possibility of their use at low temperatures causes natural doubts because of the possibility of water freezing. However, there are certain prospects. In [62] it was shown the possibility of using the start of electrolysis cells with solid polymer electrolyte at negative temperatures when using water-alcohol solutions. Alcohol also acts as an anode depolarizer and reduces energy consumption for hydrogen production.

Fuel cells (FC) with polymer electrolyte membrane (PEM) are able to function normally in the temperature range from  $-20\text{ }^{\circ}\text{C}$  to  $+50\text{ }^{\circ}\text{C}$  without additional energy supply, while maintaining high rates of output power and voltage [63]. Studies of the operation of PEMFC under low temperature conditions have been initiated for a long time [67–68] and some practical success has been achieved, namely, the launch of solid polymer fuel cells in the temperature range  $-20\text{--}15\text{ }^{\circ}\text{C}$  [69–73] is reported.

Research in this area [74-76] allows to identify 2 problems:

1. Heating (self-heating) of the fuel cell during start-up at low temperatures.
2. Degradation of membrane-electrode blocks and cells of the fuel cell as a whole in start-stop cycles at negative temperatures.

If the first problem is more technical and can be solved by an external heat source, then the second problem requires basic research, including modeling of heat and mass transfer [77, 78].

The main problem of the exploitation of membrane-electrode blocks (MEA) of these FCs at low temperatures is the formation of a crystalline water phase in the membranes and in the volume of FC elements, which leads to mechanical destruction of the membrane, namely cracks and other point defects [64-65, 79], changes in the structure and destruction of the catalytic and gas diffusion layers [80]. Repeated freeze-thaw cycles ( $-40\text{ }^{\circ}\text{C}$  -  $+80\text{ }^{\circ}\text{C}$ ) can lead to an increase in the contact resistance of the membrane, a decrease in the electrochemically active surface and a change in its hydrophilic-lipophilic properties [79, 80]. However, the authors themselves

studied the effect of cyclic temperature changes from room temperature (about 20 °C) to low -35 °C and -80 °C on the physicochemical and operational characteristics of the membrane and showed that after 5, 15, 30 freeze-thaw cycles, temperature cycling does not affect the electrochemical properties of the membrane itself and, accordingly, the more topical problem remains the preservation of the characteristics of MEA and the FC cell as a whole.

To improve the performance and durability components of PEMFC at low temperatures, a microporous layer (MPL) is used between the gas diffusion layer (GDL) and a membrane with a catalytic layer. The authors [81] showed that MPL helps to retain heat and improve water management inside the fuel cell. Also MPL allows to reduce ohmic losses and to improve the stability of fuel cell operation.

Usually, the microporous layer is made from a mixture of carbon black and a hydrophobic agent (usually polytetrafluoroethylene). If platinum is included in the MPL, and an ionomer (Nafion) is used, the MPL can also play the role of a catalytic layer of the FC. The ionomer and the MPL pores can serve as an additional reservoir for storing the water produced during cold start. The first one provides an additional water absorption, while the second one provides additional space for temporary storage of ice [82].

From the authors' point of view, alcohol additives to hydrogen fuel may reduce the negative effect of low temperatures on PEMFC operation and significantly extend the operation/storage temperature range by reducing of MEA components destruction during crystallization of the liquid phase in the MEA volume. For example, application a methanol-water solution (40 vol.%) as an antifreeze in PEMFC allowed to carry out tests up to -30 °C [83]. The FC performance during thawing-and-freezing test was much better in comparison with the performance without the antifreeze or FC air conditioning by blowing gases before freezing.

At present, PEMFC operating at low temperatures with direct oxidation of methanol are widely represented in the literature [84]. However, they have their drawbacks (in particular, higher weight and size characteristics, problems of diffusion (cross-over) of methanol through the membrane [85, 86]) and are completely unsuitable for renewable energy systems.

However, methanol FCs operating at low temperatures are sold on the Russian market by foreign companies, the main of which are SFC Energy AG, Germany [87], Pro-Power communication CO, South Korea [88], Cellkraft, Sweden [89].

The foreign market offers ready-made technical solutions for the use of alcohol fuel cells in the temperature range from -40 to +50 °C [108], which, unfortunately, have no Russian analogues. Nevertheless, the existing scientific and technical reserve in the field of fuel cells with direct oxidation of alcohols allows us to count on the successful use of this reagent as an additive to hydrogen fuel.

It should be noted that fuel cells with direct oxidation of methanol (ethanol), unlike hydrogen fuel cells, require slightly different catalysts and membrane-electrode units as a whole.

According to the literature [42-46], Pt-Ru shows the highest activity in the oxidation of aqueous-alcoholic solutions both on the carrier and in the form of mobile. For alcohol FCs, multicomponent catalysts based on Pt-Ru alloys are the most traditional, which is reflected in works [90-94]. An analysis of the literature also makes it possible to highlight the direction of research associated with the creation of electrocatalysts for FCs with direct oxidation of alcohols, the carrier of which is modified by various oxides, in particular, tin oxide, to which many modern works are devoted, for example [95–98]. So, it should be noted that the use of combined hydrogen-alcohol fuel does not create fundamental problems with catalysts, but only requires additional research and development.

Along with this, the most important task for such FCs with “combined” fuel is the optimization of the structure and composition of electrocatalytic layers [104-107]. Graphene materials should be distinguished as promising carriers for such catalysts, since in this case, in particular, effective contact between the catalyst particles is provided (see, for example, [99-103]).

It should be noted that water-alkaline electrochemical systems can be used for low temperatures, operation of which is possible at  $-30$  —  $-40$  °C, but their well-known shortcomings are inherent in them and for their use in the conditions of low temperatures no less research and development is required. The prospects for the use of high-temperature (solid oxide) electrochemical systems is not yet clear.

### Conclusion

The use of renewable energy in northern and mountain regions, for example, the arctic region, should be considered in perspective. All this is impossible without autonomous energy systems based on chemical current sources.

Intensive research and development in the field of low-temperature chemical current sources demonstrated the promise of lithium-ion batteries. Among all their varieties, the  $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$  system attracts the most attention. Due to the use of nanostructured functional materials and a special electrolyte composition, this system is efficient at temperatures down to  $-50$  °C.

Among the new battery systems, the highest expectations are placed on sodium-ion batteries, which, in addition to being able to operate at temperatures down to  $-60$  °C, will have a lower cost.

Electrochemical supercapacitors with non-aqueous electrolytes are already capable of operating at temperatures as low as  $-50$  °C due to the use of an acetonitrile-based composite electrolyte. Further work on the modification of the electrolyte and functional electrode materials will allow the production of commercial supercapacitors operable at temperatures down to  $-70$  °C.

For a wide range of tasks, it is possible to use methanol fuel cells produced industrially.

For the production of hydrogen for the purpose of long-term energy storage and the solution of a number of other problems, electrolyzers and fuel cells, and in particular, electrolyzers and fuel cells with a solid polymer electrolyte, are promising. Already, they provide an effective "cold start" at  $-20$  °C, and studies show that the temperature drop of the fuel cell to  $-60$  —  $-40$  °C is not critical for a membrane made of solid polymer electrolyte and membrane-electrode unit as a whole. Improving the performance of the fuel cell and increasing its durability at low temperatures can be achieved by optimizing the composition and structure of the catalytic layers, using additional microporous layers between the gas diffusion and catalytic layers.

Also a reduction the negative impact of low temperatures on the durability and performance of the fuel cell may be reached by use of alcohol additives to the hydrogen fuel. In this case, the development of an optimal catalyst and membrane-electrode assemblies for binary fuel becomes an urgent task.

Thus, electrochemical energy for low temperatures is an important, albeit complex, scientific task, which has undoubted prospects and scientific value.

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## ЭЛЕКТРОХИМИЧЕСКИЕ ТЕХНОЛОГИИ ДЛЯ НИЗКИХ ТЕМПЕРАТУР

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*Данный обзор посвящен анализу возможности использования электрохимических энергетических систем при низких температурах. Достичь этих целей невозможно без экологически чистых автономных источников энергии - химических источников тока, способных работать при температурах до  $-60$  °С, которые находятся в стадии разработки. Системы возобновляемой энергии в сочетании с водородными топливными элементами также могут быть использованы для этой цели, в частности с топливными элементами с твердым полимерным электролитом, которые уже могут нормально функционировать в диапазоне температур от  $-20$  до  $+50$  °С и демонстрируют некоторые перспективы для более низкой температура хранения и эксплуатации.*

**Ключевые слова:** *топливный элемент, твердополимерный электролит, мембранно-электродный блок, литий-ионные аккумуляторы, суперконденсаторы, холодный старт/остановка топливного элемента.*