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ELECTROCHEMICAL TECHNOLOGIES FOR LOW TEMPERATURES**V.N. Fateev, T.L. Kulova, E.A. Seregina, N.A. Ivanova, D.D. Spasov***National Research Center "Kurchatov Institute"**123182 Russia, Moscow, pl. Akademika Kurchatova, 1. E-mail: Fateev_VN@nrcki.ru**Received 02.06.2019*

Abstract: *This review is devoted to analysis of the possibility to use electrochemical energy systems at low temperatures. It is not possible to attain this goal without ecologically pure autonomous energy sources - chemical current sources capable of operating at temperatures up to -60 °C which are presently under development. Renewable energy systems combined with hydrogen fuel cells can also be used for this purpose, in particular with fuel cells and solid polymer electrolyte that can already operate normally at temperatures ranging from -20 to $+50$ °C and are perspective to be used and stored at lower temperatures.*

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, super-capacitors.*

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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 accounted for by environmentally "dirty" organic fuels - coal, fuel oil and firewood deliveries of which are very expensive. Therefore, the problem of ecologization of the northern energy sector is becoming ever more acute [2].

The mountain and northern regions

have a rich wind resources and a high level of solar radiation in summer, so renewable energy can play a significant role in the energy supply of these regions [3].

However, the development of autonomous and renewable energy in these regions 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

It should be noted that in the matter of "traditional" chemical current sources (CCS) it is possible to use primary lithium thionyl chloride and lithium sulfuryl chloride current sources. The operating temperature range of lithium thionyl chloride current sources is -50 - $+70$ °C [4], and there is evidence that such elements can remain operational at -100 °C [5]. However, they can only be used for solving specific cases.

A large number of modern commercial CCSs and, especially, rechargeable batteries (accumulators), are not designed to operate in the Arctic region, since at low temperatures their capacity drops significantly and the possibility of freezing of aqueous electrolytes

arises. An exception to this is nickel-cadmium batteries with alkaline electrolyte containing special additives that serve to 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 in their periodic maintenance, as well as low specific energy values [4].

In perspective, lithium-ion batteries (LIB) can also be considered as sources of energy for low temperatures use. Note that 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, at temperatures -40 and even $-60\text{ }^{\circ}\text{C}$ batteries of this type are not applicable. A temperature drop leads to a reduction of the electrical conductivity of the electrolyte, as well as rates of diffusion in the solid and liquid phases and charge transfer in electrochemical processes [6-10]. 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 [7-9, 11]. As a result, manufacturers of these battery 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 [12] which allows to thrice increase their 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 [13, 14]. 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 [15]. To increase the electronic conductivity and, as a consequence, reduce the polarization at lower temperatures, it is offered 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 [16]. 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 [17] 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 [18], especially with carbon coating [19].

Since 1997, much work has continuously been done out to optimize an electrolyte designed specifically for operation at low temperatures [20]. The electrolyte composition 1 M lithium hexafluorophosphate (LiPF_6) in a solution of ethylene carbonate-ethyl methyl carbonate-dimethyl carbonate (1: 1: 1, vol.%) is recommended in [21] for operation at temperatures lower than $-40\text{ }^{\circ}\text{C}$. In [10], it was offered 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 (LiCoO_2). Batteries of this type 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 LiPF_6 in a mixture of ethylene carbonate- dimethyl carbonate- ethyl acetate, and 87% of the nominal, if the electrolyte was used 1 M 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 [22]. Similar results were reported in [23] due to the use of methyl acetate and ethyl propionate as a diluent. Various fluorine-containing additives also contribute to the operation of lithium-ion batteries at low temperatures [24]. Important for the operation of lithium-ion batteries at low temperatures are different additives (not only solvents) including certain salts, for example, cesium salts (CsPF_6) [25].

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 delivery of energy for various weapons, in particular, naval torpedoes. Operating temperature ranges from $-40\text{ }^{\circ}\text{C}$ to $+60\text{ }^{\circ}\text{C}$ [26].

The use of low-temperature electrolyte (1 M lithium bis-trifluoromethanesulfonimide (LiTFSI) in ethyl acetate) and electrode materials based on polytriphenylamine - and 1,4,5,8-naphthalenetetracarboxylic

dianhydride -derived polyimide enable the batteries to operate at record low temperatures ($-70\text{ }^{\circ}\text{C}$). However, no commercial production of such batteries has so far 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 (NaClO_4) in propylene carbonate-ethylene carbonate mixture) with a freezing point at $-80\text{ }^{\circ}\text{C}$ [27].

Certain prospects for low temperatures have super-capacitors with their higher power density and lower energy capacity. An operating temperature of commercial non-aqueous electrolyte super-capacitors is currently limited to a freezing point of acetonitrile $-45\text{ }^{\circ}\text{C}$ [28]. The use of mixed solvent systems such as a mixture of acetonitrile, ethyl acetate, methyl formate, methyl acetate and 1,3-dioxolane, can reduce a freezing point of the electrolyte and increase a

working temperature range to $-70\text{ }^{\circ}\text{C}$ [29]. Another way to extend the low-temperature range may be use of additives of various salts [30]. The use of ionic liquids as an electrolyte is another way for super-capacitors to operate at lower temperatures [31].

Among commercial manufacturers of super capacitors there is company Eato engaged in producing super-capacitors of the XL60 series whose working temperature ranges from $-40\text{ }^{\circ}\text{C}$ to $+65^{\circ}\text{C}$. In Russia, company Partnership of Energy and Electro Mobile Projects announced the release of super-capacitors with a useful specific power density of up to 15.5 kW/kg (specific power in the mode of a pulse load of 100 kW/kg) and an operating temperature range from -55 to $+85\text{ }^{\circ}\text{C}$ [32]. Another Russian company, Titan Power Solutions, produces super-capacitor systems for starting internal combustion engines at $-50\text{ }^{\circ}\text{C}$ to $+65\text{ }^{\circ}\text{C}$ [33].

2. Electrochemical systems based on solid polymer electrolyte

Despite the significant progress in the field of batteries and super-capacitors for low temperatures, they cannot ensure long-term energy storage, so hydrogen is rather promising for this purpose in terms of northern and mountain regions [34].

Certainly, for a large number of practical problems, electrochemical systems based on solid polymer electrolyte are of considerable interest; however, of their use at low temperatures causes serious doubts because of water freezing possibility. However, there are certain prospects. In [35] it was shown the possibility of applying electrolysis cells with solid polymer electrolyte at negative temperatures when using water-alcohol solutions. Also, alcohol acts as an anode depolarizer to reduce 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 in terms of high rates of output power and voltage [36]. Studies into PEMFC operation under low temperature conditions have been conducted for a long time [37], and some

practical success has been achieved, specifically, the launch of solid polymer fuel cells in the temperature range -20 – $15\text{ }^{\circ}\text{C}$ [38].

Research in this area [39] makes it possible 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, the second problem requires basic research, including modeling of heat and mass transfer [40].

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 [41], changes in the structure and destruction of the catalytic and gas diffusion layers [42]. 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 [41, 42]. However, the authors themselves analyzed 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. It revealed 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 [43] 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 of a mixture of carbon black and a hydrophobic agent (usually polytetrafluoroethylene). While 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 additional water absorption, while the second one provides additional space for temporary storage of ice [44].

From 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 destruction of MEA components during crystallization of the liquid phase in the MEA volume. For example, application of methanol-water solution (40 vol.%) as antifreeze in PEMFC allowed to carry out tests up to -30 °C [45]. The FC performance in the course of thawing-and-freezing test was much more effective as compared 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 [46]. However, they have their drawbacks (in particular, higher weight and size characteristics, problems of diffusion (cross-over) of methanol through the membrane [47] and are completely unsuitable for renewable energy systems. However, methanol FCs operating at low temperatures are sold at the Russian market by foreign companies, the main of which are SFC Energy AG, Germany [48], Pro-Power communication CO, South Korea [49], Cellkraft, Sweden [50].

The foreign market offers ready-made technical solutions for the use of alcohol fuel cells in the temperature range from -40 to +50 °C [59], 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 [23, 24], 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 [51, 52]. 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 [53, 54]. So, it should be noted that the use of combined hydrogen-alcohol fuel makes no fundamental problems with catalysts, just requiring 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 [55, 56]. Note that graphene materials should be distinguished as promising carriers for such catalysts, since in this case the effective contact between the catalyst particles is provided (see, for example, [57, 58]).

It should be noted that water-alkaline electrochemical systems can be used for low

temperatures operation of which is possible at $-30 - -40$ °C; however, their well-known shortcomings remain inherent, so for their use in terms of low temperatures no less research and development is required. It has to be kept in mind that prospects of the use of high-temperature (solid oxide) electrochemical systems are still uncertain.

Conclusion

The use of renewable energy in northern and mountain regions, for example, the arctic region, should be considered in perspective. All these are 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 is of the great interest. 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 their capability to operate at temperatures down to -60 °C, will have a lower cost.

Electrochemical super-capacitors 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 make it possible to produce commercial super-capacitors operable at temperatures down to -70 °C.

For a wide range of tasks, it is possible

to use industrially produced methanol fuel cells. To produce hydrogen for the purpose of long-term energy storage and solve 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 through the use of additional micro-porous layers between the gas diffusion and catalytic layers. Also, reduction of negative impact of low temperatures on the durability and performance of fuel cells may be reached through the use of alcohol additives to the hydrogen fuel. In this case, the development of 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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AŞAĞI TEMPERATURLAR ÜÇÜN ELEKTROKİMYƏVİ TEXNOLOGİYALAR

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Təqdim olunan icmal elektrokimyəvi enerji sistemlərinin aşağı temperaturlarda istifadə mümkünlüyünün təhlilinə aiddir. Qoyulam məqsədə çatmaq üçün aşağı temperaturlarda (-60°C) işləyə bilən ekoloji təmiz avtonom enerji mənbələrdən istifadə etmək lazımdır. Eyni zamanda bu məqsədlə hidrogen yanacaq elementləri də, xüsusilə $-20 + 50^{\circ}\text{C}$ temperatur intervalında normal işləyə bilən bərk polimer elektrolitli yanacaq elementləri də istifadə oluna bilər.

Açar sözlər: yanacaq elementi, bərk polimer elektrolit, superkondensator.

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°C , 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 $+50^{\circ}\text{C}$ 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.