




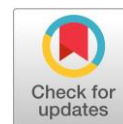


Fast-activating reserve power sources: is lead dead indeed?

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Abstract

The purpose of this research is to improve the performance and reduce the activation time of reserve power sources based on lead-acid systems at lower temperatures, down to $-50\text{ }^{\circ}\text{C}$. Physico-chemical factors affecting the activation speed of reserve power sources based on $\text{Pb-HClO}_4\text{-PbO}_2$ and $\text{Zn-HClO}_4\text{-PbO}_2$ systems are investigated using chronopotentiometry, scanning electron microscopy, and standard contact porosimetry. Two approaches to the improvement of the low-temperature performance of power sources are used. The first one is based on the substitution of lead as anodic material with zinc. This allows the increase in discharge voltage and simultaneous decrease in activation time, but brings about the instability of discharge characteristics and, finally, deteriorates the reliability of power sources. The second approach is based on the use of PbO_2 cathode material with enhanced nanoporosity. The chronopotentiometric method in galvanostatic mode is applied to the quality estimation of cathodes. The criterion of applicability of cathodes for reserve power sources consists in the low discharge overvoltage ($0.1\text{--}0.2\text{ V}$). Efficient performance of reserve power sources possessing the stable discharge voltage ($1.5\text{--}1.8\text{ V}$ per cell) and the unprecedentedly short activation time (under 30 ms) even at lower temperatures (down to $-50\text{ }^{\circ}\text{C}$) is achieved. The results are verified by fabrication and testing of pilot batches of miniaturized reserve power sources having microcells' volume of 0.02 ml . The second approach to the improvement of power sources is transferred into the industrial production.

Keywords

reserve power source
activation time
discharge
lead dioxide
lead
zinc

Key findings

- The improved low-temperature (down to $-50\text{ }^{\circ}\text{C}$) performance of reserve power sources based on lead-acid systems is achieved.
- The $\text{Zn-HClO}_4\text{-PbO}_2$ system offers the elevated discharge voltage and short activation time but exhibits an unstable performance.
- Lead dioxide cathode material with the increased nanoporosity provides the improvement of low-temperature performance of the $\text{Pb-HClO}_4\text{-PbO}_2$ system.
- The suitability criterion for electrode materials consists in the maintenance of the low discharge overvoltage ($0.1\text{--}0.2\text{ V}$) at lower temperatures.
- Improved reserve power sources of the $\text{Pb-HClO}_4\text{-PbO}_2$ system exhibit the unprecedentedly short activation time (less than 30 ms).

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1. Introduction

Reserve power sources occupy an important niche in the field of emergency, rescue, alarm, and military autonomous equipment [1, 2]. To ensure a high reliability of electronic and electromechanic devices operating under extreme conditions, power sources of this type must comply with strict requirements, stable discharge voltage and short activation time (some 40–60 ms) even at low temperature (down to $-50\text{ }^{\circ}\text{C}$) being among them. Their functional feature consists in the spatial separation of electrolyte from dry cells prior to activation, which ensures long shelf life (up to 17–20 years) without self-discharge and in the capability of fast activation by filling up the cells when needed [3].

The engineering design of reserve power sources has undergone successive development in the past decades, which resulted in creation of rather sophisticated design schemes embodied in miniaturized power sources having the outer size as small as 6–20 mm and patented by market leaders, such as Thales [4, 5], Diehl & Eagle Picher [6, 7], EnerSys Advanced Systems [8], Vitzrocell [9, 10]. JSC “NPO “Pribor” named after S. S. Golembiovsky” designed and patented [11] small-sized reserve power sources with authentic design schemes (Figure 1). Generally, the main structural elements of power sources include a sealed glass ampoule that hangs on a suspension or leans on an elastic or breakable support inside a coaxial stack of annular electrodes, including bipolar ones, which form together a battery of cells connected in series, parallel or combined mode.

The activation of reserve power sources proceeds upon an axial mechanical shock that causes the destruction of the ampule against a breaking pin, filling up interelectrode spaces with electrolyte and thus starting the electrochemical process of power generation. When lead–acid electrochemical systems ($\text{Pb-HClO}_4\text{-PbO}_2$ or $\text{Pb-HBF}_4\text{-PbO}_2$) are used, the activation process slows down at low temperatures (below $-30\text{ }^{\circ}\text{C}$), making it difficult to reach activation time shorter than 100–400 ms [12]. To some extent, the activation time was reduced by a proper design of power sources providing the decreased hydraulic resistance against the electrolyte flow, which shortens the time needed to fill up the cells. The significance of this factor is defined by a substantial increase in electrolyte viscosity at lower temperatures, by more than 8 times on decreasing the temperature from $-30\text{ }^{\circ}\text{C}$ to $-50\text{ }^{\circ}\text{C}$ [13]. Such a mechanistic approach allowed the researchers and designers [14] to reach as short an activation time as 29–45 ms at the lowest achieved temperature of $-32\text{ }^{\circ}\text{C}$. The further reduction of the activation time at even lower temperatures remained unachieved for a long time, which was attributed to the deterioration of discharge characteristics of lead–acid electrochemical systems because of the slowing down of electrochemical electrode processes at low temperatures [12] and led to the formulation of a rather categorical conclusion, “Lead is dead” [15]. All that forced researches to reject lead–

acid electrochemical systems and to employ a by far more expensive and demanding lithium–thionyl chloride system instead, despite the availability of technological and material basis for lead-containing systems and their compatibility with the well-developed and globally spread technology of lead–acid secondary power sources.

The recent studies of the properties and performance of cathode and anode materials of the $\text{Pb-HClO}_4\text{-PbO}_2$ system were limited to a temperature range down to $-30\text{ }^{\circ}\text{C}$. The application of lead dioxide coatings electrodeposited under the influence of ultrasound was shown to have advantages in some cases, consisting in the improvement of discharge characteristics [12, 16–18]. Investigations dedicated to electrodeposited lead or zinc coatings as anodic materials showed the advantage of the elevated discharge voltage of the system comprising zinc anodes [19, 20]. However, the performance of the abovementioned cathode and anode materials over a broader temperature range (down to $-50\text{ }^{\circ}\text{C}$) has remained unclear.

The current market demands motivated us to clarify if lead–acid systems can comply with strict requirements concerning short activation time at low temperatures. We aimed at the development of approaches to improving the performance of reserve power sources based on lead–acid systems over the lower temperature range (down to $-50\text{ }^{\circ}\text{C}$).

The main tasks of the research include the following:

- To find crucial factors that can help achieve short activation time (less than 50 ms).
- To establish relations between physico-chemical properties of electrode materials and discharge characteristics.
- To develop a quality estimation method that enables the selection of electrode materials with enhanced performance, usable not only under laboratory conditions but also in the industrial production.

Our aim was also to verify the industrial applicability of the results by fabrication and testing of pilot batches of small-sized power sources.

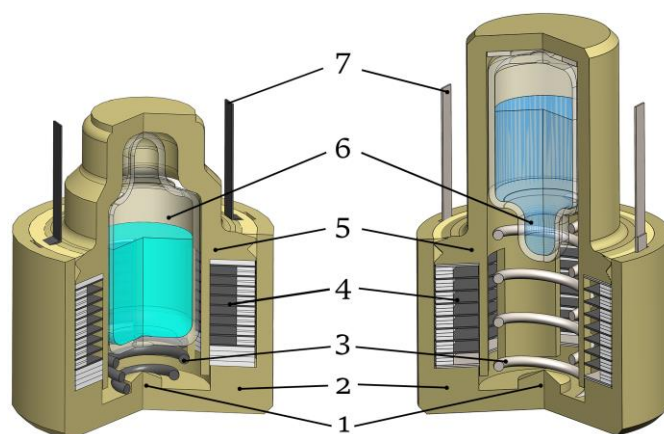


Figure 1 Small-sized reserve power sources (in axonometric projection): 1 – breaking pin; 2 – casing; 3 – spring; 4 – stack of electrodes; 5 – cap; 6 – ampoule filled with electrolyte; 7 – terminals.

2. Experimental

2.1. Materials

Cold-rolled low-carbon steel strips of grades 08, 08kp or 08ps according to the state standard GOST 503-81 were used as the substrates for the electrodeposition and fabrication of electrodes of power sources.

Lead (II) oxide, lead (II) nitrate, nitric acid, zinc oxide, sodium hydroxide, and potassium hydroxide of analytical or ultra-high grades, and purified water of the 3rd category according to the national standard GOST R 58431-2019 or distilled water according to the national standard GOST R 58144-2018 were used for the preparation of solutions for main and auxiliary processes of electrodeposition of coatings. Lead sheets of composition grades S1 or S0 according to the interstate standard GOST 9559-2021 and graphite sheets of grade MPG-6 according to technical specifications TU 1915-109-081-2004 were used in the electrodeposition processes.

The aqueous solution of perchloric acid (HClO_4) with the concentration of 40% was used as an electrolyte for the fabrication of power sources and for the tests of electrodes. This concentration prevents the freezing of the electrolyte at lower temperatures (down to ca $-56\text{ }^\circ\text{C}$) [13]. The electrolyte was prepared by the dilution of perchloric acid of ultra-high grade with concentration of 50%, complying with technical specifications TU 6-09-2878-84, with distilled water according to the national standard GOST R 58144-2018.

The following electrodes were used for potentiometric measurements using the three-electrode scheme. A glassy carbon electrode with working surface 3 mm in diameter (purchased from ElectroChemical Instruments, Russia) was used as a reference one. The platinum wire of grade Pl 99.9 M 0.50 according to the interstate standard GOST 18389-2014 was used as a counter electrode.

2.2. Methods and technologies

Electrodes for power sources were fabricated under industrial conditions as follows. Steel strips prior to the electrodeposition were subjected to subsequent chemical and electrochemical degreasing using the standardized industrial techniques [21]. Lead coatings were electrodeposited from acidic lead-containing solution according to the industrial process described in the technological card no. 33 [21]. Zinc coatings were electrodeposited from alkaline zincate solution as described in the industrial technological card no. 30 [21].

Before the electrodeposition of lead dioxide (PbO_2) the surface of steel substrate was subjected to the anodic oxidation in alkaline solution as described in [18]. The electrodeposition of PbO_2 was performed from acidic nitrate solution with $\text{Pb}(\text{NO}_3)_2$ concentration of $150\text{--}200\text{ g}\cdot\text{dm}^{-3}$. For the comparative study of the $\text{Zn}\text{--}\text{HClO}_4\text{--}\text{PbO}_2$ and $\text{Pb}\text{--}\text{HClO}_4\text{--}\text{PbO}_2$ systems we used cathodes with PbO_2 coating obtained under commonly applied anodic current density, $2\text{ A}\cdot\text{dm}^{-2}$. For the study of the influence of properties of cathodes on the performance of the $\text{Pb}\text{--}\text{HClO}_4\text{--}\text{PbO}_2$ system

we varied the current density when electrodepositing PbO_2 coating. The following anodic current densities were applied: $1\text{ A}\cdot\text{dm}^{-2}$ for variant 1; $2\text{ A}\cdot\text{dm}^{-2}$ for variant 2; $5\text{ A}\cdot\text{dm}^{-2}$ for variant 3.

The thickness of coatings was determined by calculating the difference between the overall thickness of the coated substrate and the thickness of the substrate without coating, which were measured directly. The obtained values of the thickness were $20\text{--}30\text{ }\mu\text{m}$ for zinc, $25\text{--}30\text{ }\mu\text{m}$ for lead, and $50\text{--}65\text{ }\mu\text{m}$ for PbO_2 coatings.

The adhesion strength of the coatings to the substrate was estimated using the standardized industrial techniques [22], namely the scratch method for zinc and lead coatings and the 180° -angle-bending method for PbO_2 coatings. The observed absence of the exfoliation for all coatings indicated the achieved satisfactory adhesion.

The electrodes for investigations and the fabrication of power sources were manufactured from coated steel sheets using the laser cutting industrial technique.

The electrodes were studied using the following methods. The surface morphology of coatings on substrates was determined by the scanning electron microscopy (SEM). The porosity of coatings on substrates was studied by the standard contact porosimetry (SCP) – the method developed in the A. N. Frumkin Institute of Physical Chemistry and Electrochemistry of the Russian Academy of Sciences and described in detail in [23–25]. Octane was used as the measurement liquid.

Chronopotentiometry was performed in the galvanostatic mode at the current density of $25\text{ mA}\cdot\text{cm}^{-2}$. For three-electrode and two-electrode measurements, the working electrodes with the surface areas of 0.5 and 1.0 cm^2 , respectively, were used. The three-electrode measurements consisted of two stages: (i) the open circuit and (ii) the discharge.

Pilot batches of reserve power sources of the particular design schemes (Figure 1) were fabricated and tested. The power sources in question comprised 8 microcells, each having a volume of 0.02 ml . The outer dimensions of power sources constituted 15 mm in diameter and 17.8 or 21.5 mm in height.

The testing technique consisted in the activation of reserve power sources by the mechanical impact in the axial direction accompanied by the registration of discharge voltage with the sampling frequency of at least 1 MHz . The resistivity of the load circuit was $1\text{ k}\Omega$. The activation time was determined as the time from the starting of the mechanical impact to reaching the stable discharge voltage value of 9.5 V .

2.3. Instruments and equipment

The electrodeposition processes were performed using the industrial production assembly consisting of baths with a working volume of $200\text{--}250\text{ dm}^3$ equipped with rectifying devices “Pulsar Pro 240/12” (LLC “Navicom”, Russia).

The multi-revolution dial indicator 1 MIG-0 complying with the interstate standard GOST 9696-82 was used for thickness measurements.

SEM studies were performed using the following microscopes: JSM-U3 (Jeol, Japan), ZEM 15 (ZepTools, China), and Supra 50VP (Carl Zeiss, Germany).

Potentiostat-galvanostat P-40X (ElectroChemical Instruments, Russia) was used for chronopotentiometric measurements. To maintain the temperature the cryothermostat KTKh-74-65/165 (Smolensk SKTB SPU, Russia) was used.

The discharge voltage of reserve power sources was recorded using the digital oscilloscope HMO3054 (Rohde & Schwarz, Germany).

3. Results and Discussion

3.1. The use of zinc as anode material

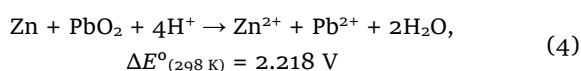
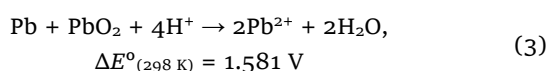
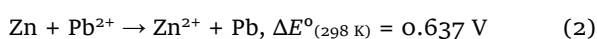
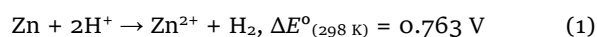
As the first approach to the improvement of the low-temperature performance of power sources, we employed the idea of using zinc as the anode material instead of lead in the Pb-HClO₄-PbO₂ system. This approach is based on the assumption that the reduction of activation time could be achieved by merely elevating the discharge voltage of a cell due to the more negative potential of the anode (cf. the values of standard potentials $E^{\circ}_{(298\text{ K})}$ for electrodes Zn²⁺/Zn and Pb²⁺/Pb being -0.763 and -0.126 V, respectively [26]).

Chronopotentiometric measurements confirm the retention of the high discharge voltage of the cells comprising zinc anodes at lower temperatures (Figure 2).

Within the temperature range of +50 to -50 °C the discharge voltage of the Zn-HClO₄-PbO₂ system exceeds significantly that of the Pb-HClO₄-PbO₂ system the typical values being 1.4–2.3 and 1.2–1.8 V, respectively.

The achieved values of the discharge capacity (237–395 mA·min·cm⁻²) constitute 37–61% of theoretical values, which is less than previously obtained (81%) [19]. This fact can be associated with the stricter conditions of our experiments, including the lower temperature limit (-50 °C compared to -30 °C) and the decreased interelectrode distance (0.5 mm compared to 1 mm).

The main drawback of the Zn-HClO₄-PbO₂ system consists in the instability of the discharge voltage that can be obviously attributed to the competition between side-reactions (1), (2), (3) and the main reaction (4).



The values of standard electromotive force $\Delta E^{\circ}_{(298\text{ K})}$ given above are calculated according to [26].

The side-reaction (1) leads to the hydrogen gas evolution that may cause a partial removal of electrolyte from the in-

terelectrode space and, in the worst case, the cell malfunction. The reaction (2) can bring about a short-circuit fault of the cell induced by the formation of fine electroconductive deposits of metallic lead. Furthermore, the instability of the discharge voltage may give rise to the cell polarity reversal. This phenomenon may arise when the voltage of a given cell in the battery drops so considerably in comparison to the other cells' voltage that the cell completely loses the stability of the power generation and switches to the consumption mode [27]. In fact, we have observed the cell reversal in some cases of profound discharge voltage instability (Figure 3).

To test the performance of the power sources the pilot batches were fabricated. The comparative tests showed a substantial decrease in the activation time (to the values shorter than 15 ms at -50 °C) of the power sources based on the Zn-HClO₄-PbO₂ system as compared to Pb-HClO₄-PbO₂ (Figure 4). However, the tests confirm the substantial disadvantages of the former system, including the instability of discharge voltage and the decreased discharge time (Figure 5). These features require that power sources for supply of sensitive microcircuits should be used in combination with electronic devices providing stabilization, accumulation or conversion of the electric power.

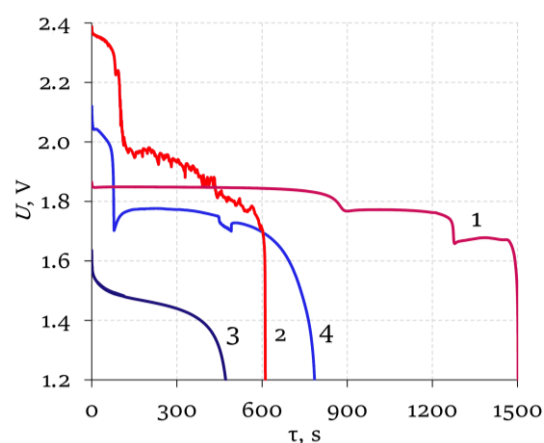


Figure 2 Chronopotentiometric discharge curves for the Pb-HClO₄-PbO₂ (1, 3) and Zn-HClO₄-PbO₂ (2, 4) systems at different temperatures: +50 °C (1, 2) and -50 °C (3, 4). Designations: U – voltage, τ – time.

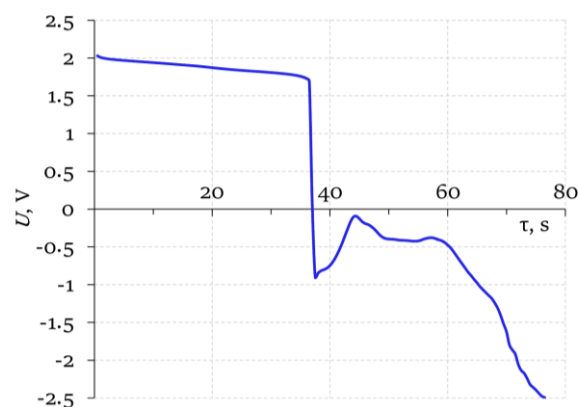


Figure 3 The example of a discharge curve for the Zn-HClO₄-PbO₂ system suffering from the cell polarity reversal at -50 °C.

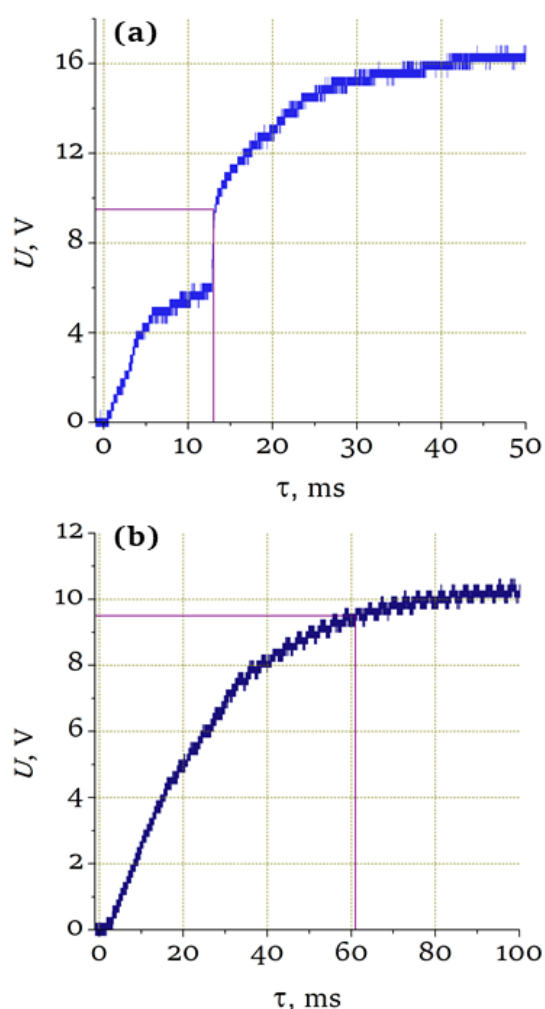


Figure 4 Initial regions of discharge curves of power sources based on the Zn-HClO₄-PbO₂ (a) and Pb-HClO₄-PbO₂ (b) systems at -50 °C.

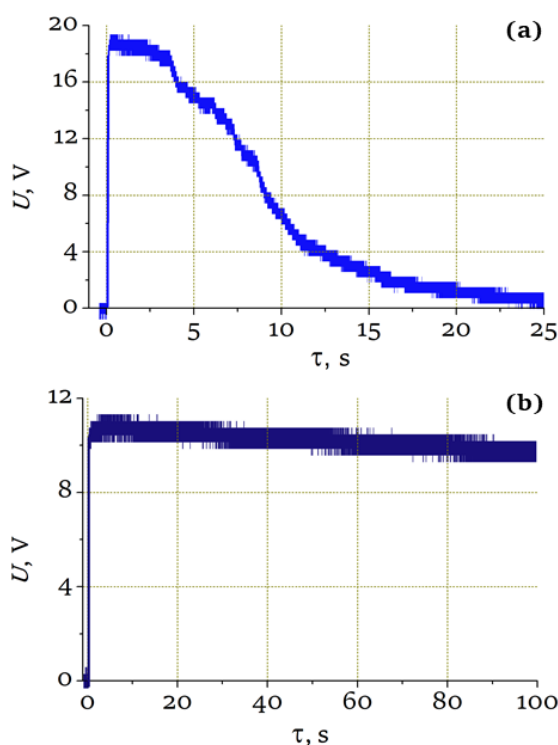


Figure 5 Discharge curves of power sources based on the Zn-HClO₄-PbO₂ (a) and Pb-HClO₄-PbO₂ (b) systems at -50 °C (discharge not completed for the second system).

The discharge performance of reserve power sources based on the Zn-HClO₄-PbO₂ system is somewhat similar to the known small-sized thermal power sources based on energy-condensed systems with molten electrolyte having the initial voltage impulse and consequent voltage decline in the course of discharge. The difference concerns the longer activation time (50–100 ms or even more) for thermal power sources [28, 29].

It is noteworthy that the instability of discharge of the Zn-HClO₄-PbO₂ system affects negatively the reliability of power sources. On testing the fabricated samples, we have observed the elevated malfunction rate, several units to tens percent. Nevertheless, we cannot exclude the suitability of this system for some applications, e.g. for power sources of larger form factors or those comprising separated anodic and cathodic spaces, which can help diminish the influence of side reactions. Despite the short activation time and satisfactory functionality at lower temperatures, one should avoid the application of this system in reserve power sources intended for critical applications, where a high reliability level is required.

Therefore, we concluded that the further research attempts should be directed to the development of another approach to the improvement of the low-temperature performance of power sources consisting in the deeper characterization and optimization of the Pb-HClO₄-PbO₂ system.

3.2. The use of PbO₂ cathodic material with different microstructure

First of all, to establish the crucial factors affecting the low-temperature performance of the Pb-HClO₄-PbO₂ system, comparative chronopotentiometric measurements for anode (Pb) and cathodes (PbO₂) obtained under different conditions were conducted using the three-electrode testing cell (Figure 6).

At +50 °C the absolute values of the overvoltage (defined as the difference between the electrode potential on discharge and that of an open circuit) for all studied samples are uniform and fairly small, being below 0.05 V. In contrast, at -50 °C the overvoltage can vary substantially for different samples (Figure 7), especially for the cathodes obtained under various conditions. For the cathode samples obtained according to variants 1 and 2, absolute values of the overvoltage approach 0.3–0.45 V, while for the sample obtained according to variant 3 the absolute value of the overvoltage is comparable to that of the anode, being just 0.13–0.15 V.

The chronopotentiometric measurements constitute a basis for the industrially applicable quality estimation procedure that enables the selection of electrode materials with enhanced discharge performance. The criterion of preferred minimal absolute values of the overvoltage is associated with the relation of the overvoltage with kinetic parameters of electrode processes [30]. Low absolute values of the overvoltage and their maintenance at lower temperatures can serve as a sign of favorable reaction kinetics, which supposedly should lead to the rapid activation of power sources.

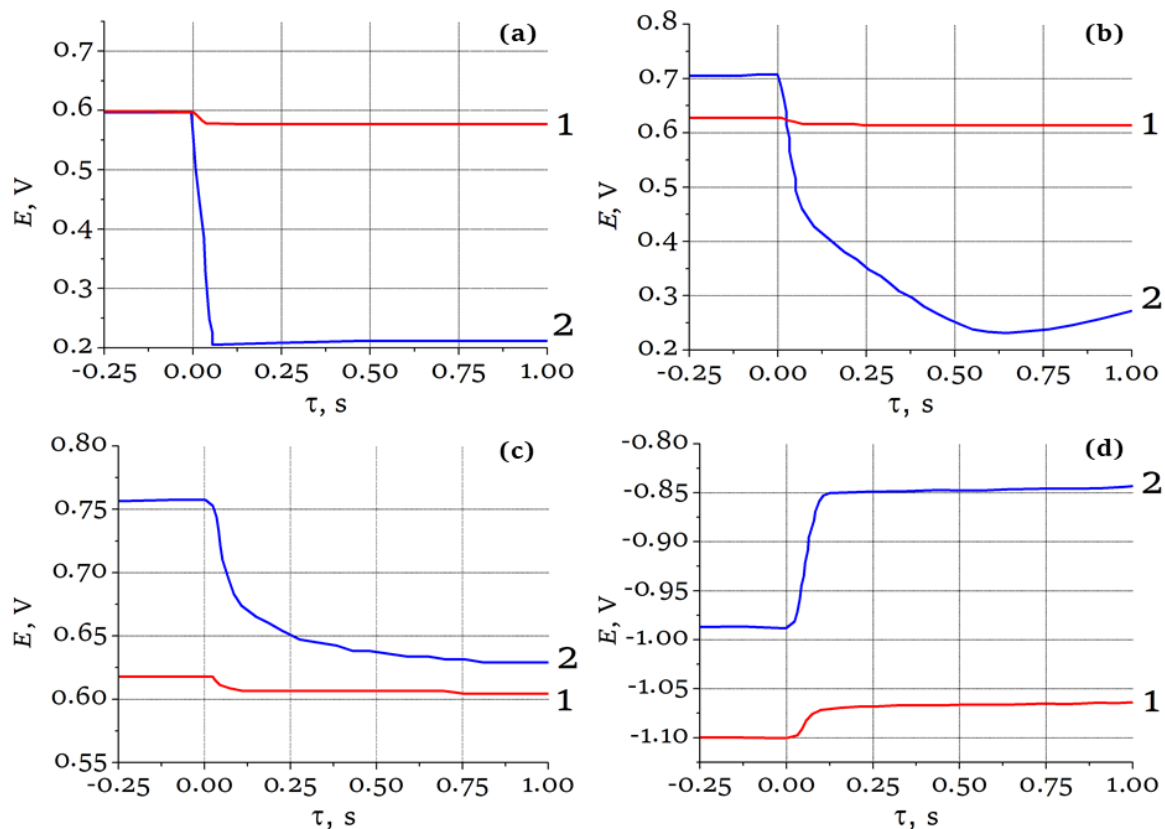


Figure 6 Chronopotentiometric curves of cathodes with PbO_2 coatings obtained according to variants 1 (a), 2 (b), 3 (c) and anode with Pb coating (d) at different temperatures: $+50\text{ }^\circ\text{C}$ (1) and $-50\text{ }^\circ\text{C}$ (2). Designation: E – electrode potential.

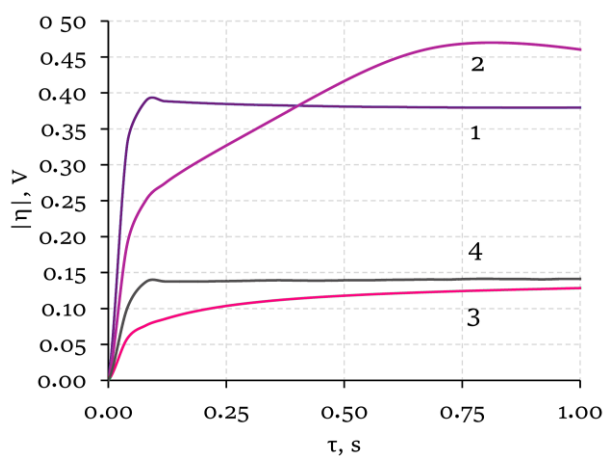


Figure 7 Overvoltage curves of cathodes with PbO_2 coatings obtained according to variants 1 (1), 2 (2), 3 (3) and anode with Pb coating (4) at $-50\text{ }^\circ\text{C}$. Designation: η – overvoltage.

The results imply that the properties of PbO_2 can be considered to be a crucial factor for achieving the satisfactory performance of power sources over the broad temperature range.

To establish relations between physico-chemical properties of PbO_2 and discharge characteristics the investigation using SEM and SCP was conducted.

SEM reveals the transformation of surface morphology of PbO_2 coatings on changing the electrodeposition conditions (Figure 8).

The sample obtained according to variant 1 (at the relatively low current density) exhibits a well-defined dense

crystalline structure formed by pyramidal blocks having the average dimension of several μm . This type of surface morphology represents the most frequently observed structure of coatings electrodeposited from acidic solutions without modifying additives [31–34]. The observed surface structure for variants 2 and 3 differs from that of variant 1. The increase in the current density leads to the formation of a granular-like structure with visible embossing structural elements having dimensions of several to ten μm . For these samples the network of submicron cracks is observed that, however, does not impair the adhesion strength of coatings to the substrate.

The high-magnification image of the surface of the coating obtained at the highest current density (variant 3) shows the fine structure at nanoscale, which is formed by aggregates of crystalline grains with the approximate size of 10 to 20 nm and has the pronounced nanoporosity.

To gain further insight into the fine porous structure of PbO_2 coatings the SCP method was employed (Figure 9). The sample obtained according to variant 1 (at the relatively low current density) has the least amount of nanopores (having the radius of up to 100 nm). For the sample obtained according to variant 2 (at the moderate current density) a significant amount of nanopores was recorded (Table 1). The largest porosity in the nanoscale was found in the sample obtained according to variant 3 (at the highest current density). The specific volume of nanopores for this sample constitutes ca 39% of the overall value.

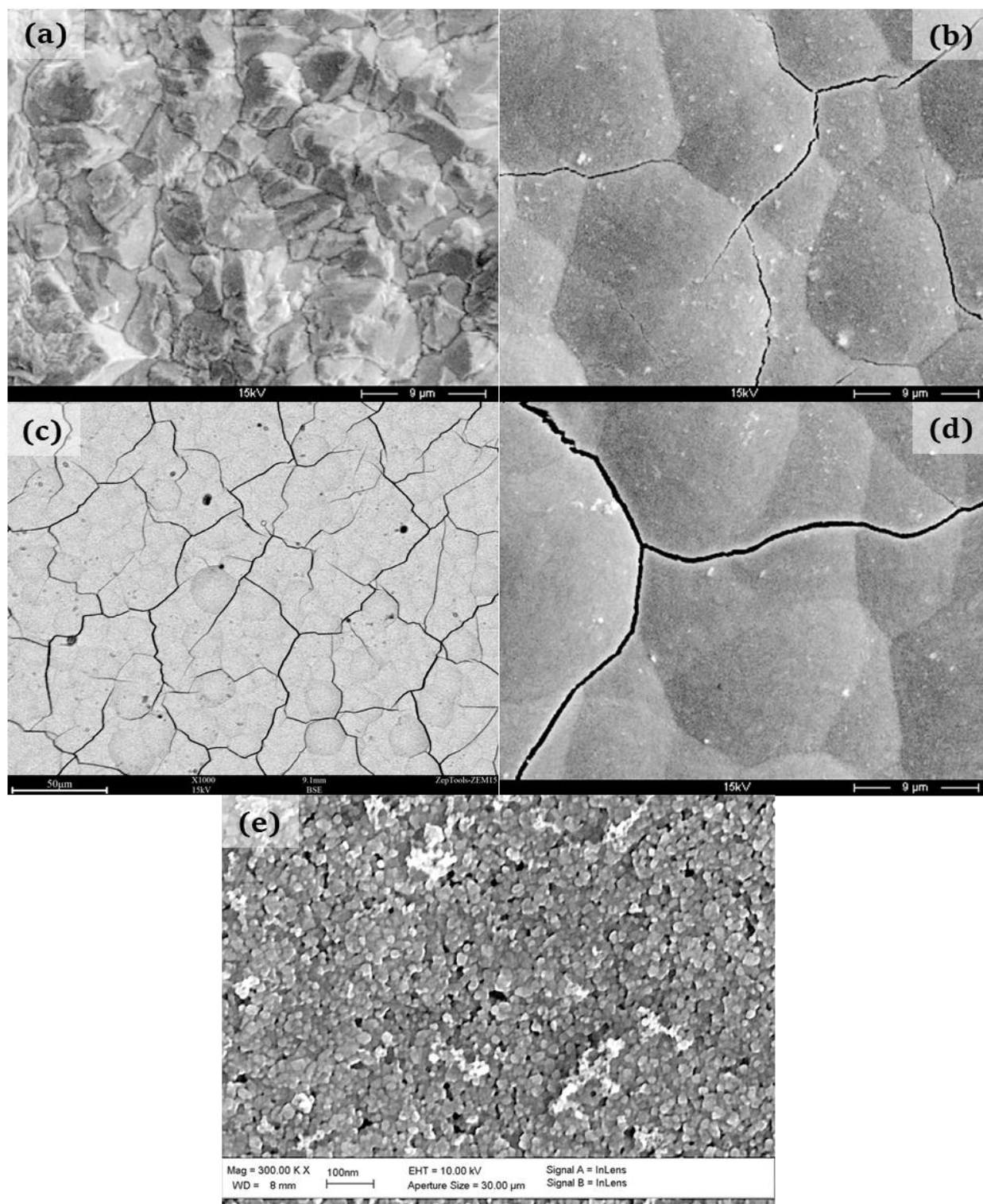


Figure 8 SEM images of the surface of PbO_2 coatings obtained according to variants 1 (a), 2 (b), and 3 (c, d, e).

Thus, the difference in the discharge behaviour of PbO_2 coatings can be attributed to different microstructure, including porosity, which is induced by the variation of electrodeposition conditions. The increased nanoporosity seems to be not the only favourable factor for the improvement of the low-temperature performance of electrodes. Our recent results obtained using X-ray photoelectron spectroscopy and X-ray diffraction analysis imply that electrodeposition conditions affect the chemical and phase composition of coatings [35, 36].

The electrodeposition at the elevated current density leads to the increase in the surface content of hydroxo and aqua groups in PbO_2 coatings [35]. According to the “gel-crystal” concept developed earlier by professor D. Pavlov for PbO_2 electrodes, this factor increases the proton mobility in the amorphous gel-phase consisting of lead hydrated oxohydroxo compounds, which is assumed to be important for improving the discharge performance of PbO_2 [37–40].

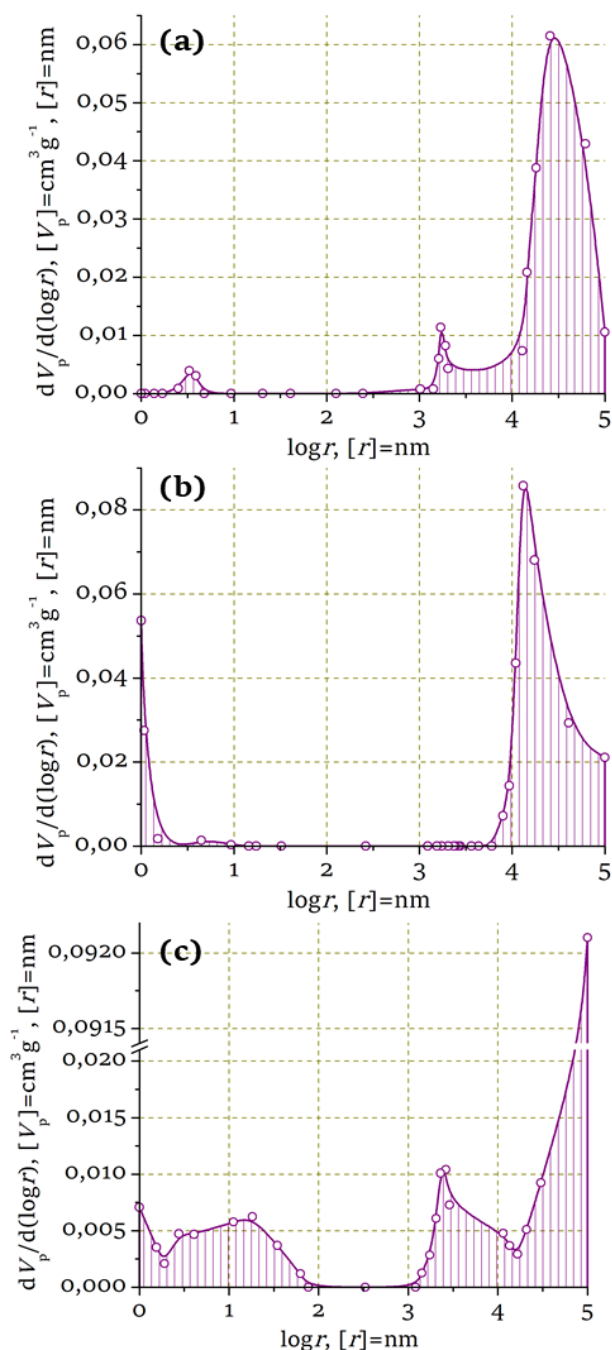


Figure 9 Differential pore size distribution of PbO₂ coatings obtained according to variants 1 (a), 2 (b), and 3 (c). Designations: V_p – specific volume of pores, r – radius of pores.

Table 1 Porosity characteristics of PbO₂ coatings obtained according to different variants.

Porosity characteristics	r (nm)	Variant		
		1	2	3
V _p (10 ⁻³ cm ³ ·g ⁻¹) ^a	up to 10	0.85	6.22	8.97
	10 to 100	0	0	3.63
	100 to 10 ⁵	44.85	41.78	19.80
	up to 10 ⁵ (overall)	45.7	48.0	32.4
α _v (%) ^b	up to 10	1.9	13.0	27.7
	10 to 100	0	0	11.2
	100 to 10 ⁵	98.1	87.0	61.1

^a Specific volume of pores with radii (r) falling within a definite range;

^b Fraction of specific volume of pores in relation to the overall value.

The equilibrium between gel and crystal zones of PbO₂ material and between gel zones, sol particles and the electrolyte, which defines the gel-crystal structure and finally the performance of PbO₂ electrode material, is dependent on the conditions of an electrochemical process, as was previously established for the PbO₂ formation in the course of the charging of Pb/H₂SO₄/PbO₂ secondary batteries [41].

The increase in the initial charge current was supposed to increase the rate of the electrochemical reaction of Pb⁴⁺ formation, which then leads to high oversaturation of the Pb(OH)₄ sol in the pores of PbO₂ material and rapid formation of [Pb(OH)₂]_m gel particles of polymeric nature, which interconnect to form stable agglomerated structures with improved contacts between the agglomerates. Ultimately, in the secondary batteries this enhances the life cycle performance of PbO₂ electrodes [41].

Despite the obvious difference in the electrolyte composition, we can infer an analogy between the electrodeposition processes during the charging of secondary power sources and the formation of PbO₂ coatings for primary power sources, as we observed the higher content of hydrated oxohydroxo lead compounds for coatings obtained at the elevated current density [35]. We did not investigate the role of other factors, e.g. temperature, additives and substrate material; this could constitute the subject of the future investigations.

The elevated current density allows obtaining of single-phase tetragonal β-PbO₂ coatings without any admixture of the orthorhombic α-PbO₂ phase [36]. The β-PbO₂ phase is believed to have a higher electrochemical activity as compared to α-PbO₂ [12, 42]. However, the electrochemical performance is influenced strongly by other factors including microstructure, which allows no unequivocal assessment as concerns to the preference of α- or β-PbO₂ [43, 44].

Considering the abovementioned, we should anticipate the best low-temperature activation performance for the sample obtained according to variant 3 (using the highest current density).

To verify this assumption, the pilot batches of power sources with different cathode samples were fabricated and tested (Figure 10). The tests show that the shortest activation time at -50 °C can be achieved indeed by using lead dioxide cathode material with the increased nanoporosity.

The recently obtained results [36] allow us to trace the influence of the porosity on the capacity of PbO₂ electrodes. For the electrode obtained according to variant 1, which possesses minor amount of nanopores and the highest amount of relatively coarse pores (with r > 100 nm), the highest discharge capacity was observed (250 mA min cm⁻², i.e. ca 50% of the theoretical value). Variant 2, which provides the noticeable amount of nanopores and somewhat lower number of coarse pores in PbO₂ electrodes as compared to variant 1, leads to inferior discharge capacity (186 mA min cm⁻², i.e. ca 37% of the theoretical value). Meanwhile, for variant 3 with the electrodes possessing the highest amount of nanopores

combined with the lowest number of coarse ones we observed the lowest discharge capacity ($121 \text{ mA min cm}^{-2}$, i.e. ca 24% of the theoretical value).

Thus, the discharge capacity is associated with the specific volume of coarse pores rather than nanopores. This observation is consistent with the capacity-limiting role of transport pores of electrode materials [45], according to which the accessibility of an electrode material for the electrochemical reaction is restricted by the retardation of mass transfer through long tortuous capillaries built up of narrow pores. Coarse pores including submicron cracks in the coatings ensure a faster transition of the electrolyte and reactant (H^+ ions) to the smaller pores, where the electrochemical process occurs, as well as the removal of product (Pb^{2+} ions).

Alternatively, one can explain the observed peculiarity of the discharge capacity in terms of interparticle contacts, which was found to be a critical factor for the discharge of PbO_2 electrodes in some cases [44]. Less tight intercrystalline contacts for the materials with the increased nanoporosity represent a factor that can diminish discharge capacity, as on the dissolution of PbO_2 crystallites in the course of the discharge process fine-porous structures tend to lose their structural integrity. This was, in fact, revealed in our direct observations of the presence of the fine PbO_2 sludge at the bottom of the cell after discharge experiments.

Further, in order to optimize the discharge stability of electrodes ensuring a reasonable balance between high capacity and fast activation, a double-layer concept was employed (Figure 11). The application of the inner dense PbO_2 layer with the decreased nanoporosity (obtained according to variant 1) hinders the access of the electrolyte to the substrate through pores and cracks in the outer layer and prevents the formation of local electrochemical cells $\text{Fe}/\text{HClO}_4/\text{PbO}_2$, thus reducing the self-discharge. The outer porous PbO_2 layer is responsible for the acceleration of the activation process, especially at lower temperatures. Submicron cracks present in this layer might obviously play a definite role in facilitating the activation process, as they could provide a faster transit of the electrolyte to the pores situated deeper from the layer surface.

Using this approach, the relatively high values of the low-temperature discharge capacity (up to $200 \text{ mA}\cdot\text{min}\cdot\text{cm}^{-2}$ at -50°C) were achieved for the $\text{Pb}-\text{HClO}_4-\text{PbO}_2$ system. These values exceed the value obtained in [12] ($91 \text{ mA}\cdot\text{min}\cdot\text{cm}^{-2}$ at -30°C).

The test results of pilot batches of power sources with double-layered PbO_2 cathodes (Figure 12) confirm the achievement of the high level of the discharge performance and short activation time complying with the requirements. These results demonstrate the effectiveness of the applied approach to the improvement of the low-temperature performance of power sources based on the study of relations between physico-chemical properties of the PbO_2 cathode material and the performance of electrochemical system. They also suggest that lead-acid systems should not be considered to be out-of-date and discarded from their application in reserve power sources.

4. Limitations

In our chronopotentiometric study, we used the glassy carbon electrode as a reference one, which is due to the absence of the classical reference electrodes capable of operating at relatively low temperatures (below 0°C).

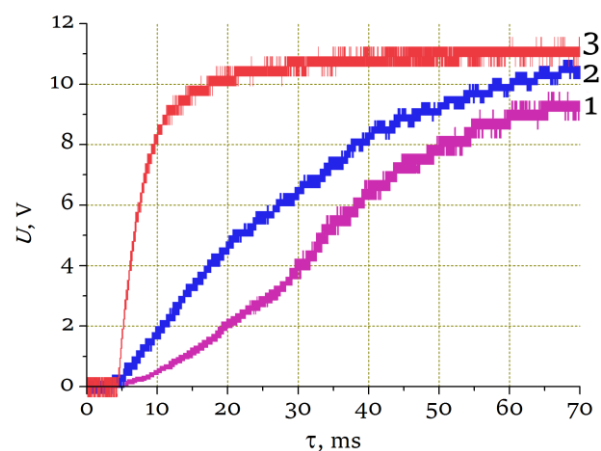


Figure 10 Initial regions of discharge curves of power sources based on the $\text{Pb}-\text{HClO}_4-\text{PbO}_2$ system with PbO_2 coatings obtained according to variants 1, 2, and 3 at -50°C (the curve's number corresponds to the variant's number).

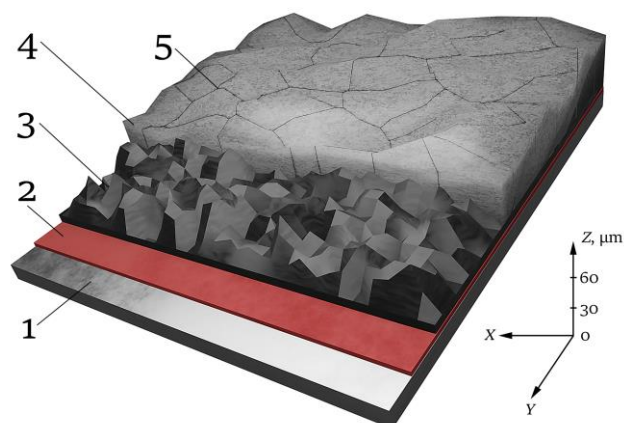


Figure 11 The model of the layered structure of PbO_2 cathodes: 1 – steel substrate; 2 – ferrous oxide barrier layer; 3 – inner dense PbO_2 layer; 4 – outer porous PbO_2 layer; 5 – submicron cracks.

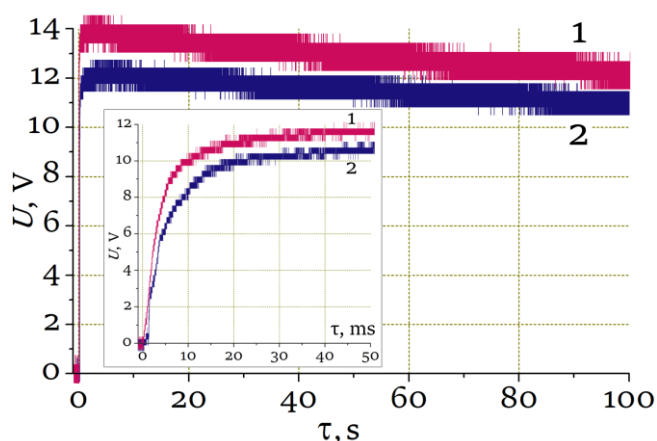


Figure 12 Discharge curves of power sources based on the $\text{Pb}-\text{HClO}_4-\text{PbO}_2$ system with double-layered cathode coatings at $+50^\circ\text{C}$ (1) and -50°C (2). The initial regions of the discharge curves are depicted in the insert.

Despite the fact that the absolute potential of the working electrode remains unidentified in this case, it is possible to determine accurately some quantitative characteristics, such as overvoltage during the discharge, due to the relative stability of the reference electrode potential in the course of measurement.

The detailed study of the kinetics of discharge processes by classical electrochemical techniques could give further insights concerning the influence of physico-chemical factors on the reaction rate, which could provide other possible ways to enhance the performance of power sources.

Regarding the stability of the obtained nanoporous PbO₂ coatings, an important practical question arises, whether the structure, composition and discharge properties of cathode PbO₂ materials preserve in the course of the long-term storage. Investigations concerning this point are currently under way. Our recently obtained preliminary results of accelerated life tests imitating the storage of power sources for 15 years in the heated and unheated depots showed the maintenance of the performance of power sources, which indirectly confirms the stability of coatings.

Appropriate physico-chemical properties of components of the electrochemical system impose necessary but not sufficient conditions for obtaining the high performance level of power sources. For instance, the role of engineering materials used for the fabrication of structural components is of high importance. Although some significant results were achieved in this field recently [46], one cannot exclude further advance.

5. Conclusions

The low-temperature (down to -50 °C) discharge performance of reserve power sources based on lead-acid electrochemical systems involving lead dioxide and perchloric acid was improved. Two approaches to the improvement were applied.

The first one employs the use of zinc instead of lead as the anode material, which increases the discharge voltage at lower temperatures and thereby decreases the activation time. The main disadvantage of this approach lies in the instability of the discharge voltage.

The second approach consists in the study of physico-chemical properties of PbO₂ cathodes and the choice of cathode coatings, enabling the improvement of the performance of power sources. The key criteria of applicability of cathode coatings consist in the high content of nanopores and low overvoltage (0.1–0.2 V) during discharge.

The fabrication and tests of pilot batches of miniaturized reserve power sources based on the Pb–HClO₄–PbO₂ and Zn–HClO₄–PbO₂ systems confirm the high level of the low-temperature performance (including the unprecedentedly short activation time of less than 30 ms at -50 °C) and the applicability of the results of this study to the industrial production.

• Supplementary materials

No supplementary materials are available.

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• Conflict of interest

The authors declare no conflict of interest.

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