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CHEMICAL CURRENT SOURCE EXPRESS DIAGNOSTICS USING NOISE SPECTROSCOPY ON THE EXAMPLE OF LITHIUM-THIONYL CHLORIDE BATTERY

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Abstract

Lithium-thionyl chloride battery voltage is practically not changing during the discharge process and drops sharply being completely discharged. In this regard, the problem of non-destructive quality control of the chemical current sources (first of all, the discharge degree) before installation thereof in the equipment becomes of particular importance. Microcalorimetric studies make it possible to rather correctly determine the current source internal self-discharge rate, predict the LCCS shelf life and its performance term. However, the heat release absolute value in current sources with sufficient storability, i.e., with low self-discharge, is very small; therefore, it is necessary to use sensitive, stationary and large-sized equipment. This makes such diagnostics impossible when operating in the stand-alone conditions. The impedance spectroscopy method could be proposed to solve this problem. However, satisfactory results are only obtained in the 0–70 % residual capacitance range. Determination of residual capacitance in the 70–100 % range appears to be rather difficult due to the absence of noticeable alteration in the informative parameter within the limits of its absolute deviation from the mean value. In this regard, it looks advisable to use noise spectroscopy as a physically independent method in diagnosing the state of chemical current sources to expand the residual capacitance diagnostics range to the 70–100 % domain, as well as to increase reliability of the chemical current source diagnostic estimate in the range of 50–70 %. Results of the electrochemical noise measurement analysis confirm promising application of the noise spectroscopy method in estimating current state of the primary chemical current sources in their low discharge domains

Keywords

Primary chemical current sources, lithium batteries, noise spectroscopy, discharge degree, residual capacitance

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Introduction. Chemical current sources (CCS) long ago became the basis for the power supply in stand-alone equipment, which performance characteristics significantly depend on the CCS electrical parameters and storage capacity. In recent years, the problem of diagnosing the lithium CCS (LCCS) became of great scientific and practical interest. Lithium-thionyl chloride chemical current source possessing stable discharge characteristic and high specific energy value are of considerable interest in the LCCS line. Voltage value during operation is not depending on their discharge degree and drops sharply at full discharge. Therefore, estimation of their current state is of significant importance from the point of view of a possibility to use these devices in the equipment with high reliability requirements imposed. First of all, such estimation should provide information on the discharge degree of current sources proposed for use. Its determination is especially important in primary (non-rechargeable) current sources.

Scientific research results demonstrated that two methodological approaches are currently used to solve the problem of diagnosing the primary LCCS current state (their discharge degree), and they include: 1) microcalorimetry [1–5] and 2) impedance spectroscopy [6–10].

CCS storage capacity is largely determined by the rate of side chemical processes that lead to consumption of the active substances. As a result of these processes, part of energy contained in the CCS active masses is being converted not into electrical energy, but into thermal energy; i.e., the CCS is self-discharging. Microcalorimetry makes it possible to determine intensity of the CCS thermal radiation, which in turn is proportional to the intensity of side processes and, consequently, to self-discharge rate of the current source. This makes it possible to predict its service life. Disadvantage of this method lies in the fact that it could only be used in laboratory conditions, since its implementation requires using bulky and sensitive equipment.

Impedance spectroscopy is a rather informative and sensitive method of the CCS non-destructive testing in the residual capacitance values range of 0–70 %. Diagnostics of a CCS with low discharge degrees (residual capacitance of 30–100 %) based on the impedance spectroscopy results is not possible, since in this range values of the considered correlates remained unchanged within the measured values range.

To diagnose a CCS in the low discharge degrees range, it is necessary to include results of other independent approaches, in particular, the noise spectroscopy method.

In the general case, noise appears to be random (fluctuation) oscillations of various physical nature characterized by complex temporal and spectral structures that are present in any systems and media. In electrochemical systems, which include CCS, noise is closely related to physical and chemical processes there. Violation of relationships between molecules is accompanied by motion and interaction of the charge carriers, excitation and emission of electromagnetic oscillations that are changing with alteration in the object state, both in the open circuit mode and under load. Exposed to discharge and self-discharge, electrode state and composition is changing, as well as degree of micro- and macroheterogeneity, local or general passivation of the electrodes, which is reflected in the voltage fluctuations. All of this is manifested by the corresponding noise alteration.

At present, noise spectroscopy method is used to study corrosion [11], escape of gas [12], changes in the reagent concentration [13] or in the process kinetics occurring in the electrochemical systems [14, 15].

Including electrochemical noise spectroscopy in consideration was determined by desire to ensure reliability of the CCS diagnostic estimations by increasing the accuracy in determining the discharge degree thereof, which is the most important characteristic of the current source state.

Electro-noise method in determining discharge degree of the $Li/SOCl_2$ system primary batteries was tested in [16–18]. The authors studied the direct current impact on the low-frequency spectral characteristics of the $Li/SOCl_2$ system primary batteries electrochemical noise at various discharge degrees thereof.

Distinctive feature of the method under consideration differing it from that proposed in [16–18] is that measurements to analyze the internal physicochemical processes characterizing the CCS current state do not imply any disturbance of the electrochemical system by the external probing signals, i.e., spectral characteristics of the primary lithium-thionyl chloride CCS electrochemical noise at their various discharge degrees were determined in the no-current state. Such a diagnostic estimation is also decisive at the stage of current sources rejection before their installation in critical units of special equipment, which reliable operation should be ensured in the course of long-term operation in stand-alone and hard-to-reach conditions.

Experimental technique. The developed device [19] was used to measure and register the LCCS noise signals, which took into consideration the need to register low-level signals; these signals level was comparable to the fundamental Johnson noise. High level of the LCCS DC voltage component (more than 3.6 V) significantly suppressing extremely low noise signals (less than ± 1 μV) was also taken into account. In addition to high sensitivity, this device does not require compensation for the noise signal constant component, i.e., influence of noise inevitable, when using any compensator, is eliminated. Alteration in the LCCS open circuit voltage was registered depending on the time, when using the device.

Noise dependence subsequently subjected to mathematical processing is presented in Fig. 1. Special software was developed that implements the Fourier transform and is based on a system of harmonic orthogonal functions according to the algorithm considered in [20].

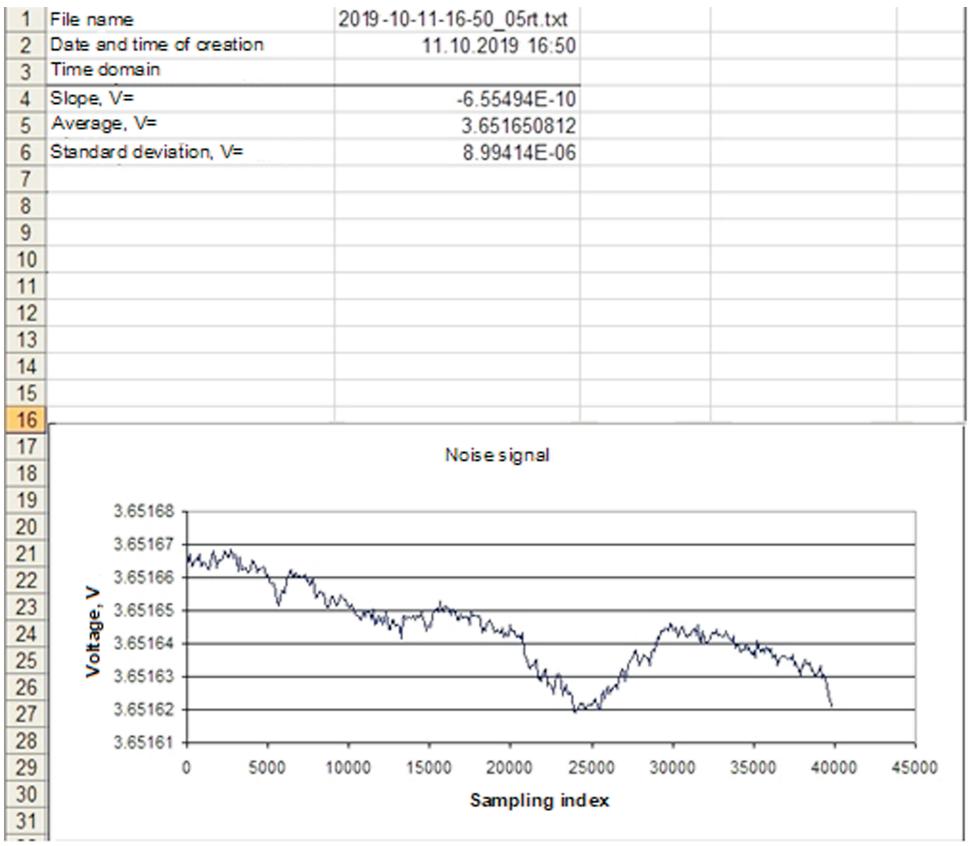

Fig. 1. Results of measuring the CCS noise characteristics

Developed software makes it possible, along with the required functions of setting and measuring the experiment parameters, to construct for each type of CCS a calibration curve, which appears to be a dependence of the informative characteristic on the battery residual capacitance.

Before proceeding to removal of noise characteristics, which are forming the basis to construct a calibration curve for this type of a battery, influence of external destabilizing factors on the noise characteristics was considered, including significant alteration in the ambient temperature, natural electromagnetic and microseismic background. These factors are able to distort, and in some cases block the signal under investigation. It was established that although they are of insignificant effect, but, when measuring noise signals in the LCCS under study in order to exclude their influence on the results obtained, it was necessary to ensure shielding, thermal stabilization and damping of the CCS and the measuring device under investigation.

Results and discussion. Primary LCCS batteries type SL-2780 manufactured by *Tadiran* (Israel) were used as the research objects in this work, a batch consisting of 80 pcs.

Using the proposed method for processing the received noise signal made it possible to identify informative parameters that could be promising to estimate the discharge degree.

Mathematical processing of noise signals (see Fig. 1) made it possible to obtain the averaged dimensional Fourier spectra. According to the spectra in Fig. 2, they meet monotonicity condition in the frequency range of 10–100 Hz. However, monotonicity in dependence of the spectral density on the discharge degree in the low-frequency band (less than 10 Hz) is missing.

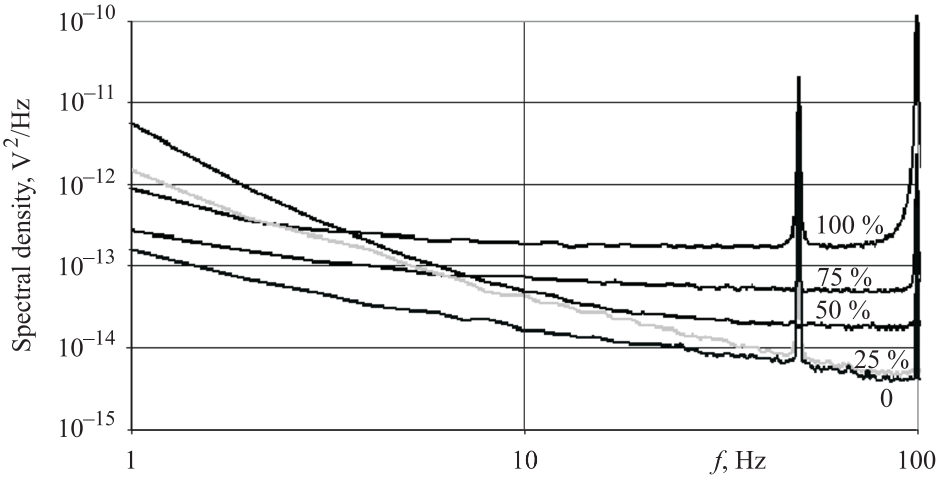

Fig. 2. Average dimensional noise spectra for different LCCS density degree

Monotony is a required prerequisite in estimating the battery current state. Therefore, harmonics of more than 10 Hz were selected as an informative parameter to construct the calibration curve.

Besides, to construct a calibration curve, it was also necessary to take into account the fact that any information on the battery charge level at the initial stage was missing, while the charge level depended both on storage conditions and time, and on production conditions and other technological factors.

This was confirmed by results obtained during the battery discharge indicating that deviations from the nominal capacitance value for individual cells were ± (10–20) %. Therefore, construction of a calibration curve became possible only after the batteries were completely discharged making it possible to attach them to a single point corresponding to the battery charge zero value. Residual capacity intermediate values were determined by discharging a battery with the nominal current; discharge period corresponded to the interest point on the "residual capacitance" axis.

Spectral noise density dependence on the LCCS residual capacitance is shown in Fig. 3. According to the dependence, it is possible to rather accurately determine the battery residual capacitance in the 30–100 % range of values. In the 0–30 % range of values, any noticeable alteration in the informative parameter is missing. Thus, possibility of estimating residual capacitance in primary lithium-thionyl chloride chemical current sources using the method of noise spectroscopy in the domain of their discharge low levels was demonstrated.

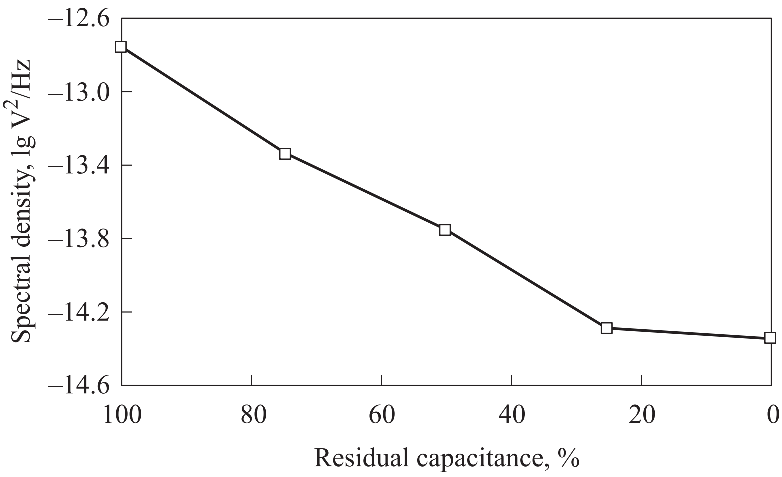

Fig. 3. Spectral noise density dependence on the LCCS residual capacitance

Conclusion. Possibility of using the noise spectroscopy method to estimate residual capacitance of the primary lithium-thionyl chloride chemical current sources in their discharge low degrees domain is presented.

Determination of the LCCS residual capacitance during their operation in the stand-alone mode is of both scientific and practical interest.

Special software was developed that implements the Fourier transform making it possible to construct a calibration curve for each type of a CCS, which actually is the informative characteristic dependence on the battery residual capacitance.

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