RESIDUAL CAPACITANCE ESTIMATION
IN LITHIUM-THIONYL-CHLORIDE CHEMICAL CURRENT SOURCES
USING IMPEDANCE SPECTROSCOPY

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Abstract

Purpose of this work is to elaborate operational and reliable method for ensuring non-destructive control over primary lithium-thionyl-chloride chemical current sources (LCCS) using the impedance spectroscopy. Results and conclusions presented in this work are based on a series of experimental studies. Result reliability was experimentally proven on models and samples with known characteristics. Mathematical apparatus used in processing experimental data using the Fourier transforms allows obtaining information on impedance in a wide frequency range based on results of a single experiment and prompt calculating its main parameters (impedance imaginary value at the hodograph extreme point, its frequency, high-frequency resistance and phase). Ways to reduce the passive film influence, which is appearing on the lithium electrode during storage and operation, on the impedance characteristics are shown. Based on the electrochemical impedance spectra analysis, most informative frequency ranges were determined, and correlates were found connecting the impedance characteristics with the investigated current source state. It is proposed to use the phase angle value measured at the impedance hodograph extreme point as a correlate allowing to estimate the LCCS residual capacitance. It was determined that in assessing the LCCS discharge degree in the range of 0–70 % residual capacity, results of impedance spectroscopy are being quite informative

Introduction. Chemical current sources (CCS) still remain the main power sources used with equipment; therefore, their diagnostics in the autonomous mode is of scientific and practical interest. CCS operational status control

is usually carried out according to the discharge curve. However, this control method could be successfully used only, when the voltage dependence first derivative on the system electric discharge significantly differs from zero. Main advantages of a lithium-thionyl-chloride CCS (LCCS) include: exceptional energy characteristics; low self-discharge; long shelf life; wide operating temperature range. It should be mentioned that due to the missing slope of discharge curve in these cells, conventional control is impossible.

Control methods used today, such as microcalorimetry [1–4], require sophisticated equipment and take a long time, which makes it difficult to introduce them outside the laboratory. Elaboration of methods for predicting the LCCS behavior is rather relevant, in particular, when these devices are rejected before installation in the critical equipment nodes. Based on results of microcalorimetric studies, it is possible to rather correctly predict the current source service life and safety. Disadvantages of this method include long measurement duration and need to use the high sensitivity equipment, since the absolute heat release value for current sources with low self-discharge, i.e., with high storage stability, is very small. In this regard, using these diagnostics is practically impossible, when working in autonomous conditions, for quick and accurate determination of the LCCS state of discharge.

Development of a technique for the LCCS state diagnostics requires the use of other methods, in particular, the impedance spectroscopy.

Information on instantaneous state of the current source as an electrochemical system is provided by an estimate of its total internal resistance, which includes both active and reactive components, and each of them has a well-defined physical meaning. CCS electrochemical impedance spectroscopy [5–9] makes it possible to obtain a large number of parameters under conditions of the online non-destructive testing. Each of these parameters, as well as their functionally related values, could be used as correlates of their state of discharge. This provides possibility to solve an urgent problem associated with ensuring reliable and prompt determination of the CCS state.

Main criterion in estimating any current source performance is the electricity volume provided to ensure regular functioning of the energy-consuming facility. This parameter could be defined as the state of discharge or the source residual capacitance, which is of great importance in regard to primary (non-rechargeable) current sources.

Obviously, such a diagnostics assessment is extremely important at the stage of rejecting the current sources before their installation in critical units of the special equipment, which reliable functioning should be ensured during long-term operation in autonomous and hard-to-reach conditions.

According to results presented in [10–13] and results of studies carried out in this work, using the impedance spectroscopy method appears to be rather promising in solving the problem posed.

Possibility of determining the lithium-ion battery electrochemical impedance spectrum using the digital signal processing methods is described in [13]. However, this method in determining residual capacitance and performance of the lithium-thionyl-chloride cells did not provide sufficiently significant results, since none of the investigated impedance parameters correlates with the state of discharge [14]. The main reason for this lies in the specific feature of this type of elements associated, in particular, with strong oxidizing ability of the thionyl chloride. As a result, the lithium anode is passivated during storage, which leads to result irreproducibility and loss of expected correlation between the element state of discharge and its impedance characteristics. In addition, irreproducibility of the impedance characteristic values could depend on the inevitable LCCS technological parameters spread.

LCCS uses metallic lithium as an anode, and the cathode is made of a chemically inactive material, for example, of graphite or glass carbon. LCCS distinctive feature is the use of liquid oxidants, which include, first of all, the $SOCl_2$ thionyl chloride in aprotic solvents. Lithium in such solutions stays in the semi-passive state as a result of generating protective film on the surface. Electrode self-discharge in this case is minimal even after long term contact between the lithium electrode and the oxidizing agent. Protective film is having sufficient conductivity for lithium ions and does not interfere with lithium anodic dissolution.

In situ impedance measurements providing information about two interphase boundaries (anode and cathode) and electrolyte resistance provide information on the LCCS internal resistance.

Equivalent electrical circuits are used to describe the element impedance, and they include capacitance and resistive cells.

Any electrochemical system impedance consists of electrolyte volume resistance, geometric cell capacitance and electrode impedances. Electrode impedance is determined by redox processes directly on the electrode, charging the double near-electrode layer, diffusion of oxidized and reduced reagents to and from the electrode, as well as by specific adsorption processes on the electrode surface, if the oxidized and reduced reagent flows from the electrode (to the electrode) are not equal to each other.

In case electrochemical reaction occurs on the electrodes, the current could pass across the electrode/electrolyte interface in two ways: 1) due to the Faraday

reduction (oxidation) process; 2) due to charging the double layer. Thus, a parallel *RC*-circuit from the R_F resistor corresponding to the redox reaction active resistance and from the C_d capacitor, which is equivale to the double electric layer capacitance (C_d', R_F' describe the cathode, C_d'', R_F'' describe the anode)

Fig. 1. Equivalent circuit of electrochemical cell with two electrodes

would be present in the equivalent circuit (Fig. 1) of an electrochemical cell with two electrodes along with the R_e, electrolyte active resistance.
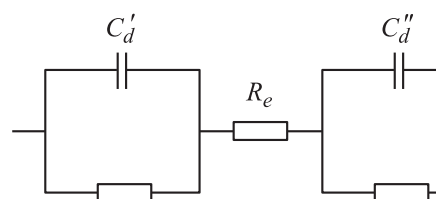
It is impossible to separate impedance components at the anode and at the cathode without special assumptions, one of which states that impedance of a cell with smooth anode and porous cathode is determined primarily by the anode impedance. Porous electrode has the phase boundary low ohmic resistance and large differential capacitance; therefore, its contribution to impedance is insignificant and could be neglected in the first approximation. Then, the equivalent circuit contains only the R_e electrolyte active resistance, the R_F resistance and the C_d lithium anode capacitance.

The equivalent circuit impedance is theoretically calculated according to the rules for calculating the electrical circuit resistance. All mathematical operations are performed according to the rules of operations with complex numbers.

To check reliability of the measuring complex and of the proposed method for processing the resulting *I–t* and *V–t* dependences, control measurements were carried out on the electrical equivalent. Discrete Fourier transform algorithm from the time domain to the frequency domain was used to process data files containing records of changes in the *I* current and in the *E* potential versus *t* time.

Experimental procedure. Experimental part of this work was carried out on an installation based on the EL-02 multifunctional research device[*]. This device is designed to solve fundamental and applied problems in various areas of science and technology, primarily, in electrochemistry. To confirm correct operation of the device and of the proposed method for processing the results, measurements were performed on the electrical equivalent.

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[*] Device was included in the Rosstandard Register and certified to comply with TU 4215-001-11431364–99 standard.

Theoretical dependences compared to impedance values obtained by measurements and subsequent processing according to the proposed methodology for the electrical equivalent are provided in Fig. 2.
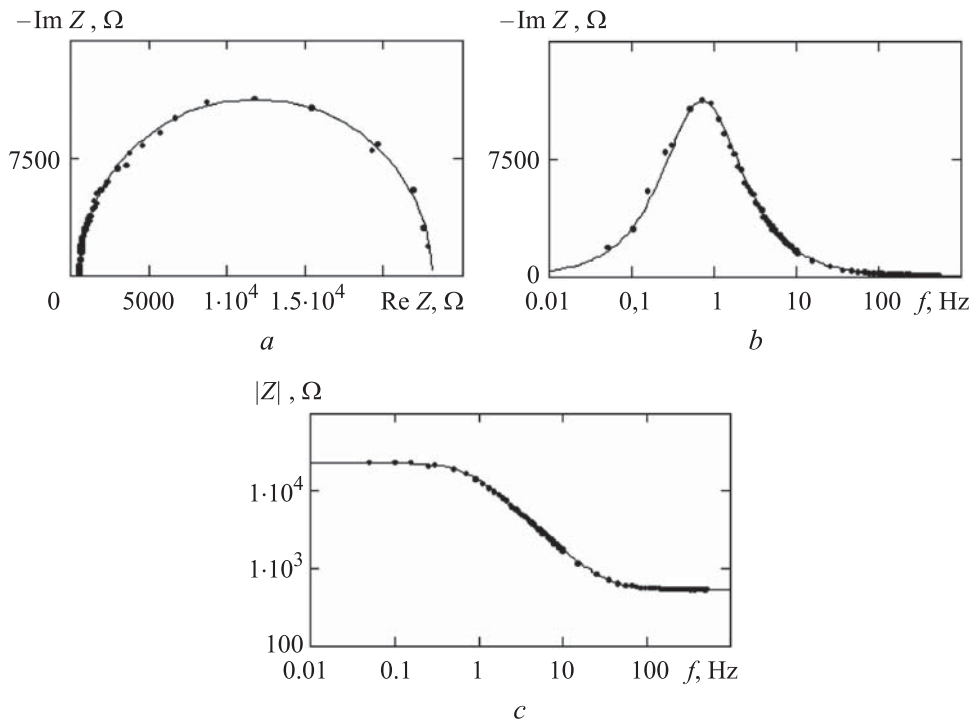

Fig. 2. Results of theoretical calculation and control impedance measurements on the electric equivalent:

a is impedance hodograph (Nyquist diagram) obtained experimentally (points) and theoretically (line) on the electric equivalent; *b* is Bode diagram showing dependence of the impedance imaginary part (–ImZ) obtained experimentally (points) and theoretically (line) on the *f* frequency; *c* is Bode diagram showing dependences of the impedance modulus ($|Z|$) obtained experimentally (points) and theoretically (line) on the *f* frequency

Impedance hodograph (Nyquist diagram) in the complex plane is described by a semicircle shifted along the real axis by the R_e resistance value; and the semicircle diameter is equal to the R_F resistance (Fig. 2 *a*), where the impedance real part is plotted along the abscissa axis, and the imaginary part is plotted along the ordinate axis. Coincidence in the hodographs measured impedance with theoretical values is a required condition. For this condition to be sufficient, frequency dependences of the impedance components should coincide. According to the Bode diagrams (Fig. 2 *b* and *c*), this is really taking place. Thus, control measurements performed indicate reliability of the impedance measurements carried out.

Fourier transform was used according to the algorithm considered in [15] in mathematical processing of the results obtained.

To determine the LCCSs impedance, pulsed method of stepwise alteration in the current passing through them was used with registration of voltage changes over time (galvanostatic mode). In this method, potentiostat in the galvanostat mode is being programmed in such a way that a step disturbance (current) of small amplitude 5 mA is superimposed on the CCS under consideration. This function could be expanded in the Fourier series as a total of sinusoids, where the odd harmonics are not equal to zero. Records of alterations in potential and current transformed in this way are complexly divided. As a result, spectrum of impedance values is obtained at the first, third, fifth and further harmonics (ω, 3ω, 5ω, where $\omega = 2\pi / T$ is the fundamental (first) harmonic and T is the pulse duration). Consequently, measurement range in the high-frequency area is limited by the potentiostat frequency discrete sampling (practically 20–40 kHz), and it is virtually unlimited in the low-frequency area.

Data processing software algorithm uses the *Microsoft Office* package and *Excel* software implemented in the *Visual Basic for Applications* (VBA) environment. The program processes the data file containing records of alterations in the I current and in the E potential over the t time (Fig. 3).

Fig. 3. Current and potential alterations registration over time

As a result of mathematical processing, a file is obtained containing the ReZ and ImZ dependences, as well as the θ phase and the $|Z|$ impedance modulus dependences on the f frequency. Experimental results demonstrated that the most informative correlation dependence is the impedance phase dependence measured at the hodograph on the LCCS state of discharge.

Results and discussion. Primary SL-2780 type LCCSs (manufactured by *Tadiran*) with the 19 Ah capacitance were used as objects of research. Measurements carried out on the LCCS series of 80 pcs. made it possible to propose a calibration curve for this type of elements provided below.

Due to specifics of objects under investigation, measurements were taken in the 1.6–175 MHz frequency range, where processes in LCCS are limited primarily by the diffusion of reagents and reaction products in the interelectrode space and in the porous cathode.
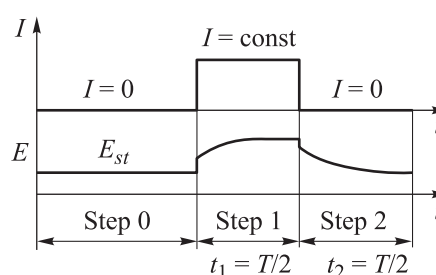
As indicated above, assessment of the LCCS internal resistance is hampered due to the presence of a passive film on the lithium electrode. It is very difficult to ensure reproducible and unaltering state of a passivated lithium electrode during measurements. This is connected not only to technological features of the lithium-thionyl-chloride cell manufacture, but also to the specificity of chemical processes occurring in these cells during their discharge and self-discharge [16].

To minimize the passive film influence on the measurement results, i.e., to ensure that each experiment is carried out under the same conditions, it was proposed to affect the cells with a preliminary galvanostatic pulse before the measurement, and its amplitude was close to the maximum permissible value of the cell discharge current (120 mA), while duration (300 s) guaranteed a decrease in the cell charge during exposure to a value not exceeding 1 % of its nominal capacitance. As a result, the passive film influence on the impedance characteristics of the current sources under investigation should significantly decrease.

To determine the impedance, pulsed method was used of stepwise alteration in the current flowing through the LCCS accompanied by registration of voltage changes over time at the source terminals (galvanostatic mode) with subsequent Fourier transformation of the influencing signal and of the response to it.

The measuring pulse (5 mA) amplitude was set equal to nominal value of the cell discharge current, and duration was selected in such a way to observe the extremum in the low-frequency region on the impedance hodograph.

Amplitude of the second half-period was selected to be equal to zero. Second half-period running time was set equal to running time of the first half-period. Each period was digitized with 4000 points. It was found out that the half-period duration of 300 s was the closest to the optimal value. At shorter values, it was not always possible to obtain information about the extremum of the impedance imaginary part. Increase in the half-period duration led to significant time expenditure and to additional measurement errors.

After the measurement were finished, results were processed in accordance with the method described above to obtain the LCCS frequency characteristics and the corresponding Bode diagrams, as well as the impedance hodographs. Impedance hodographs were constructed during the SL-2780 element discharge (Fig. 4).

According to hodographs presented in Fig. 4, LCCS state of discharge could be estimated by the phase angle value measured at the extreme point of the impedance hodograph. For a cell with the 0 state of discharge, the hodograph is characterized by the θ_1 phase angle. With an increase in the LCCS state

of discharge, the phase angle value decreases from θ_1 to θ_2. Decrease is observed in this area in the impedance imaginary part. At higher degrees of the cell discharge, alterations in the impedance imaginary part are practically not observed. Decrease in the phase angle (from θ_2 to θ_3 and θ_4) occurs due to an increase in the high-frequency resistance.
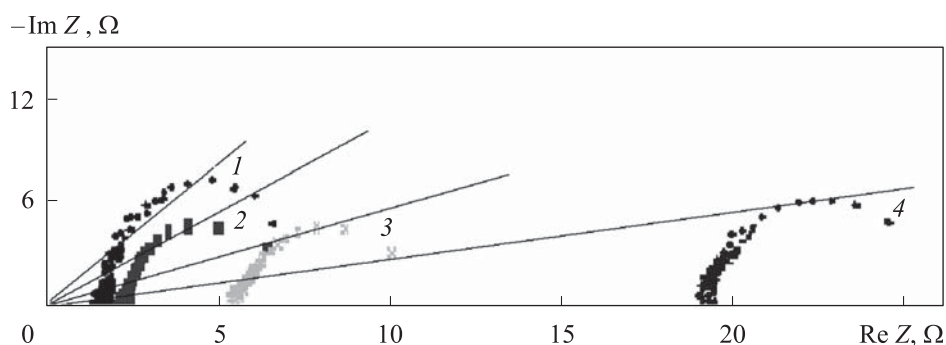
Fig. 4. SL-2780 impedance hodographs obtained during the cell discharge (measurements were taken in the frequency range of 1.6–175 MHz) at 0 (*1*), 50- (*2*), 75- (*3*) and 95 % (*4*) state of discharge

Thus, a conclusion was made on possibility to determine the LCCS state of discharge by the phase angle value measured at the impedance hodograph extreme point. Measurements taken on the LCCS series made it possible to propose a calibration curve for this type of cells, which is presented in Fig. 5.

Phase angle dependence measured at the impedance hodograph extreme point on the LCCS group residual capacitance is shown in Fig. 5. Measuring the phase makes it possible to determine residual capacitance of the sources in the range of

Fig. 5. Phase dependence at the impedance hodograph extreme point on the SL-2780 CCS residual capacitance

0–70 %. It is rather difficult to identify residual capacity in the range of 70–100 % by this method, since noticeable correlate alterations within its absolute value distortion from the average is missing.

Consequently, the impedance spectroscopy method could be used to determine the LCCS residual capacitance at high state of discharge values. In the of low state of discharge values (up to 30 %), this method could be proposed for rejecting an LCCS (incoming control).
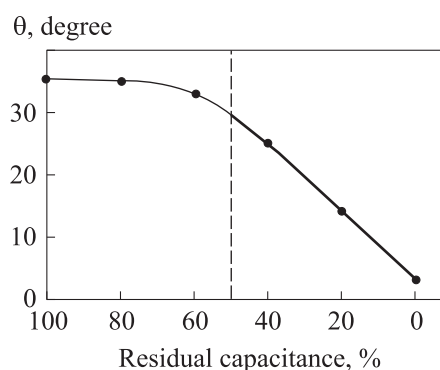
Conclusion. Using the LCCS impedance hodograph phase value at the extreme point as an information parameter makes it possible to estimate the state of discharge in primary LCCSs.

It is indicated that reducing the influence of a passive anode film is required by preliminarily LCCS exposure to a galvanostatic rectangular pulse.

Results obtained are of both practical and scientific interest for determining the state of discharge and predicting the behavior of LCCSs studied in this work. When a LCCS is operating in the autonomous mode, our proposed technique allows saving time and expenditures.

Translated by K. Zykova

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