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ASSESSMENT OF MECHANICAL DAMAGES IN THE PRIMARY Zn–MnO₂ BATTERIES BY ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

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The mechanically destroyed elementary primary Zn–MnO₂ batteries were studied using electrochemical impedance spectroscopy, scanning electron microscopy and elemental analysis of the surface. It has been experimentally proved that the change of the average capacity of the destroyed elements in time is a function of not only the geometry of the surface, but also its component composition. During study the correlation of the photomicrographic images of the electrodes surface with three-dimensional contour diagrams in coordinates: changing of capacitance means value, dispersion of capacitance and frequency was found.

K e y w o r d s: primary batteries, electrodes, mechanical destruction, impedance spectroscopy, capacitance dispersion.

INTRODUCTION. Today the modern methods of electrochemical impedance spectroscopy (EIS) are widely used for measuring and investigation interphase and bulk electrochemical properties of materials and devices based on them [1]. The most well-known method is the construction of equivalent electrochemical circuits with the corresponding set of elements that simulate the behavior of components of the electrochemical system (electrodes, interphase interactions of the electrode and electrolyte, ion diffusion, etc.). But disputes over the interpretation of the elements of these chains, especially of the constant phase element (CPE), are continued [2–6]. It is well known, that a perfectly polarized electrode is an electrode without any RedOx reactions on the surface. According to impedance theory such electrodes are modeled by the element of capacitance [3–6]. The formation of the perfectly polarized electrode is possible only

on the geometrically and atomically homogeneous surfaces such as liquid mercury or single crystals (monocrystal) electrodes. The surface of polycrystalline solids is never completely homogeneous on an atomic level — as a result, energy heterogeneities along the surface are formed. Such lack of homogeneity is reason of the formation of kinks, dislocations, and on a much larger scale corrugation, scratches, pits, grooves, etc. This makes the surface "disordered" from a geometric point of view, so it has two types of geometric irregularities: on the atomic level and level, that is much bigger than 10 nm [7]. Superficial disorders and roughness are interrelated because the mechanically rough surface has a large number of dislocations. Therefore, on polycrystalline solid electrodes (even on smooth ones) the impedance is not purely capacitive. This is connected with such effect as the double electric layer frequency dependent capacitance formation

named as "frequency capacitance dispersion", or simply — a "capacitance dispersion", which depends on the geometry of the surface and its roughness. Thus, the total impedance of the electrode is the sum of the real and complex functions of the resistive and capacitive elements formed in the volume of the solution and on the electrode/electrolyte interphase, respectively, the interfacial capacity become a frequency dependent. Assuming a certain geometry of the electrodes (porous [3–5] or fractal [6]), the CPE element is often used to calculate this capacity. However, according to [7] these calculations were to give inflated results which can not be used for interpreting the actually existing relationship between roughness and the capacitance dispersion. The second physicochemical explanation for the occurrence of the capacitance dispersion is the formation of a double electric layer (DEL) at the electrode/electrolyte boundary with the atomic inhomogeneities due to the specific adsorption of ions. The presence of such adsorption causes the distribution of the activation energy during kinetic processes on the electrode surface [8–10]. The relatively narrow distribution of the activation energy causes a wide distribution of reaction speed constants (or time constants), because they are connected by the exponential relationship. This relationship gives a more pronounced frequency dependence of capacitance [11]. This dependence with combination of Kirgoff's laws makes possible to use the principles of commutation [12–14] for calculation of the impedance spectra of batteries electrodes after changing surface geometry (mechanical destruction). So the purpose of the current study is to obtain regularities between the changing of the capacitance in time, the frequency capacitance dispersion and the degree of mechanical destruction of the electrodes of the primary current sources.

EXPERIMENT AND DISCUSSION OF THE RESULTS. We chose the new commercial alkaline zinc–manganese batteries 6LR61, with a voltage of 9.0 V as the samples under investiga-

tion. Such elements consist of the six primary current sources, which are connected in series by a sequential circuit. Each primary current source has the form of the square tablet and consists of a cathode — the mixtures of MnO_2 (pyrolusite) with graphite (95 %) impregnated with an alkaline electrolyte (mixtures of KOH and NH_4Cl) and an anode — the powder metal zinc (fig. 1).

Fig. 1. Scheme of the elementary element.

According to the design of the elementary battery, the cathode with a current collector (graphite) is inside of the tablet, and the anode is on its surface. Therefore, the level of mechanical destruction should change not only the electrochemical characteristics of a single source, but also the chemical composition of the surface. Thus, the nine-volt batteries are a good system for investigating the effect of mechanical damage on the electrochemical and chemical properties of these energy sources. Mechanical impact on elements with varying degrees of depth and area was made by force using a scalpel. Electrochemical impedance spectra were measured in two electrode cells on an electrochemical module Autolab-30 PGSTAT302N Metrohm Autolab, with FRA (Frequency Response Analyzer) installed in the range of 10^{-3} – 10^6 Hz. Wrecking

electrodes were further impregnated with 1M aqueous solution KCl to ensure good contact during measurements. Control of the FRA module was carried out using the program Autolab 4.9 at an amplitude perturbation signal of ± 5 mV with further processing of the obtained results in the package Zview 2.0. Calculations of the capacity dispersion were performed using impedance spectra in Bode coordinates based on the Zview 2.0 software package, using the formulas:

$$C(\omega) = ([Z(\omega) - Z(\omega \rightarrow \infty)]/\omega), \quad (1)$$

where $C(\omega)$ – dispersion of capacitance; $Z(\omega)$ – impedance data on preset frequency; $Z(\omega \rightarrow \infty)$ – impedance data on high frequency.

$$C = \frac{1}{Z'2\pi f}, \quad (2)$$

C – capacitance data on fixed frequency; Z' – data of real part of impedance; f – frequency.

Photomicrographic images and chemical composition of the surface were obtained by a scanning electron microscope (TESCAN VEGA 3) with Bruker Company software, which is used for determination the local chemical composition and building a “map” of distribution of chemical elements on the electrodes surface. The degree of the surface destruction of the element was calculated by the ratio of the visual area of the destroyed surface (S_d) to the total surface area (S_T):

$$\alpha_d = \frac{S_d}{S_T} \times 100 \%. \quad (3)$$

During comparison of the impedance spectra of elements with different degrees of destruction with their chemical composition and surface photomicrographs were determined that the radii of the semicircles of the spectra correlate with the degree of surface destruction (fig. 2, 3). It was found that the values of the capacitances calculated according to equation 2 are a function of the radius of the semicircle of the impedance spectra (table 1).

Fig. 2. SEM images of the elements surface.

Fig. 3. EIS of the elements in the Nyquist plots, numeration of samples according fig. 2.

Increasing of the capacitance and the degree of the element destruction has an antiparallel character.

The capacitance of samples is increased in following way: № 2 > № 1 > № 4 > № 3, and the degree of destruction is decreased in similar way: № 3 > № 4 > № 1 > № 2. Thus, a decreasing of the value of the capacitance is correlated with an increasing of the degree of destruction of the

Table 1

The degree destruction and the calculated capacitance of the elementary elements

Sample	α_d , %	C, F
1	5	$1.34 \cdot 10^{-5}$
2	7	$1.28 \cdot 10^{-5}$
3	25	$7.46 \cdot 10^{-6}$
4	85	$9.94 \cdot 10^{-6}$

electrode surface. The subsequent studies of the chemical composition of the surface found that the mechanical destruction of the electrodes leads to a change in the Zn : Mn ratio, which had changed the value of the capacitance (table 2). The maximum value of the capacitance is reached at the ratio Zn: Mn = 2:1 and accorded with the minimum destruction of the electrode surface. The minimum capacity is observed in sample № 3, which has the maximum concentration of Manganese on the surface (Zn: Mn = 1:3) and the maximum degree of destruction (fig. 2). That is, the destruction of the electrode surface leads to a change in the ratio of Zinc and Manganese. With strong volume destruction of the sample, the number of Manganese increases significantly. But the anode surface destruction

Table 2

Chemical composition of the samples surface, mas. %

Sample	[Zn]	[Mn]	[C]	Zn:Mn
1	45.29 ±0.01	21.32 ±0.03	33.39 ±0.01	2:1
2	26.66 ±0.01	42.96 ±0.03	30.37 ±0.01	1:2
3	17.46 ±0.01	46.92 ±0.03	35.62 ±0.01	1:3
4	60.76 ±0.01	16.40 ±0.03	22.84 ±0.03	4:1

Fig. 4. SEM images and components "map" of the samples: minimum (a) and maximum (b) of the surface and volume destruction.

has influence, which comparable with volume destruction (sample № 4) (table 1, 2, fig. 4). So, the capacitance is a function not only of the geometry of the surface, but also of its components composition. This gives grounds for its further use as a test parameter for the assessment of the state of art and the degree of destruction of the batteries. It is possible to use a capacitance's dispersion as a second test parameter to account for a certain electrode surface geometry for increasing the self-descriptiveness of the analysis [3–5]. Moreover, the using of only this testing function leads to high errors gaining, which allows it to use only for qualitative evaluation of the electrode surface [7]. Based on the exponential relationship between the impedance value and frequency — dependent capacitance:

$$Z_w = \frac{1}{Y_0(j\omega)^n}, \quad (4)$$

Y_0 — frequency-dependent factor; n — level of frequency dependence. With $n \rightarrow \infty$, the frequency dependence is increased. So, such dependence gives reason to use imaginary part of impedance as a concentrated parameter. It is means, that it is possible to consider the changes in

the AC wavelength from the moment of its occurrence to a certain point in time as function of the impedance of the system in the assign frequency range. Then, based on Kirchhoff's circuit laws, the dependence between changing of the capacitance, current and voltage will be looking as:

$$\frac{du_C}{dt} = \frac{1}{C} (-i_2 + i_1 + J) = \frac{1}{C(-\frac{u_C}{R_2} + i_2 + J)}. \quad (5)$$

To solve this equation at different time intervals we suggesting to use Duhamel's integrals:

for the interval $0 < t < t_1$:

$$u_C(t) = \int_0^t ae^{-a(t-\tau)}u_1(\tau)d\tau; \quad (6)$$

for the interval $t_1 < t < t_2$:

$$u_C(t) = \int_0^{t_1} ae^{-a(t-\tau)}u_1(\tau)d\tau + \Delta u_1 \frac{1}{R} (1 - e^{-a(t-t_1)}) + \int_{t_1}^t ae^{-a(t-\tau)}u_2(\tau)d\tau; \quad (7)$$

for the interval $t > t_2$:

$$u_C(t) = \int_0^{t_1} ae^{-a(t-\tau)}u_1(\tau)d\tau + \Delta u_1 \frac{1}{R} (1 - e^{-a(t-t_1)}) + \int_{t_1}^{t_2} ae^{-a(t-\tau)}u_2(\tau)d\tau - \Delta u_2 \frac{1}{R(ae^{-a(t-t_2)})}. \quad (8)$$

So, if impedance spectra of samples separate into three frequency zones, which satisfied for such mathematical conditions, it has been obtained an integral picture of the sample. Moreover it can be possible to register the surface changes of the destroyed electrodes using this method. For obtaining EIS images the capacitance value and capacitance dispersions calculated in the three frequency ranges: 10^{-3} – 10^1 Hz, 10^2 – 10^4 Hz and 10^4 – 10^6 Hz, after that, the obtained value was used for building contour diagrams in coordinates: capacitance means value, dispersion of capacitance and frequency. So, the obtained picture gives the ability to trace the layer-by-layer change of the electrical parameters of the research objects and to establish the inter-

nal structure of the electrode/electrolyte boundary. That is, according to existing ideas [15], such dependence falls under the signs of a tomogram. Also, the comparison of the obtained diagrams with photomicrographs showed the correlation between them. The general appearance of the obtained diagrams repeated the contours of surface damage (fig. 5). It is fixed a presence of sections with local concentrated deviations from the total distribution of capacity in the specific frequency range in the case of deep damage of the samples on the obtained diagrams.

Moreover, the ratio of the capacitance values (C_0) and the dispersion of the capacitance

Fig. 5. Photomicrographs of samples surfaces (SEM images) and integral diagrams of capacitance changes on their surface (EIS images).

ce (C_d) are correlated with the component composition of the surface of the destroyed samples (table 2, fig. 4, 5). Thus, these diagrams can be used to estimate the type of damage to the electrodes of chemical current sources.

CONCLUSIONS. The results of the current study show that the changes in the capacitance and dispersion of capacitance of destroyed primary Zn–MnO₂ batteries in wide frequency range is a function not only of the geometry of the surface, but also of its chemical composition of the surface. The using of the second frequency-dependent value (dispersion of the capacitance) as a concentrated parameter allowed the application of the principles of the electric current commutation to register the layer-by-layer changes of the destroyed electrodes and obtained a visual picture of the quantitative and qualitative changes of the destroyed samples. The images gained through calculation of the impedance spectra have a strong correlation with SEM images.

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ВИЯВЛЕННЯ МЕХАНІЧНИХ ПОШКОДЖЕНЬ ПЕРВИННИХ Zn–MnO₂ ХІМІЧНИХ ДЖЕРЕЛ СТРУМУ СПЕКТРОСКОПІЄЮ ЕЛЕКТРОХІМІЧНОГО ІМПЕДАНСУ

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Результати проведених досліджень показали, що зміна середньої ємності зруйнованих електродів хімічних джерел струму в часі є функцією не тільки геометрії поверхні, а й її компонентного складу. Максимальне значення середньої

ємності досягається при співвідношенні Zn:Mn = 2:1 та мінімальній зруйнованості поверхні електрода. Мінімальна ємність має максимальну концентрацію марганцю на поверхні (Zn:Mn = 1:3) та максимальний ступінь зруйнованості. Тобто руйнування поверхні електродів приводить до зміни співвідношення цинку та марганцю. При сильному руйнуванні поверхні кількість марганцю значно зростає. Використання другої частотно-залежної величини (дисперсії ємності) в якості зосередженого параметру дозволило застосування принципів комутації електричного струму для реєстрації пошарової зміни ємносних характеристик зруйнованих електродів та отримання наочної картини кількісних та якісних змін, що відбуваються в результаті руйнування. Загальний вигляд отриманих діаграм відтворював контури пошкоджень поверхні. У разі глибоких пошкоджень на діаграмах спостерігається наявність ділянок з концентрованими відхиленнями від загального розподілу в часі показників ємності. Отже, отримана картина дає можливість відстежувати пошарові зміни електричних параметрів об'єктів дослідження та встановлювати внутрішню структуру межі електрода/електроліту. Тобто, згідно з існуючими ідеями, і така залежність підпадає під ознаки томограми. Також порівняння оброблених діаграм з мікрофотографіями показало кореляцію між ними. Загальна характеристика отриманих діаграм повторила контури поверхневого пошкодження. На одержаних діаграмах також фіксується наявність секцій з локальними концентрованими відхиленнями від загального розподілу ємності у конкретному діапазоні частот у разі глибокого пошкодження зразків.

К л ю ч о в і с л о в а : первинні хімічні джерела струму, електроди, механічне руйнування, спектроскопія імпедансу, дисперсія ємності.

ОБНАРУЖЕНИЕ МЕХАНИЧЕСКИХ ПОВРЕЖДЕНИЙ ПЕРВИЧНЫХ Zn–MnO₂ ХИМИЧЕСКИХ ИСТОЧНИКОВ ТОКА СПЕКТРОСКОПИЕЙ ЭЛЕКТРОХИМИЧЕСКОГО ИМПЕДАНСА

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Проведено исследование механически поврежденных электродов первичных химических источников тока с использованием спектроскопии электрохимического импеданса, сканирующей электронной микроскопии и элементного анализа поверхности. Экспериментально доказано, что изменение средней емкости разрушенных электродов во времени является функцией не только геометрии поверхности, но и ее компонентного состава. Найдена корреляция между микрофотографиями поверхности и тройными контурными диаграммами скорости изменения емкости, дисперсии емкости и частоты.

К л ю ч е в ы е с л о в а: первичный химический источник тока, электроды, механическое повреждение, спектроскопия импеданса, дисперсия емкости.

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