INFLUENCE OF A PULSED MAGNETIC FIELD ON THE ELECTRICAL PROPERTIES OF NANOPOWDER SYSTEM BASED ON ZIRCONIA

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Abstract
A technique for studying of electrical characteristics based on electrochemical impedance spectroscopy of sealed nanopowder compact sets from a powder based on ZrO_2 was proposed. The possibility of using this technique for studying of influence of pulsed magnetic field on a charge state of the surface of zirconia nanoparticles is shown. It is established that the action of a weak pulsed magnetic field leads to redistribution of free charge carriers between the volume and the surface of nanoparticles. In particular, different processing times lead to different impedance behaviour: treatment of a pulsed magnetic field with a pulse repetition frequency f = 1 Hz and an exposure time t <15 min leads to an irreversible decrease in the conductivity of the nanoparticle surface by two times (from $3.47 \cdot 10^{-5}$ to $1.72 \cdot 10^{-5}$ $Ohm^{-1} \cdot m^{-1}$), and processing with exposure time 15 <t <90 min leads to its increase by 10 times. Thus, the treatment of PMF causes formation in the near-surface zone of nanoparticles of a region depleted of charge carriers.

Keywords: zirconia, nanopowder, impedance, pulsed magnetic field

1 Introduction

At the present stage of scientific and technological development the methods of electrochemical impedance spectroscopy (EIS), based on the analysis of a response of the system under study to disturbing effects are becoming increasingly important in fundamental and applied physical research. Obtained experimental data can be used to estimate a wide range of electrophysical / electrochemical processes in condensed media with different aggregate phase states [1-6]. The main goal at studying of impedance is obtaining information about near-electrode processes, i.e. processes occurring at the electrode / electrolyte interface [7, 8].

Taking into account the proximity to aggregate state of phases of nanopowder compacts and dispersed nanopowders, there is reason to believe that compacts as EIS objects can also be used to characterize the electrical and physical properties of nanopowders from which they consist [9, 10]. Despite a large number of authentically established macroscopic effects, it is practically impossible to directly detect changes of physical properties of nanoparticles caused by pulsed magnetic field (PMF), even by means of a modern methodological base.

The development of a technique that makes it possible to study the effect of weak pulsed magnetic fields on electrical properties of nanopowder system was the main goal of this work.

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2 Experimental material(s) and methods

As a research object compact sets from nanopowder of composition ZrO_2 + 3mol% Y_2O_3 were used. The technology for obtaining nanopowders contains several technological operations [11]. At first, hydrated zirconium hydroxide was obtained by co-precipitation method from a chloride raw material. After dehydration in a specialized microwave oven (T = 120°C, t = 0.4 h), the amorphous powder was subjected to crystallization annealing at a temperature of 400°C for 2 hours. Then from the powder by uniaxial pressure (P = 40MPa) a samples – compact sets in the form of tablets with a diameter of 20 and a height of the order of 2 mm (m = 1 g) was obtained. After compacting the tablets were sealed with a high hydrostatic pressure (HHP, 500 MPa).
EIS measurements [12] were carried out at room temperature ($T \approx 20^0C$) in automatic mode using a precision virtual meter-analyzer of the impedance parameters type 2B-1 [13]. Frequency range 1 Hz - 1 MHz. Approximation of the model and experimental impedance spectra was carried out using a computer program published on the website of the European Internet Center for Impedance Spectroscopy [14]. Carbon contacts were deposited mechanically on surface of samples.
Unipolar exponentially increasing pulses of the magnetic field with a repetition frequency of 1 Hz were used as PMF (H = 10^5-10^6 A / m) [15]. EIS measurements were carried out directly during the treatment by PMF. Also relaxation processes after PMF influence were investigated.

3 Results

A typical spectrum of impedance of sealed compact sets is shown on **Fig. 1**. Two sections can be clearly distinguished. At the bottom left, in the region of high frequencies, a part of a semicircle with shifted below the abscissa axis centre is located. Further, in the direction of frequency decrease, a rectilinear part in the form of a ray is disposed. Each segment of the hodograph can be analytically approximated by a specific electrical circuit that resonantly interacts with an external electrical signal. Each such element has its own time constant [16]. The high-frequency part of the curve describes processes with a small time constant, low-frequency part with a larger one.

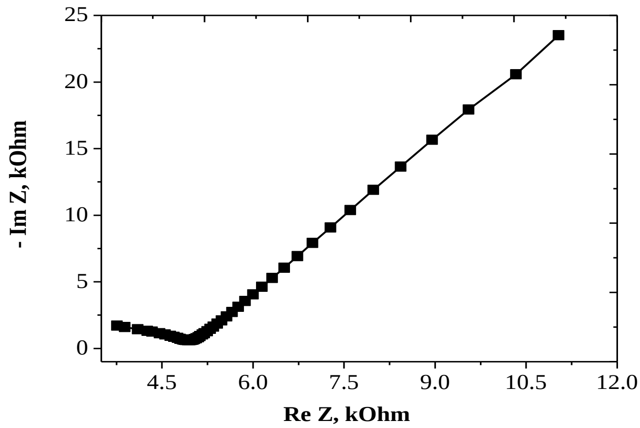

Fig. 1 Impedance spectrum of compact set from the powder ZrO_2 + 3mol% Y_2O_3, 400^0C, 2h, obtained from the chloride raw material

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The segment of the hodograph in the form of a semicircle is interpreted as a parallel RC circuit and characterizes the contribution to impedance of processes associated with electrical polarization of the material. The rectilinear section, as a rule, reflects the contribution of diffusion processes on the surface to the overall impedance of the system [17, 18, 19]. Polarization processes have a smaller time constant than diffusion. It follows that the high-frequency region of the spectrum (semicircle) characterizes the resistance of the nanoparticles volume. The linear low-frequency region of the impedance spectrum in this case probably characterizes the diffusion processes in interparticle space, including particles surface and surface of electrodes.
The equivalent electrical circuit of each layer - the elementary unit - is consists from a resistance and a capacitance connected in parallel with it. The time constant of the layer is determined by the time constant of RC circuit with the given parameters. The resulting two-link model corresponds exactly to Vojta's structure.
The distortion of the shape of the semicircles with the center located below the abscissa on the hodograph indicates that the frequency properties of the samples can not be modeled by an equivalent circuit containing exclusively frequency-dependent elements in the form of capacitors. The experimental hodographs correspond to the Vojt model, in which the frequency-dependent elements (C) are replaced by constant phase elements (CPE) [20]. Equivalent circuit that simulates the above experimental data is shown on **Fig. 2.**

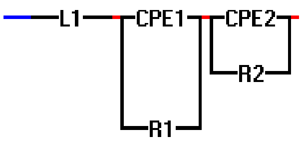

Fig. 2 Equivalent electrical circuit of the investigated object

A good agreement between the model and experimental impedance spectra after approximation by means of a computer program confirmed the validity of choice of the theoretical model. Calculated by means of a computer parameters for calculating the impedance spectrum of a sample are given in **Table 1**.

Table 1 Parameters for calculating the impedance spectrum of a sample

Parameter	Value
R1,Ohm	1.50E+06
R2,Ohm	5.38E+03
P1, F	4.31E-08
n1	0.851
P2,F	1.81E-10
n2	0.848
L1, Hn	9.92E-06

3.1 Determination of volume and interparticle conductivity of sealed compact sets

Taking into account the geometric dimensions of the samples and the previously performed simulation of the impedance parameters of compact set, it is possible to calculate the volumetric σ_v and interparticle σ_b values of specific conductivities by the formulas:

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$$\sigma_v = L / SR_v , \quad (1.)$$

$$\sigma_b = L / SR_b \quad (2.)$$

Where R_v and R_b are the values of volume and surface resistances of nanoparticle, respectively; L is the length of a sample; S is the cross-sectional area of a sample.
The indicated values was $\sigma_v = 9.35 \cdot 10^{-6}$ $Ohm^{-1}m^{-1}$ and $\sigma_b = 1.87 \cdot 10^{-3}$ $Ohm^{-1}m^{-1}$, respectively.
Thus, an analysis of the character of EIS spectra allows us to conclude that in the samples the conductivity is carried out predominantly by the ions of dispersion medium.

3.2 Investigation of influence of a PMF on the electrical properties of nanoparticles

To determine the nature of processes in the volume and on the surface of nanoparticles caused by the influence of a pulsed magnetic field, the time dependences of impedance directly during and after treatment by PMF were studied.
On **Fig. 3** the EIS spectra of samples as a function of the treatment time (**Fig. 3, a**) and after-effect time (**Fig. 3, b**) are shown. Significant differences in the nature of the impedance spectra indicate the possibility of fixing using the EIS technique the processes caused by PMF. This property was used to study the processes of charge transport in the near-surface zone of nanoparticles in the process of PMF treatment in order to identify the corresponding physical kinetic processes in the system.

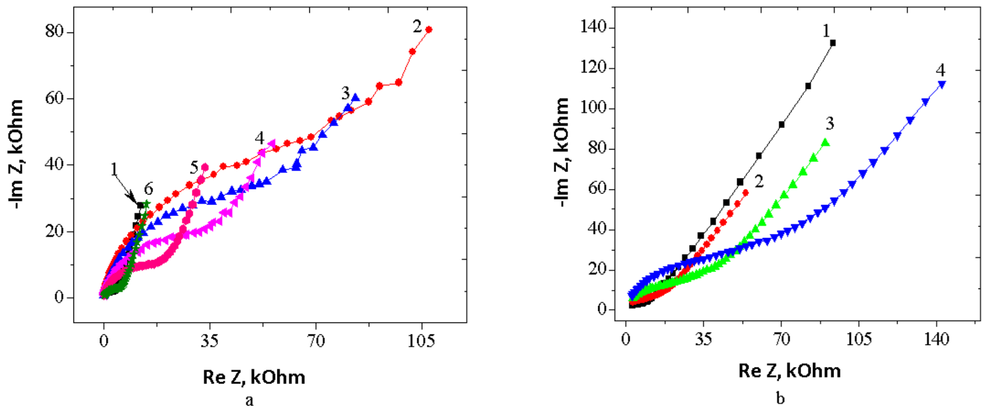

Fig. 3 Influence of PMF treatment on the nature of impedance of samples:
A) in the process of relaxation: 1- before processing; 2 - immediately after treatment; 3 - after 10 min; 4 - after 30 min; 5 - after 60 min;
B) during the treatment: 1- before processing; 2 - after 35 min; 3 - after 65 min; 4 - after 95 min

3.3 Dynamics of the charge state of nanopowder compact sets in the process of PMF treatment

Changes in the shape of the hodograph during PMF treatment are shown on **Fig. 3, a, b**. At first minutes (5-10 minutes) of processing the spectrum is scaled in the direction of decreasing resistance (curve 2 on **Fig. 3, b**). Then the high-frequency part of the hodograph begins to bend

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and pressed against the ordinate axis (curve 3 on **Fig. 3, b**). After 25 minutes of treatment constant current plateau begins to increase; a shelf begins to form, which simultaneously propagates to the low-frequency region of the spectrum (curve 4 on **Fig. 3, b**). At the end of processing slope angle of the plateau to ordinate axis increases, and the shape of mid-frequency part of the spectrum approach the characteristic for the diffusion process.

Thus, we can distinguish three main stages of the process caused by the treatment with a pulsed magnetic field. At the initial stage resistance of the sample decreases (**Fig. 4**, curve 2). Then the dynamics of the process goes to saturation (**Fig. 4**, curve 3), a plateau of constant current conductivity is formed. After this, the resistance begins to increase and the plateau scales into the low frequency region. In this case the impedance increases (**Fig. 4**, curve 4).

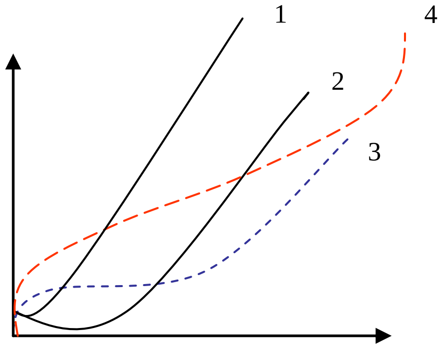

Fig. 4 Schematic diagram, that reflecting the trend to transformation of impedance of samples during PMF processing: 1 - the initial state; 2 after 45 minutes processing; 3 - after 55 minutes processing; 4 - after 95 minutes of treatment

3.4 Hodographs interpretation (The nature of the plateau according to the EIS data)

With the purpose of revealing the nature of frequency-independent plateau β on the example of PMF treatment, we consider model representations that allow us to interpret the shape of the EIS spectra. For the convenience of interpretation, we take the spectrum obtained after the PMF treatment with a frequency of 10 Hz (processing time - 1 h). PMF treatment in the above mode did not lead to such significant changes in the shape of the spectrum as at a frequency f = 1 Hz, but the plateau of constant current conductivity on it is the most pronounced (**Fig. 5**).

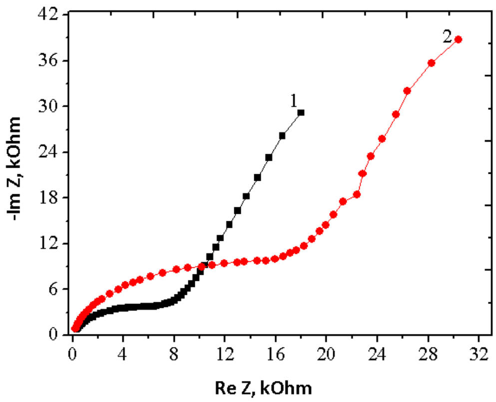

Fig. 5 Typical spectra of the sample: 1 - before processing by a pulsed magnetic field; 2 - after processing by a pulsed magnetic field in the mode: 10 Hz, 1 hour

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3.5 Modelling and spectrum analysis

Calculated using the Kramers-Kronig transform, the parameters for calculating the impedance spectrum of the sample are given in **Table 2**.

For initial state of the sample the conductivity over the volume of the nanoparticles was $\ln\sigma_v$ = -8.97 $Ohm^{-1}m^{-1}$, and the interparticle conductivity was $\ln\sigma_b$ = -14.924 $Ohm^{-1}m^{-1}$. After processing by PMF, these values became $\ln\sigma_v$ = -9.583 $Ohm^{-1}m^{-1}$, $\ln\sigma_b$ = -15.435 $Ohm^{-1}m^{-1}$, respectively.

Table 2 Parameters for calculating the impedance spectrum of a sample after PMF treatment

Parameter	Value
R1,Ohm	77888
R2,Ohm	3.00E+07
P1, F	4.55E-10
n1	0.798
P2,F	5.40E-09
n2	0.791
L1, Hn	2.33E-20

4 Conclusion

1. It was found that the action of pulses of a weak magnetic field causes a change in the charge state of an ensemble of nanoparticles based on zirconia. The relaxation process caused by this influence is accompanied by a change in its electrical conductivity.

2. Impedance spectroscopy measurements has shown that the treatment of a pulsed magnetic field with a pulse repetition frequency f = 1 Hz and an exposure time t <15 min leads to an irreversible decrease in the conductivity of nanoparticles surface by two times (from $3.47 \cdot 10^{-5}$ to $1.72 \cdot 10^{-5}$ $Ohm^{-1} \cdot m^{-1}$), and processing with exposure time 15 <t <90 min leads to its increase by 10 times. On the impedance spectrum this manifests itself in the appearance of a frequency-independent region.

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