

THE EFFECT OF PERCOLATION ELECTRICAL PROPERTIES IN HYDRATED NANOCOMPOSITE SYSTEMS BASED ON POLYMER SODIUM ALGinate WITH A FILLER IN THE FORM NANOPARTICLES $ZrO_2 - 3mol\% Y_2O_3$

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Abstract. Using the methods of liquid deposition the operating laboratory models of humidity sensors with a functional layer based on Alginate biopolymer and $ZrO_2 - 3mol\% Y_2O_3$ nanopowder of particles size 7.5, 12 and 35 nanometers were obtained. Their electrical properties were investigated on a direct current mode under the conditions of dynamic changes of the atmospheric humidity. The threshold of percolation of electric properties of the studied metal-oxide nanostructured systems in the conditions of gas-phase adsorption equilibrium was established. It was shown a possibility of using of the specified nanodimensional systems for the development of non-volatile humidity sensors for the needs of a bionanoelectronics and modern sensory.

Keywords: Nanopowder, humidity sensor, alginate, polymer nanocomposite, heterogeneous physical and chemical processes, adsorption.

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Received: 2 August 2019;

Accepted: 20 October 2019;

Published: 30 December 2019.

1. Introduction

Nanomaterials based on zirconia are of interest for powder nanotechnologies, both in fundamental and in applied aspects because of the combination of its unique physical and chemical properties. In particular, the value of dielectric permittivity, rather high for plain oxides ($\epsilon = 25$) and high chemical activity of the surface, results in broad spectrum of heterogeneous processes during interaction with the atmosphere gases, involving, high-energies (up to 5 - 6eV (Zainullina & Zhukov, 2001)) processes, and localizations on nanoparticles surface of a large number of ions. Therefore, ZrO_2 nanoparticles have potential in a number of the functional applications assuming energy

and material exchange with the external environment, for example, in alternative energy systems (Kammler & Kupfers, 1999; Styrov & Simchenko, 2012).

Reversible adsorption processes on developed surface of nanopowder systems which are accompanied by the change of the charge carriers concentration in the interstitial space can be used in the sensor technologies as unhysteresis gas sensors (Styrov & Tyurin, 2003). Such sensors will favourably differ from semiconductor analogs due to the absence of the need for to desorb adsorbates during the operating cycle, higher response performance and technological effectiveness of productions. Development of such sensors as a perspective alternative to semiconductor sensor elements is extremely relevant at the moment.

However, physical and chemical processes on a surface of a disperse phase of nanopowder sensor systems are studied insufficiently at the moment. Thus, creation and investigation of electrical properties of the ZrO₂-based powder humidity sensors was the aim of this work.

2. Methods and Materials

Planar nanopowder humidity sensors based on hydrophilic biopolymer Alginate (sodium alginate) filled with ZrO₂-3mol% Y₂O₃ were deposited on dielectric substrates with straight gilded electrodes. The distance between electrodes was 1mm, the total area of a reactionary zone 12 mm. Powders were obtained by co-precipitation method using ammonia from chloride solutions of zirconium and yttrium with the following crystallization at temperatures of 400, 600 and 1000°C (Konstantinova *et al.*, 2011) to obtain nanopowders with a size of particles 7.5; 12 and 35 nm, respectively. The nanopowders used in the work are a commercial product. («Nanomaterials Research & Development Sp.Z.O.O», Poland). Nanopowders of 3mol% Y₂O₃ in the ZrO₂ composition were obtained in two stages. First an amorphous hydroxide of the appropriate composition were obtained by co-precipitation method from mix of chloride solutions of zirconium and yttrium using ammonia/ Then the three powder batches was dehydrated in a specialized microwave oven and annealed at a temperature of 400, 600 and 1000°C to obtain crystalline nanopowders with a particles size 7.5; 12 and 35 nm, respectively. The indicated particle sizes are provided by the manufacturer («Nanomaterials Research & Development Sp.Z.O.O», Poland) and are guaranteed by them.

The functional layer of sensors was obtained by spraying on a hot substrate (140°C) of water suspension of polymer Alginate (a weight ratio 1/25), with the nanopowder filler (a weight ratio 1/10).

Electric properties of obtained humidity sensors were investigated using VICTOR-VC9808 multimeter on a direct current in the dynamic mode. Each measurement has been repeated three times. Related humidity was varied 20 ÷ 95%. For humidity measurement the CENTER 311 RS232 Meter was used. The thickness of a functional film were determined by the optical Contour GT profilometer. Optical microscopy was carried out by using Digital Microscope Electronic Magnifier. SEM measurements of samples was conducted on the TM-3000 (HITACHI) scanning electron microscope. The X-ray diffraction analysis was carried out using the Empyrean (PANalytical) diffractometer. Mass fractions of humidity in samples under various conditions of saturation were measured using CPA225D (Sartorius) gravimetric balances on powder hinge plates of 1 g.

3. Results and discussion

3.1 Structure of materials

The nanopowders used for production of sensors in accordance with the X-ray diffraction data presented on Fig. 1 have a tetragonal crystal syngony (a class of symmetry $P4_2/nmc$). It is possible to observe the proportional dependence of integrated intensity and inversely proportional dependence of half-width of peaks on powders crystallization temperature caused by a size effect.

Polymer Alginate (Sodium alginate) powder is an amorphous substance. In general, all powders have almost identical structure and a particle size can be considered as the key target parameter of obtained samples of models of sensors.

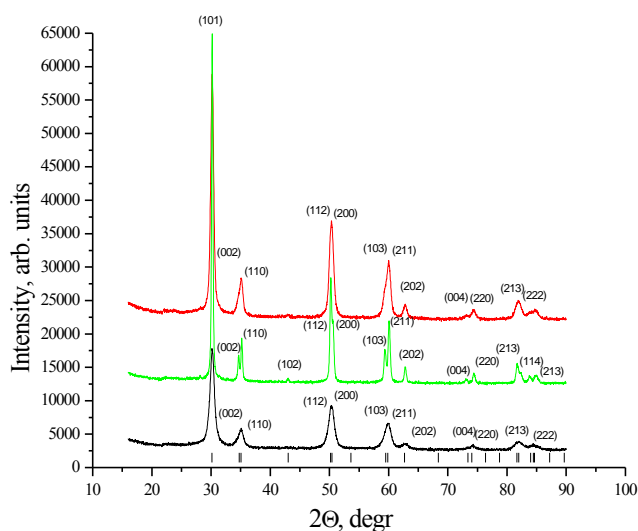


Fig.1. X-ray patterns of $ZrO_2 - 3mol\% Y_2O_3$, powders with a size of particles of 7,5 nm(a), 12 nm (b) and 35 nm (c)

3.2. Microstructure and morphology of a functional layer

Fig. 2. shows surface of deposited sensors. As can be seen, suspension on the basis of nanopowders with a particles size of 7.5 nanometers (Fig. 2, a) forms the most dense layer with good adhesion to electrodes. Such behavior of a nanopowder system is probably caused by the high specific surface area and, as a result - chemical activity of nanoparticles. Suspension on the basis of powder with a particles size of about 12 nanometers (Fig. 2, b) has bad adhesion both to electrodes, and substrate (glass fiber plastic) that can happened due to specific superficial active cites and, as a consequence of the functional condition of the nanopowder system (Doroshkevich *et al.*, 2006, 2008). Nevertheless, it can be seen, enough blinded areas in electrode space.

Suspension with particles size of 35 nanometers forms the thinnest layer (Fig. 2, c), that, is caused obviously, by higher bulk density of this nanopowder type.

SEM - images of the samples surface are shown on Fig. 3. As can be seen the functional layer has an appearance of rather uniform porous structure with the developed relief. Also, it is observed the densest film structure for the sample made with nanoparticles size of 7.5 nanometers, while the most friable for the sample with nanoparticles of size 35 nm. The film made with nanoparticles of about 12 nanometers

consists of the largest agglomerates. It is possible to assume that the difference in morphology of the films obtained from suspensions with various particles size is caused by different charging conditions and chemical activity of nanoparticles (Doroshkevich *et al.*, 2008).

It is visible an extensive network of rather large (about 1 micron) pores network. Thus, water easily gets into the volume of a functional layer.

3.3 Electrical properties

The results of investigation of electric properties of obtained sensors under direct current mode are shown on Fig. 4. In case of 7.5 nm – powder dependence of resistance with humidity have an appearance, close to the exponential law.

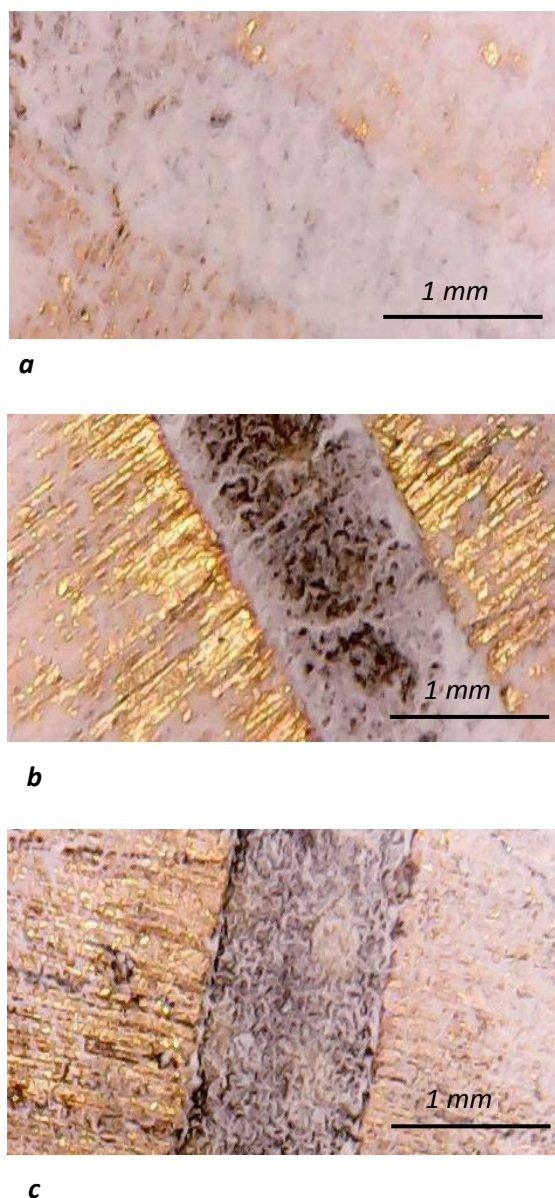


Fig. 2. Images of sensors with $ZrO_2-Y_2O_{3m}$ particles size of 7.5 nm (a), 12 nm (b) and 35 nm (c).
1 - gold electrode,
2 - functional layer.

Direct and return curves of dependence (Fig. 4, a - b) do not coincide with the variation of humidity at $\eta = 35 - 60$ and $65 - 85\%$ respectively, i.e., the hysteresis is most probably caused by nonzero energy of the water molecules desorption (Doroshkevich *et al.*, 2015).

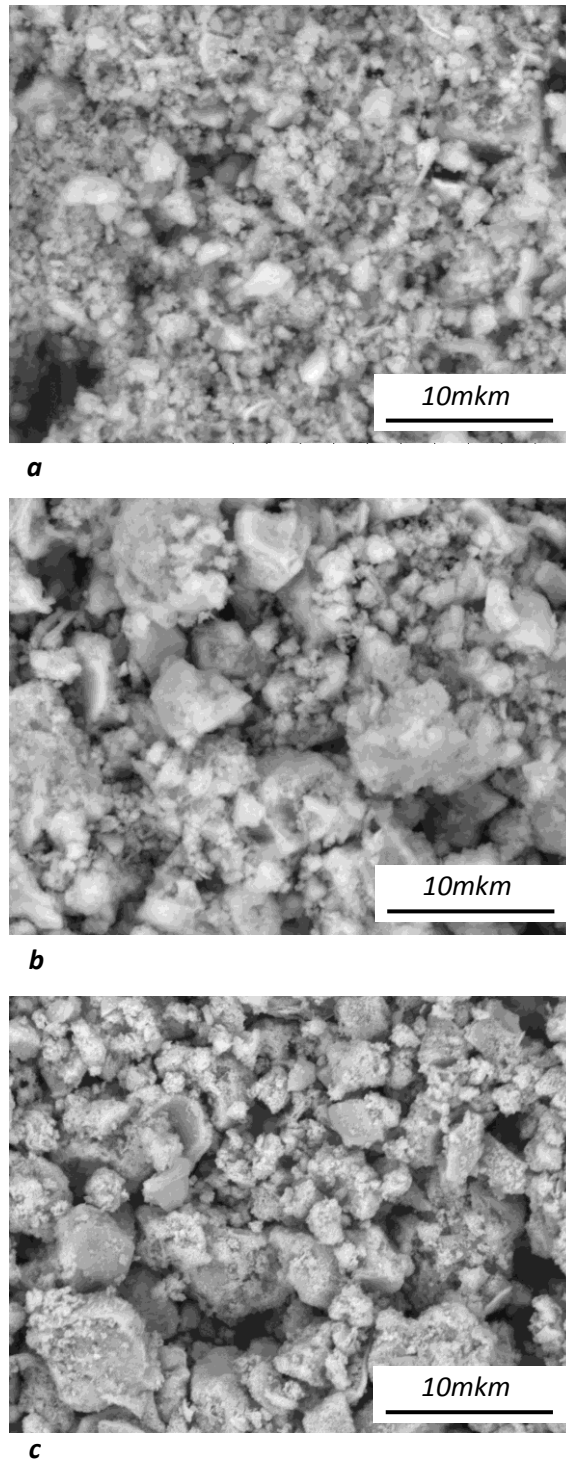


Fig. 3. A typical SEM images of the surface microstructure of the humidity sensors made using powders with different nanoparticles size of 7.5 nm (a), 12 nm (b) and 35 nm (c)

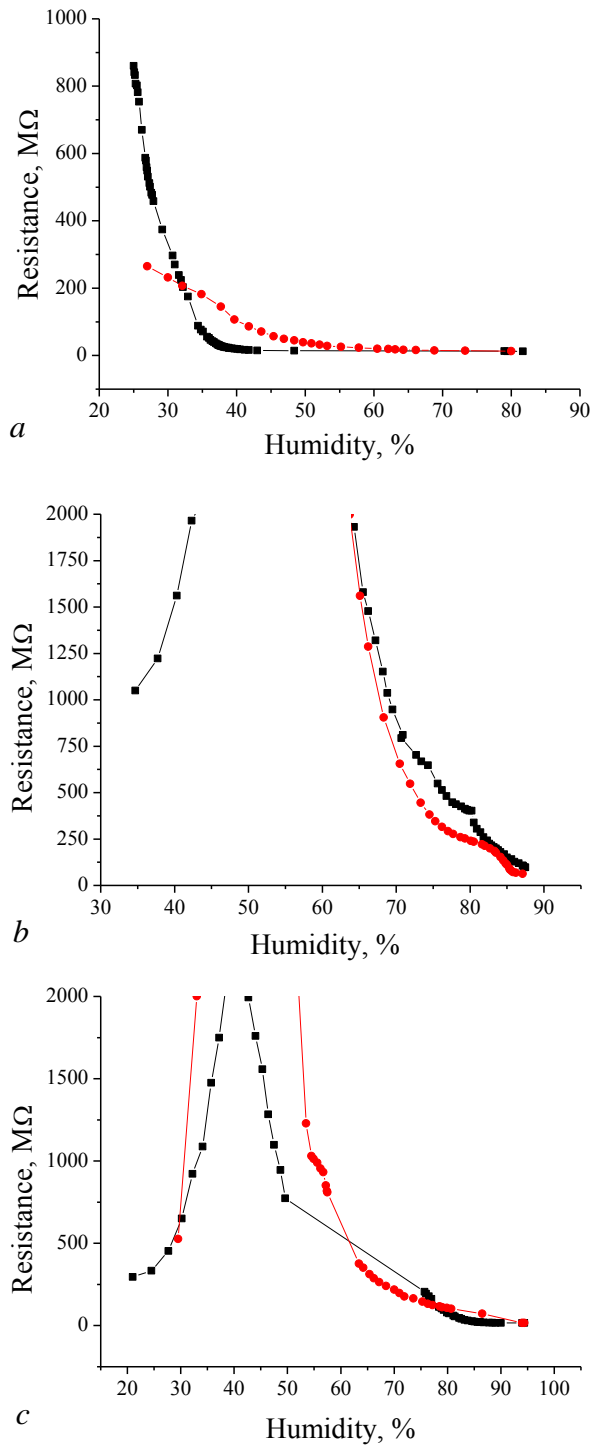


Fig. 4. Variation of resistance the sensors layouts made from powders with a size of 7.5 nm (a), 12 nm (b), 35 nm (s) on atmospheric humidity. Black line dependence of sample resistance on humidity when humidity changes upwards, red line– dependence of sample resistance on humidity when humidity changes in the direction of decrease

Nevertheless, taking into account the dynamic nature of change of atmospheric humidity and especially qualitative nature of the experiment, it is possible to conclude that not optimized laboratory model of the sensor of humidity without application of external temperature influences is reverts to the initial state (Fig. 4).

That confirms our findings on possibility of development on the basis of the nanopowder systems non-volatile sensors of humidity. Reversibility of the state at cyclic changing of the environment is important property for sensory materials.

Fig. 4 shows two curves of resistance to humidity. The black curve is obtained by increasing humidity in the system. Red is obtained by dropping the humidity readings in the system. Thus, these curves show the presence of hysteresis. The presence of hysteresis is a characteristic phenomenon for all sensory systems. The nature of hysteresis in this system requires a separate consideration. Apparently, from Fig. 4, the test nanopowder systems, with particles size of 7.5 nm have the highest sensitivity in the range of small concentration of water vapors (humidity less than 30%) whereas systems based on powders with a particles size of 12 nm have higher value of resistance and the extreme nature of dependence of conductivity on external humidity.

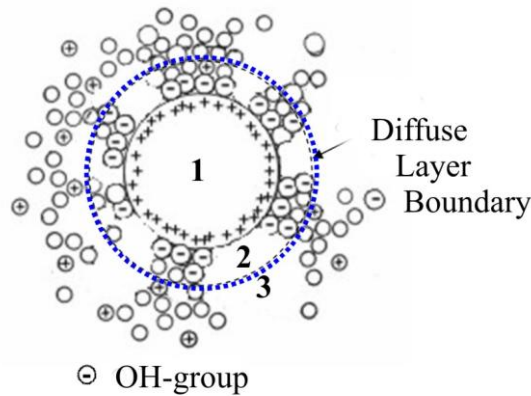


Fig.5. The schematic representation of nanoparticle $ZrO_2 \cdot 3mol\% Y_2O_3$ (1) surrounded with the ionic atmosphere including adsorptive (2) and diffusion (3) layers.

The threshold of percolation is observed for nanopowder systems with a particles size of 12nanometres at relative humidity range $\eta = 45 - 60\%$, and for systems with a particles size of 35 nm at relative humidity range $\eta = 38 - 42\%$. The percolation behavior of electric properties, for sensors based on ZrO_2 - nanopowders obtained by annealing at 600 and 1000°C with high probability is a consequence of insular nature of distribution of hydrate covers of nanoparticles size more than 12 nm. That indicates the dimensional nature of the conductivity effect of the studied nanopowder systems.

3.4. Structure of reaction zone

The particle of disperse phase together with DEL (double electric layer) forms so called micelle (Fig. 5). The unit of substance $\{m \cdot [ZrO_2]\}$ with potential-forming ions, (mainly OH^- for $ZrO_2 \cdot 3mol\% \cdot Y_2O_3$ (Blumenthal, 1958, Lisichkin, 1996) forms the core of such a micelle $\{m \cdot [ZrO_2] \cdot n \cdot OH\}$.

Potential-forming ions are linked to the surface through ($E > 0.3eV$) chemical bonds. According to (Strekalovsky, 1987), the adsorptive layer can be presented in the form of bridged hydroxyls with the "socialized" oxygen where oxygen atoms formally

trivalent as for surface of $\text{Al}_2\text{O}_3\text{-SiO}_2$ (Patrilyak, 2001), however, are not assigned to concrete cations, but migrate abruptly along the surface of the nanoparticles. The diffusion layer (Fig. 5) is linked to micelle core physically by electrostatic interaction forces and consists generally of protons H^+ and polarized water molecules. Diffusion layer is the receiver of molecules from the external atmosphere and it provides the electric continuity of properties of a system by means of the "relay" mechanism or the Grotusmechanism (Markovitch & Agmon, 2007). The hydrate layer between atoms contains hydrogen bonds due to which an ionic exchange between particles (Fig. 6) is provided.

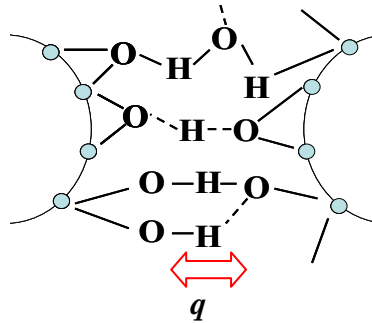


Fig. 6. Schematic representation of the closed hydrate layer covered nanoparticles, as the continuous environment for charges transportation.

The adsorbates on a surface of ZrO_2 are in thermodynamic balance with atmosphere (Okamoto, 2008). Therefore, when equilibrium shifts due to change of external conditions the charge state of a near-surface layer of micelle undergoes changes. Due to the specific coordination of surface atoms the coefficient of ions surface diffusion on a surface of nanoparticles D_r can be more than 10 orders of magnitude higher the corresponding coefficient of ions diffusion in volume of the objects D (Gladkikh *et al.*, 2004). Therefore, processes of charge transfer in nanoscaled substances proceed almost in real time. It is possible to reveal density of a hydroxyl cover of nanoparticles from the content of adsorbed moisture Δm and the value of specific surface area of the system S_{BET} (Tab. 1). This means the area measured by the BET-Brunauer - Emmet - Teller method

Apparently from Tab. 1, for nanopowder of 7.5, the size of specific surface area of the S_{BET} system = $113.8 \pm 6.8 \text{ m}^2 / \text{g}$. (Blumenthal, 1958). At 35% of relative humidity value and pressure of 760 mmHg the sample of mass $m_s = 1 \text{ g}$ adsorb $\Delta m = 0.032 \text{ g}$ of moisture, or 3.2% of specific amount of moisture.

Molar weight of OH^- groups is: $M_{\text{OH}} = 17 \text{ g/mol}$. Number of moles of water in a sample: $N_{3.2} = m_{\text{H}_2\text{O}} / M_{\text{OH}} = 0.032 / 17 = 0.0019 \text{ mol}$, quantity of OH^- molecules: $N_{m3.2} = N_A \cdot N_{3.2} = 1,14 \cdot 10^{21}$ units, where $N_A = 6,02 \cdot 10^{23} \text{ mol}^{-1}$ is Avogadro's number.

The contact area of OH^- groups according to (Keltsev, 1976; Tarasevich & Malyshev, 2008) is $S_{\text{OH}} = 10.2 \text{ \AA} = 10.2 \cdot 10^{-20} \text{ m}^2$. Thus, the total area occupied by the molecules is $S_{\text{OHsum}} = S_{\text{OH}} \cdot N_m = 10.2 \cdot 10^{-20} \text{ m}^2 \cdot 1,14 \cdot 10^{21} = 116 \text{ m}^2$. Therefore, under normal conditions the surface filled at a size $k = (S_{\text{OHsum}} / S_{\text{BET}}) \cdot 100\% = (116 / 113.8) \cdot 100\% = 101\%$.

So, we can assume that quasimolecules of water are located in the form of a monolayer on a surface of nanoparticles and can move freely in volume of the functional environment by means of superficial diffusion even at low humidity, i.e. percolation of electric properties in the studied range of humidity is not observed. Another situation is observed for sensors made using nanopowder of bigger sizes (12 - 35nm). Apparently from Tab. 1 these powders hardly reach 50% of surface filling most probably due to passivation of the adsorption sites by higher temperature processing. Existence of local ruptures of a continuous hydrate cover leads to emergence of spatial restrictions of ionic diffusion and hence to loss of its electric continuity decreasing conductivity of the environment. Apparently from Tab. 1 and Fig.4, when filling of the surface of nanoparticle is less than 30% the threshold of percolation of electric properties occurs and system from ionic conductor passes into a dielectric.

Table 1. The parameters of the hydrate layer of nanoparticles

Size of particles, nm	7.5	12	35
S_{BET} (m ² /g)	113	60	30
Filling of a surface, at $\eta = 20\%$ (%)	26	50	32
Filling of a surface, at $\eta = 35\%$ (%)	54	73	35
Filling of a surface, at $\eta = 50\%$ (%)	123	91	37
Filling of a surface, at $\eta = 75\%$ (%)	210	150	40
Filling of a surface, at $\eta = 95\%$ (%)	271	171	44

The curves on Fig.4b and c, indicate existence of a point of singularity on the physical and chemical diagram of the studied dispersed systems. Emergence of this point is obviously caused by change of the mechanism of charge- and mass-transfer with variation of extent hydration of the system. In particular, emergence of effect of conductivity in the field of concentration of moisture below a threshold of percolation can be caused by emergence of electronic conductivity between nearly placed nanoparticles as a result of interphase issue of the electrons localized spatially in near-surface area (Tamm's Levels (Tamm, 1933; Shockley, 1939) at emergence of phase contacts as a result of a desorption of the moisture forming an interphase hydrate layer.

4. Conclusion

1. A set of the operating laboratory models of nanopowder sensors of humidity based on monodispersed powders of $\text{ZrO}_2 - 3\text{mol}\% \text{Y}_2\text{O}_3$ with particle sizes of 7.5, 12 and 35 nm, was obtained.
2. Existence of hysteresis on dependences of resistance from humidity in the range of a relative humidity values $\eta = 35 - 60\%$ and $65 - 85\%$ for systems based on nanoparticles size of 7.5 and 12 nm respectively was observed. Also, the presence of a threshold of percolation of electrical properties for nanopowder systems with a particle size over 12 nm in the relative humidity range $\eta = 38 - 60\%$ were established.

3. The dependence of degree of a covering of a nanoparticles surface by water molecules from atmosphere humidity and particle size were made. The emergence of a threshold of electrical properties percolation for nanopowder system is caused by formation of incoherent areas in a hydrate cover complicating the diffusion charge transfer was established.
4. Existence of conductivity of the studied nanopowder systems at extent of moistening when charge transfer by means of diffusion of ions is extremely complicated was established. The assumption regarding an electron nature of electric conductance in the field of values of humidity which nature is connected with a size effect of interphase electron emission was made.
5. The conclusion concerning the possibility to overcome the basic fundamental restrictions of traditional constructions of gas sensors on energy consumption value, operating frequency and sensitivity by means of use of nanodimensional metal-oxide systems was made. Moreover, obtained devices are fully biocompatible.

Acknowledgements. The work was supported through the project H2020/MSCA/RISE/HUNTER/691010 and RO-JINR Project No. 395/27.05.2019 item 19, 20.

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