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Laboratory of Neutron Physics named after I.M. Frank

FINAL REPORT ON THE SUMMER STUDENT PROGRAM

Research of technological features of obtaining chemo-electronic converters

Supervisor:
A.S. Doroshkevich

Student:
Oksana Poliakova, Ukrain,
Donetsk Public institution
"L.M. Litvinenko Institute of Physical Organic and Coal Chemistry"

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Abstract

The sharp increase in the growth of energy consumption over the past decades has led to the depletion of traditional energy resources, which has given impetus for the search for new renewable energy sources. In this aspect, one of the urgent tasks of our time is the development of promising areas of alternative energy. In addition to hydropower (mechanical energy from the flow of rivers and oceans), wind or solar energy (electrical, thermal), methods of obtaining energy from the external environment / thermostat are of particular interest [1, 2]. Thus, adsorption energy represents a new promising direction of alternative energy. In this regard, the adsorption of atmospheric moisture, as a potential channel for extracting energy from the environment by objects of residential and industrial infrastructure of a person, is of scientific and practical interest for alternative energy. One of the new alternative methods for generating electricity is the exothermic heterogeneous electrochemical conversion of energy into electrical one due to the interaction of a nanopowder system based on ZrO_2 with atmospheric humidity. In this work it was developed on the base of ZrO_2 + 3mol% Y_2O_3 (YSZ) nanopowders an experimental series of samples of nanopowder convectors of the energy of chemical adsorption of atmospheric moisture molecules into an electric current has been obtained. The time dependences of the voltage of the chemoconverter on the concentration and conditions of obtaining the working layer have been studied.

1. Introduction

Water is one of the most frequently and traditionally used source of electricity by mankind. In its liquid state, water is used to convert electricity from an external thermostat by means of hydroelectric power plants. Until recently, it was considered that direct conversion of gaseous water (atmospheric humidity) into electrical energy was not feasible. It was assumed that in the process of exothermic chemical interaction of the surface of a solid with gas molecules from the outside, the excess energy is transformed into heat due to the significant difference in the masses of the electron and molecules – adsorbates. Only at the end of the 20th century it turned out to scientifically justify and practically realized the idea of creating a "chemo-electronic" electricity generator based on a semiconductor 2 D – heterojunction. Hydro – electricity converters are currently being developed [1, 2], as a rule, includes intermediate energy forms, which leads to relatively low efficiency. The prospect of further applications of such devices, due to extremely low energy efficiency, has not been determined at the moment.

The development of nanotechnology has opened up prospects for the creation of adsorption chemoelectronic converters with a reasonable efficiency. In this regard nanopowder system based on zirconium dioxide (ZrO_2) is a promising functional medium for hydroelectric direct converters [1]. This statement follows from thermodynamic considerations.

It is known that the surface of nanodispersed oxide systems, in contrast to the surface of bulk bodies, is in a state of dynamic charge and adsorption equilibrium. Considering that the adsorption shell of nanoparticles consists of ions, a change in the material balance should be accompanied by a change in the total charge of the system. Considering the exothermic nature of adsorption, saturation of the dispersed system with moisture should be accompanied by the release of energy, including electrical energy. The reverse loop should return the system to its original state. Therefore, in a cyclic mode in a transient nonequilibrium state, a nanopowder system can theoretically convert the chemical energy of adsorption of water molecules into an electrical form [1-4]. As a possible physical mechanism of charge separation in the system, the phenomenon of injection of hot electrons in the course of a high-energy (energy more than 4-5 eV) heterogeneous catalytic chemical reaction can be considered [5].

In the general case, the phenomenon of conversion of the energy of heterogeneous exothermic chemical reactions into an electrical form is called "chemo-conversion", and the generated EMF-chemo-EMF (the prefix chemo emphasizes the non-thermal nature of the phenomenon) [6-9]. This method of converting chemical energy into electrical form occurs directly, bypassing intermediate stages. However, it remains unclear in which act of the physicochemical process a free electron is formed.

Within the framework of the international project "HUNTER" within the framework of the European program "Horizon 2020", an attempt was made to practically implement a converter of the energy of water molecules adsorption into an electrical form with direct conversion type based on nanosized ZrO_2 particles. On the base of the high chemical activity of the surface of porous objects based on YSZ nanoparticles, their polymorphism (specific structural β - α transition of the adsorption type), and new physical principles for constructing the functional cell of the converter, resulting from the size effects, it was possible to successfully solve the problem. At this stage, experimental samples of chemovoltaic converters have been obtained, however, the problem of optimizing the technology of their production and unification of performance characteristics remains unsolved.

Investigation of the technological features of obtaining chemo-electronic converters based on the nanopowder system ZrO_2 + 3mol% Y_2O_3 and the development of recommendations for optimizing the technology of their production was the purpose of this work.

2. Materials and methods

To obtain a series of chemo-electronic converters, polymeric glass-textile substrates with gold-plated electrodes were used. Powders of stabilized zirconium dioxide ZrO_2 + 3mol% Y_2O_3 were used as the functional material. The functional layer was applied by the drip method from the liquid phase. The suspension was consisted of PVA polymer dissolved in water and YSZ nanopowder. The ratio of solid and liquid phases were varied. Three different compositions: 1 g to 250 mg (composition № 1), 2 g to 250 mg (composition № 2) and 3 g to 250 mg (composition № 3) were made. The average size of YSZ particles was about 7.5 nm (Fig. 1). The powder was obtained by co-precipitation of zirconium and yttrium chlorides with ammonia with drying in a specialized microwave oven (T = 120°C, t

= 0.4 h) and subsequent crystallization annealing of the insoluble precipitate at 400°C for 2 h.

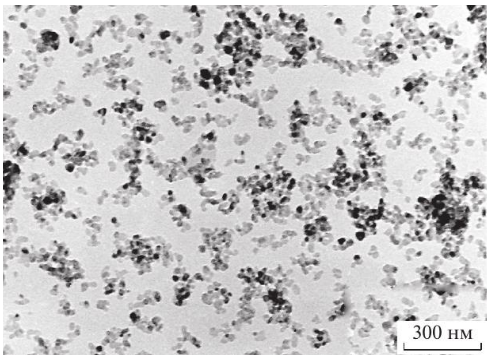
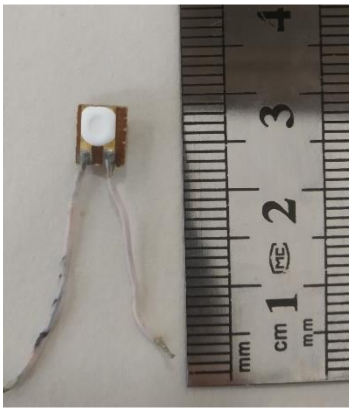


Fig. 1. TEM image of ZrO_2 – Y_2O_3 nanopowder (3 mol%) annealed at 400°C for 2 h

An aqueous solution of a polymer based on PVA was obtained by dissolving the polymer component with constant stirring on a ULAB® US-1500S or TAGLER MM-135H magnetic stirrer for 4 hours at room temperature until complete dissolution. Then, with continuous stirring, a weighed portion of the powder was added, and stirring was continued for 4 hours until a homogeneous mixture was obtained (Fig. 2a). The resulting suspension was applied to a substrate and left in air until complete drying (Fig. 2b).

a



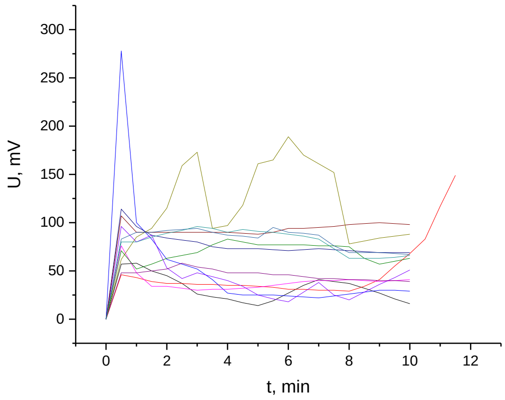
b

Fig. 2. Obtaining a test sample: a – obtaining a working area; b – laboratory model of a chemoconverter

The dependence of the voltage of a chemoelectronic converter based on PVA with a working layer in the form of YSZ of various concentrations in Fig. 3.

3. Experiment Results

3.1. Influence of the concentration of nanopowder in the composition of the functional layer on the efficiency and period of operation of hydroelectric converters.



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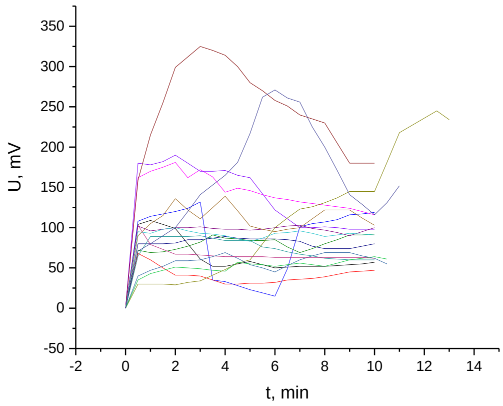

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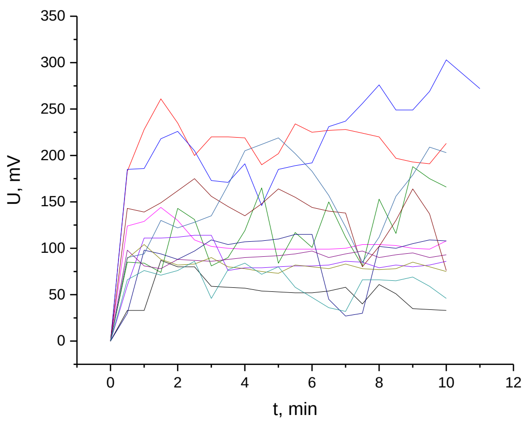

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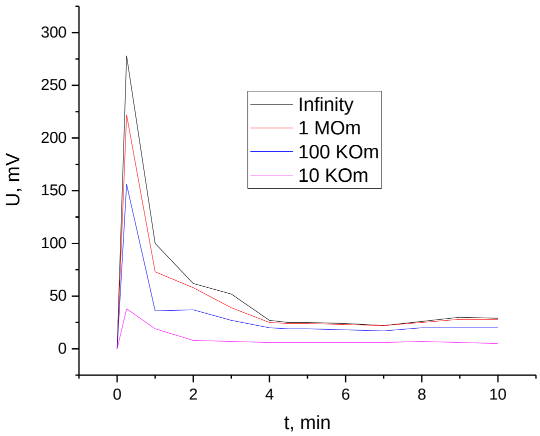
Fig. 3. Time dependences of the voltage of the chemo converter at maximum humidity and different concentrations of YSZ with PVA polymer binder:
a – composition № 1; b – composition № 2; c – composition № 3

As can be seen from the graphs, an increase in the concentration of nanopowder in the composition of the functional layer from 1 to 2-3 g / 250 mg leads to an increase in the average EMF voltage of the working cells from 100 to 200 mV. The maximum voltage of 325 mV was reached in chemo converters with a working layer of composition № 2, while in composition № 1 and № 3 the maximum voltage reached 278 mV and 303 mV, respectively (Fig. 4). It should be noted that at the concentration of YSZ and polymer of composition № 3, deformation and peeling of the working layer from the substrate occurs, presumably as a result of polymerization hardening.



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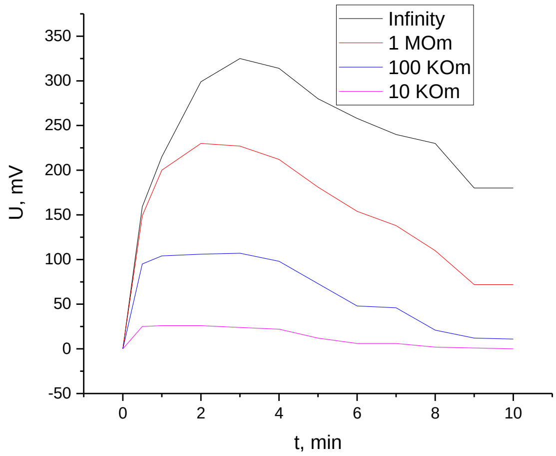

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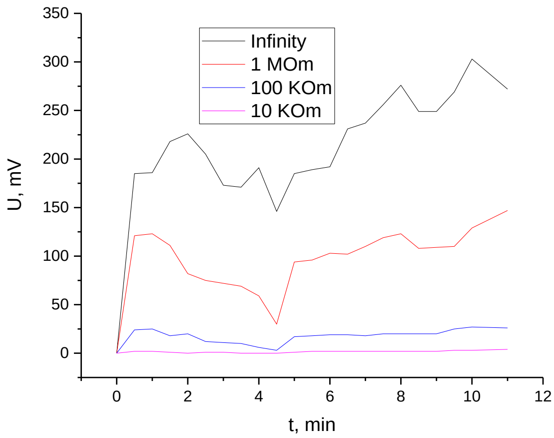

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Fig. 4. Maximum voltage in chemo convectors with working layer of different concentration: a – composition № 1, b – composition № 2, c – composition № 3

During the study, an increase in the quantitative yield of working samples with a working layer of composition №2 was noted (Fig. 5).

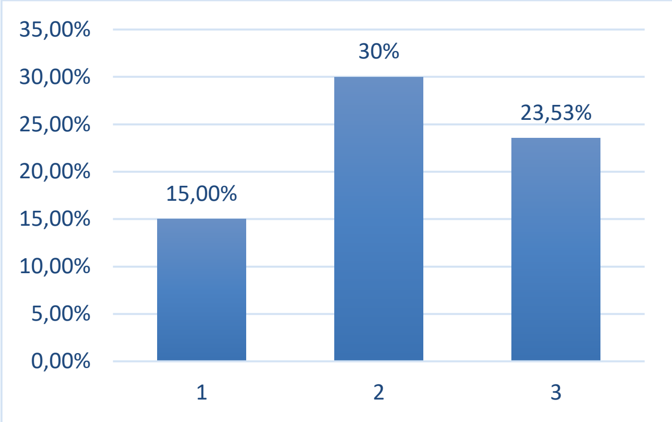
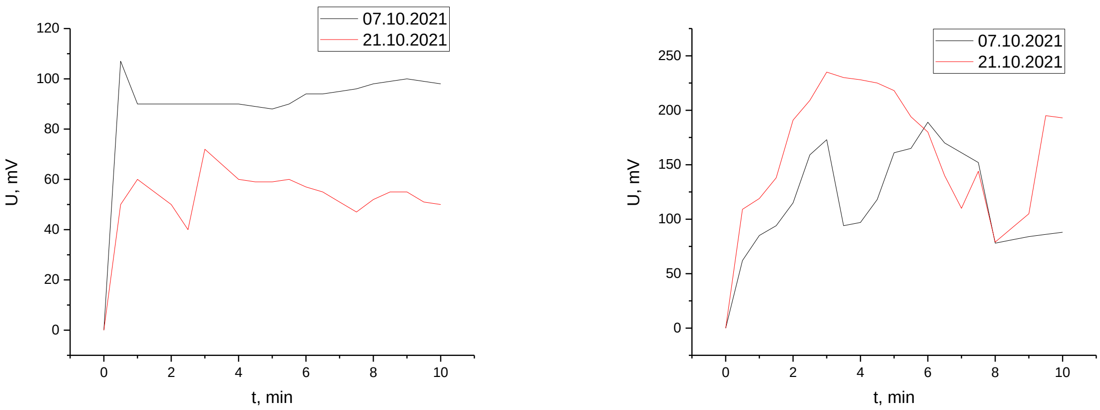


Fig. 5. Percentage output of working chemoconverters:

1 – composition № 1; 2 – composition № 2; 3 – composition № 3

The obtained samples were examined for repeatability depending on the number of cycles of operation of the chemoconverter cels (Fig. 6-8). The data obtained indicates that the properties of workspace are change during cycling. It should be noted that for Series № 1 and № 2, the cycling and decontamination are tend to increase the maximum EMF voltage (Fig. 6).



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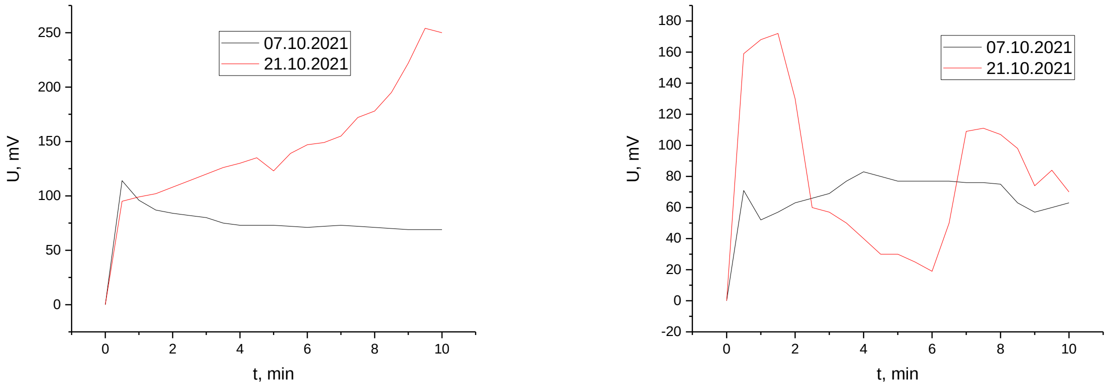

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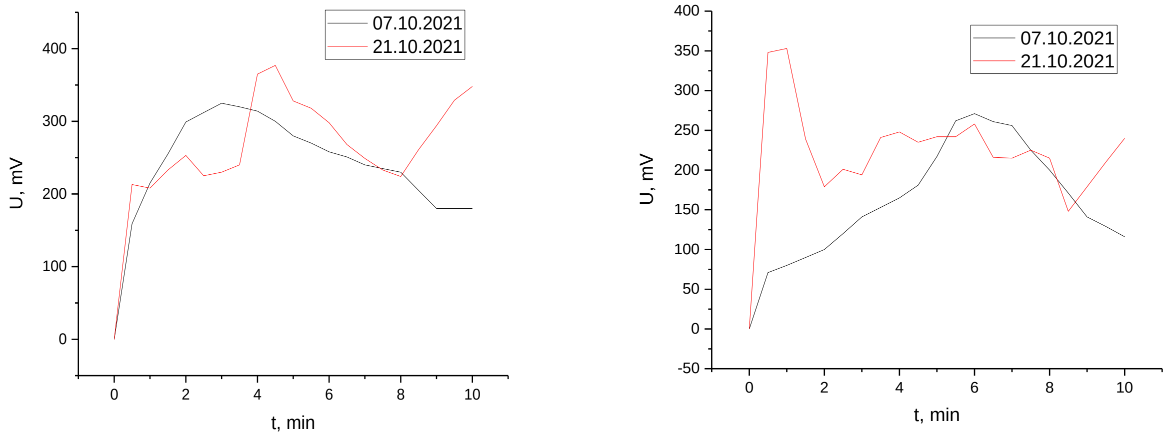
Fig. 6. The results of study of the repeatability of the properties of the chemo converter cells of composition № 1: Dependences of EMF on time obtained at different times: a – sample № 1, b – sample № 2, c – sample № 3, d – sample № 4

As can be seen from Fig. 7, this trend is most pronounced for samples of series № 1.



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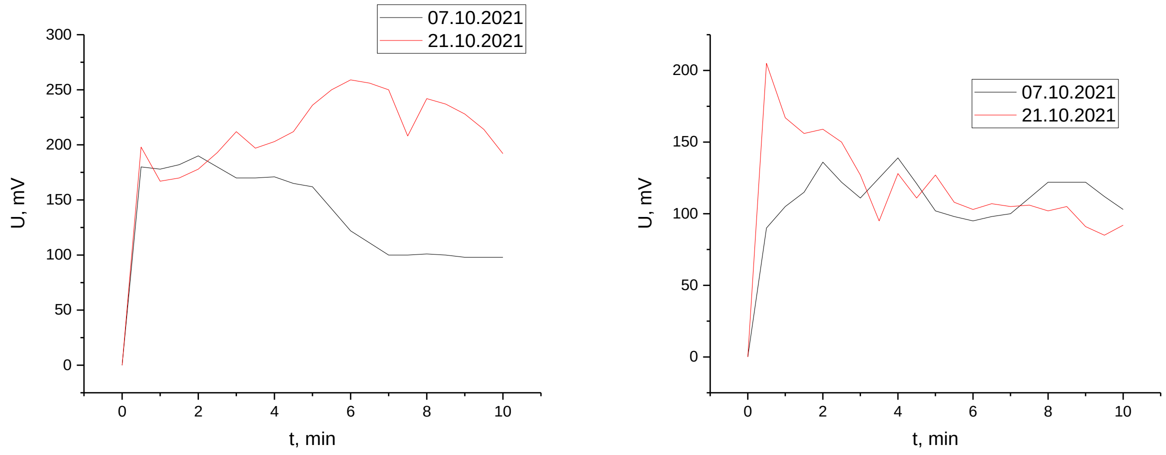

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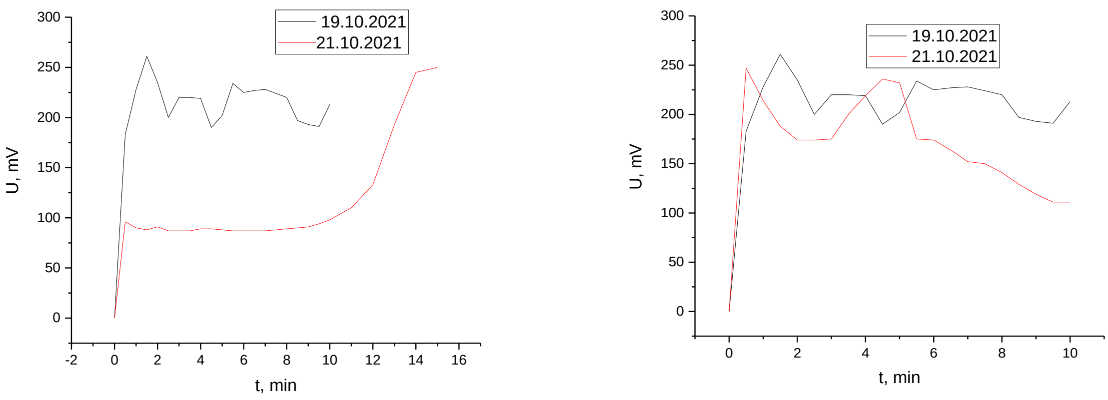
Fig. 7. The results of study of the repeatability of the properties of the chemo converter cells of composition № 2: Dependences of EMF on time obtained at different times: a – sample № 1, b – sample № 2, c – sample № 3, d – sample № 4



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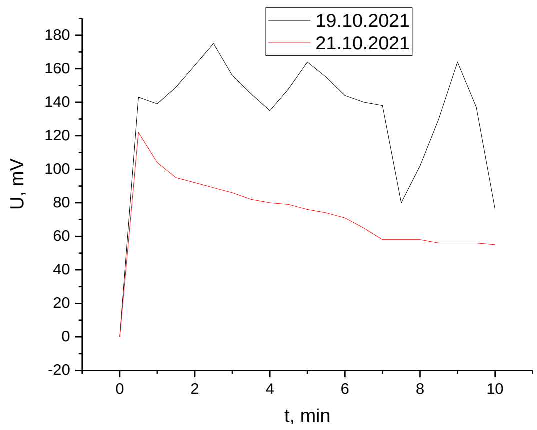

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Fig. 8. The results of study of the repeatability of the properties of the chemo converter cells of composition № 2: Dependences of EMF on time obtained at different times: a – sample № 1, b – sample № 2, c – sample № 3

Based on all the above data, it can be concluded that the functional layer with the ratio of solid and liquid phases: 2 g/250 mg (series № 2) has the best technical characteristics, as well as the highest quantitative yield of working samples and it's time of life.

3.2. Affect of storage time of polymer solution on performance characteristics of hydraulic converters.

During the study, it was revealed that the technical characteristics of the working layer and the quantitative output of the working samples are significantly influenced by the storage time of the pre-prepared aqueous solution of the polymer binder (Fig. 9-10). Preparation of the working layer of composition № 1 was carried out according to the procedure described above. The subsequent addition of a suspension of YSZ powder was add to a freshly prepared aqueous solution of PVA (batch 1), a solution of PVA after 5 days (batch 2) and 8 days (batch 3).

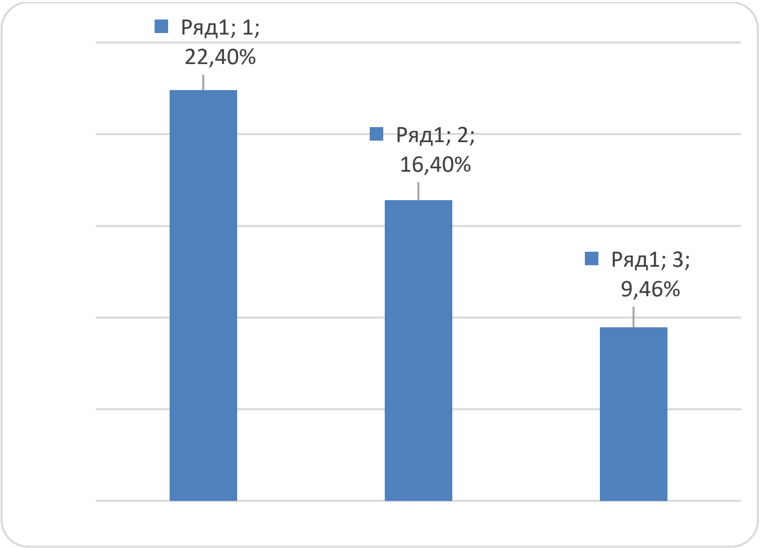
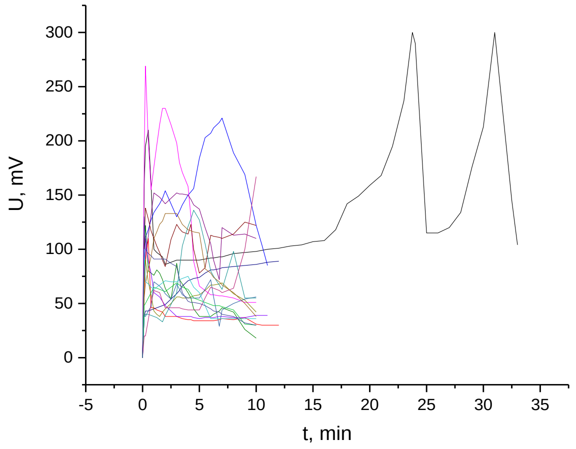


Fig. 9. The amount of reduction of percentage yield of working chemo converters cells in case of using PVA solution prepared at 8 days before use in comparison to the freshly prepared one, where: 1 – series № 1; 2 – series № 2; 3 – batch № 3.



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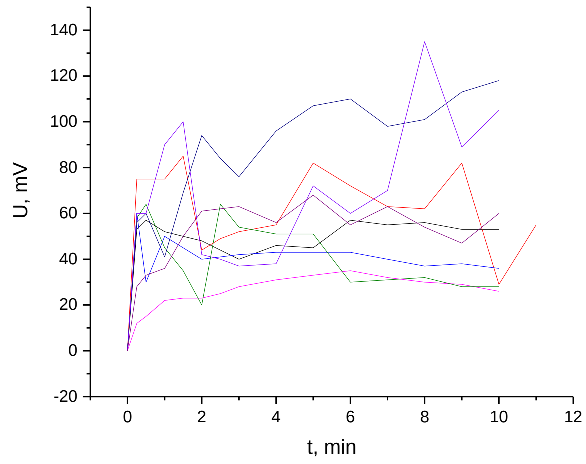

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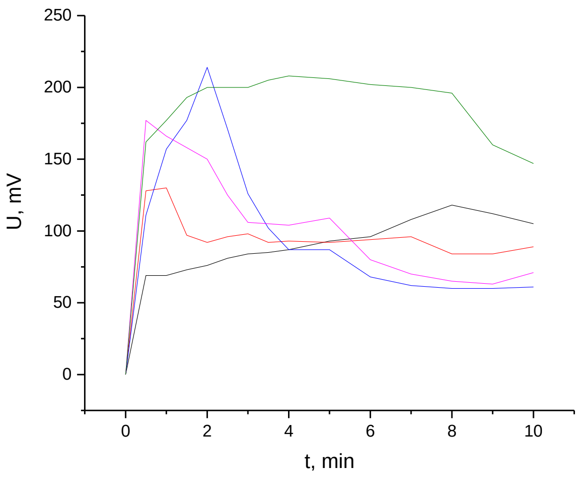


c

Fig. 10. Temporary dependences of tension of EMF of cells chemoconverters at the maximum humidity for bath № 1 (a), party № 2 (b) and parties № 3 (c).

3.3. Affect of degree of homogenization of working suspension on technical characteristics of chemo-converter cells.

The effect of the mixing time of the working slurry on the performance and quantitative yield of the working samples was also investigated. Preparation of an aqueous solution of the polymer binder was carried out according to the described procedure for 4 hours, after which a slurry of stabilized YSZ powder was added with mixing for 2 and 4 hours. For the study, working mixtures of composition № 1 and composition № 2 were taken. The results of the study are shown in figure 11.

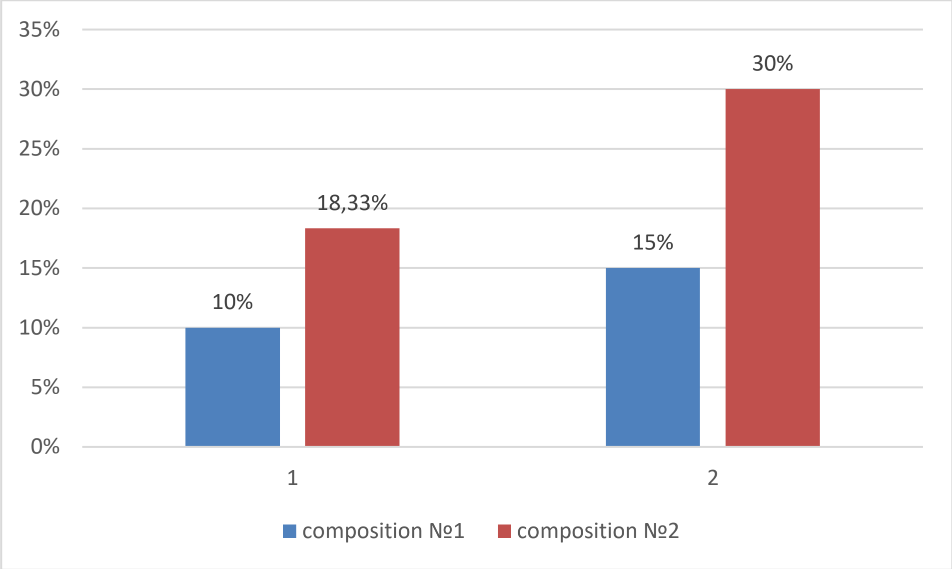
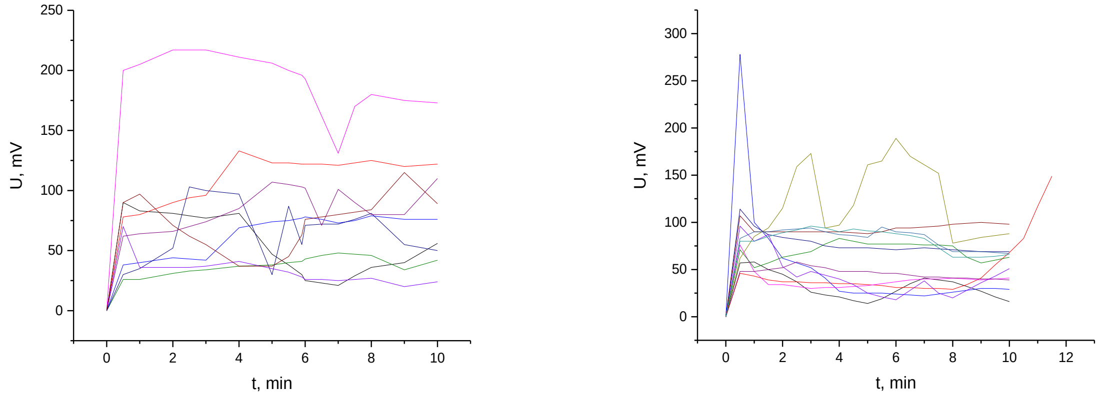


Fig. 11. Percentage yield of working chemo converter cells, wpere: 1 – preparation of the working layer mixture within 2 hours; 2 – preparation of the working layer mixture within 4 hours

Based on the obtained data, it can be concluded that the reduction of the preparation time of the mixture for the working layer leads to a decrease in the quantitative output and maximum voltage of the working chemoconverters (Fig. 12).



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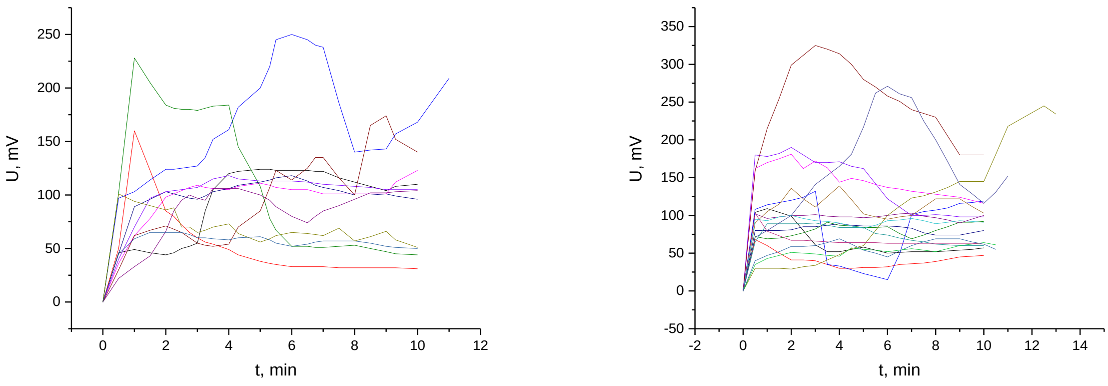

c d

Fig. 12. Time dependencies of chemo-converter voltage at maximum humidity and different mixture preparation time for the PVA-based working layer: a – preparation of working suspension within 2 hours of composition № 1; b – preparation of working suspension within 4 hours of composition № 1; c – preparation of working suspension within 2 hours of composition № 2; d – preparation of working suspension within 4 hours of composition № 2.

As can be seen from Fig. 12., the maximum voltage 278 mV and 325 mV was reached in the chemoconverters with the working layer of composition № 1 of composition № 2, respectively, with the duration of mixing the suspension for 4 hours (Fig. 12 b, d), while at 2 hours stirring the maximum voltage reached 217 mV and 250 mV, respectively (Fig. 12 a, c).

Conclusion.

During the work, the Adsorption hydroelectric converter (chemoelectronic converter) were obtained, optimal technique and the chemical composition of the functional layer of the chemoconverter were selected. Time dependencies of voltage of converters cells were studied and limit number of operating cycles of elements was determined. The set of working chemoconverter cells which is capable to produce an electric charge stored on the electric capacitor was made, The statement about the possibility of obtaining electricity from atmospheric moisture was confirmed.

Acknowledgements

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