Chemistry, Physics and Technology of Surface. 2022. V. 13. N 4. P. 415-424

PACS numbers: 77.84.Lf doi: 10.15407/hftp13.04.415

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ELECTRICALLY CONDUCTIVE COMPOSITES BASED ON TIO_2 AND CARBON NANOSTRUCTURES MANUFACTURED USING 3D PRINTING OF CJP TECHNOLOGY

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The mechanical mixtures of titanium oxide (TiO_2) with carbon nanostructures for 3D printing of CJP technology, which are used as consumables for the manufacturing of electrically conductive composite 3D products, are created in this work. Various carbon nanostructures (single- and multi-walled carbon nanotubes and carbon nanofibers) were used in the creation of composite 3D products (TiO_2–CNS) by CJP 3D printing technology. Optimal conditions for processing of mechanical mixtures (TiO_2/MWCNT) on a planetary ball mixer for composite 3D products (CJP) were studied and proposed. The dose of the deformation influence on the mechanical mixture under optimal conditions of mechanochemical processing (76 J/g), which allows not to deteriorate the electrical conductivity of the material, is determined.

The dependence of the electrical conductivity of composite 3D products (CNS/TiO_2, where the CNS content is 3 wt. %) on the type of carbon nanostructures (SWCNT, MWCNT and CNF) contained in ceramics (TiO_2), is constructed. The exponential dependence of the specific electrical conductivity (G) of composite 3D products (TiO_2–MWCNT) on the mass content of multi-walled carbon nanotubes, is also recorded in the work.

In the framework of the study of the electrical conductivity of composite 3D products (CJP), a fuel cell cathode based on a Pt/TiO_2–MWCNT composite was created. It was found that the catalyst Pt/TiO_2–MWCNT, which contains 5 wt. % of carbon nanotubes, has the best catalytic activity in oxygen recovery. At the same time, the average particle size of platinum (Pt) is 5–10 nm, while the content of Pt in the EDX samples is approximately ~10 wt. %. Also, studies were carried out from the mixing of Pt/TiO_2-MWCNT composites with MWCNT content 15 and 50 wt. %. Samples were analyzed by transmission and scanning electron microscopy.

***Keywords**: carbon nanostructures (CNS), nanocomposite (TiO_2–CNS), titanium oxide (TiO_2), electrical conductivity, catalytic activity, carbon nanotubes (CNT), Pt/TiO_2–CNT, 3D printing, CJP, fuel cell, additive technology, hydrogen energy*

INTRODUCTION

The main problems of hydrogen energy are the process of transporting and storing hydrogen [1–6], as well as reducing the cost of equipment for obtaining electricity when using hydrogen. Today, the use of nanotechnology also allows breakthroughs in the field of hydrogen energy. For example, carbon nanomaterials can accumulate hydrogen [7–13] and preserve it no less efficiently than advanced materials for hydrogen storage [14–33].

The key to the success of carbon nanomaterials lies in a large number of various methods of their synthesis, which allow creating a wide range of their modification [34–40]. This increases the possibility of creating new composites based on carbon nanostructures (fullerenes [26], fullerene-like nanostructures [27–30], carbon nanofibers (CNF), single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs) [31–32], nanocomposites [33–34], graphenes and their packets) [54–55].

Composites based on the ceramics and carbon materials have broad perspectives for modern industry [35–41]. The electrical conductivity of such composites can be useful for creating of various electrochemical devices [39].

The creation of electrically conductive composites by the method of 3D printing will allow to design the cheap fuel cells for fuel elements of any configuration, which will make it possible to refusal the expensive "Nafion" membranes, which are used in fuel cells today. The fuel cell is the most expensive element of the hydrogen cycle for obtaining hydrogen electricity, therefore reducing its cost is the main step for the introduction of hydrogen energy into the life of all countries and society.

Thus, imparting the conductive properties to the composite through the introduction of small additions of carbon nanomaterials is attractive compared to other composite systems. And the using of such composites in CJP 3D printing technology will allow not only to automate the system of creating complex 3D products and reduce their cost due to the economical use of consumables, but will also allow to give a sufficient impetus for their mass production and application.

In the production of electrically conductive composite 3D products of the CJP technology with a dielectric matrix and a conductive filler, the internal conductivity, shape and size of the particles of the introduced filler, as well as its amount, are of particular importance.

The carbon black, carbon nanofibers (CNF), multiwall and single-walled nanotubes (CNT) and graphene structures are used as fillers for 3D products [38–52]. All of these ceramic matrix fillers can be used in CJP 3D printing technology with some pre-processing. But when creating electrically conductive ceramics using CJP 3D printing technology, carbon nanostructures (CNS) require the special processing, since damaged (defective) CNS change their electrical conductivity.

To create highly effective composite 3D materials, it is necessary to introduce additives that will either improve the properties of the basic material (matrix), or give to it new properties without changing or improving the original properties of the base material (supporting matrix). Therefore, to achieve the best effect, it is necessary to introduce a minimum quantity of additives that gives the new properties to composite materials. In the work of other researchers, the content of carbon materials in composites ranged from one to several tens of percent. In this regard, one of the problems is to determine the minimum content of carbon nanostructures in the composite material, which will ensure the maximum effect of the predicted properties in the 3D product.

MATERIALS AND EQUIPMENT

To create composite 3D products, the carbon nanofibers with a diameter of 100–200 nm (brands C1234NMG) [1], multi-walled carbon nanotubes (MWCNT) with a diameter of 10–50 nm (brands C1214NMGS) [1], thin carbon nanotubes with a diameter of 5–10 nm (brands C1226NMG) [1] were synthesized by the pyrolytic method, and TiO_2 powder (brand "Degussa P25", which includes the phase of anatase and rutile in the ratio of 3:1) [2] was also used. CJP (Color Jet Printing) or 3DP (3D Printing) technology is an additive technology of injection manufacturing of three-dimensional objects by the method of discrete layer-by-layer printing, where the consumables have a loose powder form (ceramics, plaster, plastic, CNS, *etc*.). Each layer of printing is impregnated with an adhesive. The mechanical mixture for 3D printing of CJP technology was prepared by mixing of carbon nanostructures with metal oxide (TiO_2) in a planetary ball mill. Such parameters as rotation speed, milling time, type and mass content of CNTs were changed.

The samples were examined using transmission electron microscopy (TEM) on EMW–100B and JEOL JEM–100 CX instruments. A field emission scanning electron microscope (SEM) Zeiss LEO SUPRA 25, equipped with an EDX nozzle for X-ray microanalysis of the elemental composition of the sample surface, was used to study the surface of mechanical mixtures (CNS/TiO_2). A QUADRASORB SI analyzer was used to measure the specific surface area. The electrical conductivity of 3D products was determined on a P–30S potentiostat (Elins Co) using four- and two-zone cells with electrodes with a diameter of 0.5 and 0.3 cm. To create samples in the form of 3D products, a 3D printer of CJP technology of the ProJet 860 Pro brand with an industrial-scale printing chamber (508×381×229 mm) was used, which will allow for quick adaptation of the developed technology on a production scale.

To study the electrocatalytic activity during oxygen reduction of the obtained composite 3D products, the platinum (Pt) clusters were deposited on their surface. Tests were performed with a cathode for simulating fuel cells. Cyclic voltammograms were recorded at different speeds with a potential sweep, which blowing air through gas channels. After registration, the stationary currents were recorded on cyclic voltammograms in potentiostatic mode. A P-30S potentiostat and a Z-500PX impedance meter (Elins Co) were used for this purpose.

RESULTS AND DISCUSSION

To study the dependence of the electrical conductivity of 3D products on the content of carbon nanomaterials, mixtures with a MWCNT content of 1 to 5 wt. % were prepared. After processing on a planetary ball mill, the samples of oxide powders and nanotubes had a same form, but in the study by transmission electron microscopy (TEM) the carbon nanotubes were not observed alone in samples of mixtures containing 1 and 2 wt. % MWCNT. At a MWCNT content of 3 wt. % both bundles of nanotubes and individual tubes were observed. In mixtures with a MWCNT content of 5 wt. % there was a large number of nanotube bundles distributed between the titanium oxide particles (Fig. 1). As a result of planetary ball mill processing, the homogeneous mechanical mixtures (TiO_2 / MWCNT) were obtained, which are ideal for application in CJP 3D printing technology. Optimal conditions were determined and selected - the processing time, degree of loading, type and content of carbon nanomaterial.

The study of specific electrical conductivity (G) of composite 3D products from mechanical mixtures based on titanium oxide (TiO_2) with different content of carbon nanotubes showed that the dependence has an exponential form. With a MWCNT content of 1–2 wt. %, the specific electrical conductivity remains practically unchanged and is approximately 5×10^{-6} Siemens/centimeter (S/cm). An increase in the content of nanotubes to 5 wt. % leads to a sharp increase in the value of G (2.2×10^{-2} S/cm). It is also possible to observe a jump in specific electrical conductivity up to 2.2×10^{-3} S/cm at 3 wt. % CNT (Fig. 2).

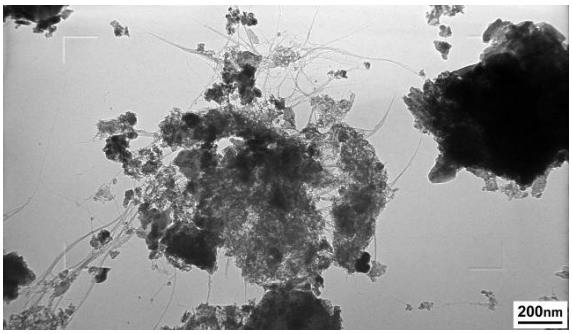

Fig. 1. Composite based on ceramics filled with 5 wt.% MWCNT (TEM)

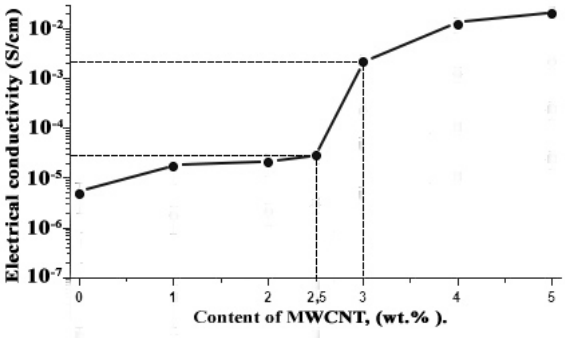

Fig. 2. Dependence of the electrical conductivity of composite (MWCNT / TiO_2) 3D products on the mass content of carbon nanotubes

To select the optimal speed (wheeling number) and milling time in a ball mill, a mechanical mixture was used, where the carbon nanostructures content was 3 wt. %. Experiments showed that the highest electrical conductivity of 3D products made of floured mechanical mixtures (CNS/TiO_2) was achieved at a rotation speed of 100 rpm. within 30 min. (Figs. 3, 4). A further increase in the processing time or the mill rotation speed leads to the creation of defective carbon nanostructures and the rearrangement of the CNS, therefore, all this reduces the electrical conductivity of 3D products.

At the studying of the electrical conductivity of the created 3D products made from mechanical mixtures that differed in the type of used carbon nanostructures (SWCNT, MWCNT and CNF), it was found that the composite 3D products with multi-walled carbon nanotubes have the best electrical conductivity (Fig. 5). At the same time, the value of G of composite 3D products with single-walled carbon nanotubes is two orders of magnitude lower, and the composite with carbon nanofibers has the worst electrical conductivity. We think that this

is due to the deformation effect of ball mill processing on the mechanical mixture that contains carbon nanostructures.

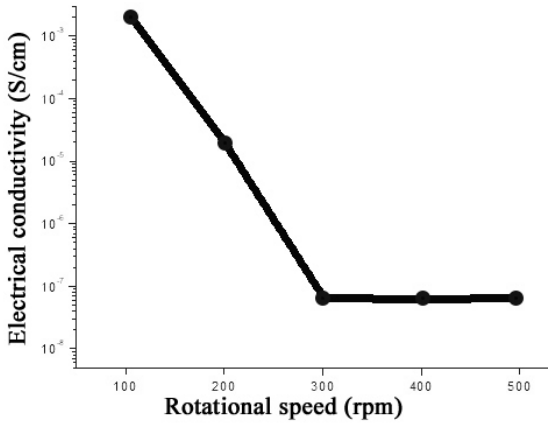

Fig. 3. Dependence of the conductivity of composite 3D products (TiO_2–MWCNT, where content of MWCNT is 3 wt. %) on the speed (wheeling number) on the ball mill

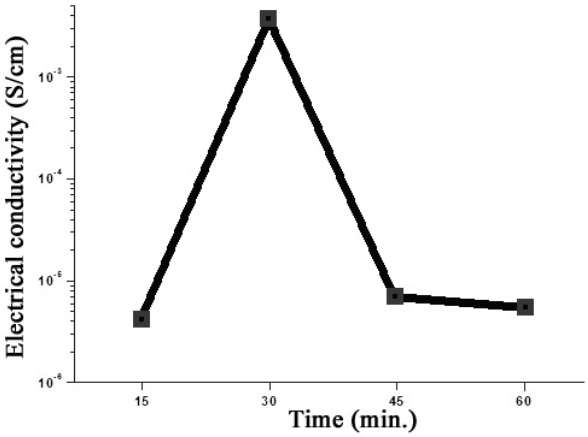

Fig. 4. Dependence of the conductivity of composite 3D products (TiO_2–MWCNT, where MWCNT content is 3 wt. %) on the time of milling (processing) on a ball mill

That is why, for a detailed description of the conditions for the formation of composite 3D products with using a ball mill, the magnitude of the deformation effect on the mechanical mixture during mechanical processing was determined. To determine the magnitude of the deformation effect, it is necessary to calculate the energy which is transferred to the sample during milling in a ball mill. This method uses a universal value, that allows you to ignore the type of mill and to a certain extent facilitates the production and optimization of the processes of forming mechanical mixtures (metal oxide/CNS) in the conditions of various grinding and mixing machines.

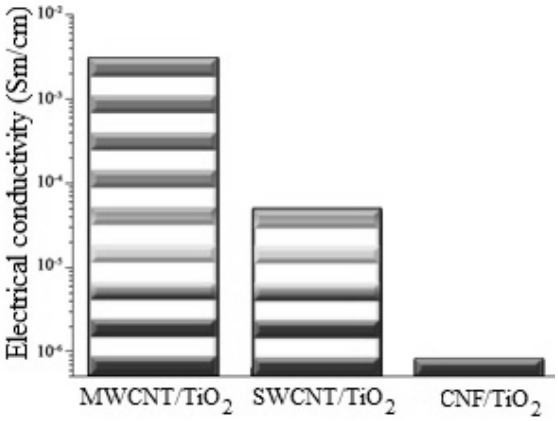

Fig. 5. Dependence of the electrical conductivity of composite 3D products (CNS–TiO_2, where the content of CNS is 3 wt. %) on the type of carbon nanostructures contained in ceramics

According to the results of the calculations of the deformation effect dose and the electrical conductivity data of the mechanical mixtures, the graphs of the dependence of the electrical conductivity of composite 3D products (MWCNT-TiO_2) on the deformation effect dose on the composite samples were plotted (Fig. 6).

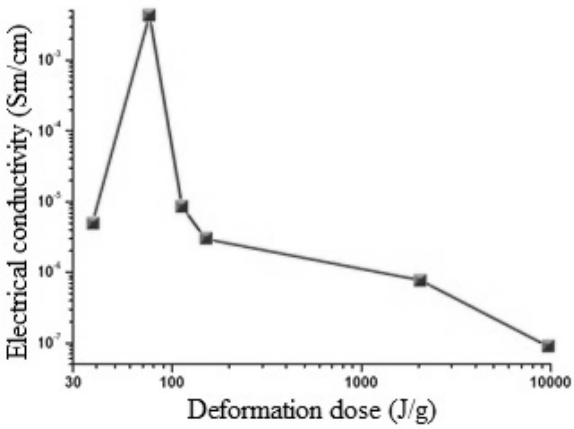

Fig. 6. Dependence of the electrical conductivity of composite 3D products (MWCNT–TiO_2, where the content of MWCNT is 3 wt. %) on the deformation effect dose of the ball mill on the mechanical mixture

As can be seen from Fig. 6, composite 3D products obtained by mechanical processing of mechanical mixtures at the deformation effect dose of 76 J/g have the highest specific electrical conductivity (4.5×10^{-3} S/cm). A further increasing of the load and time of mechanical mixtures (MWCNT/TiO_2) processing with a ball mill leads to a decrease in electrical conductivity, which, obviously, occurs due to the grinding of the oxide and the destruction of carbon nanostructures. This assumption is confirmed by the value of the specific surface of the composites, which has a value from 55 m^2/g for composites obtained at the deformation effect dose (mechanical action) of 38 J/g, to a specific surface of 80 m^2/g for composites obtained at the deformation effect dose of 9.6 kJ/g.

The main thing is the fact that when processing of mechanical mixture (titanium oxide / CNT) in a ball mill at the speed of 100 rpm for 30 minutes, the dose of deformation effect (76 J/g) is reached. Such value is insufficient for impairment of electrical conductivity of the formed composite. In addition, such mechanical treatment contributes to the formation of a sufficiently homogeneous mechanical mixture for use in 3D printing technology CJP and for creating of electrically conductive composite 3D products with a specific surface area of 55 to 80 m^2/g.

To evaluate the effectiveness of using the CNT-TiO_2 composite for 3D printing as a catalyst bearer in electrochemical devices, the samples of 3D products Pt/TiO_2–CNT with different percentages of carbon nanotubes were prepared and their electrocatalytic activity was investigated using an electrode modeling cathode of a fuel cell. Platinum was applied by plasma spraying. According to the data of scanning electron microscopy (SEM), Pt particles are distributed on the surface of the composite 3D product (TiO_2-CNT) quite uniformly, where their average size is 5–10 nm (Fig. 7). According to EDX data, the content of Pt in 3D products is approximately ~10 wt. %.

The volt-ampere characteristics of the Pt / TiO_2-MWCNT composite systems with different mass content of carbon nanotubes (3, 5, 15, and 50 wt.%) are shown in Fig. 8.

Composite 3D products with 5 wt. % MWCNT content are the most effective for creating an electrically conductive composite. Composite 3D products with MWCNT content of 3 wt. % have a smaller number of extended carbon structures that provide electron transfer, and in 3D products with MWCNT content of 15 and 50 wt. %, they show low efficiency of the Pt catalyst, which may be related with difficulties in contact with the reaction environment due to the large amount of carbonaceous material.

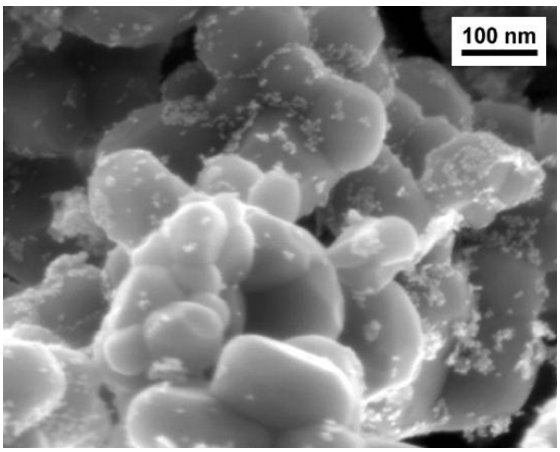

Fig. 7. Composite 3D products (MWCNT-TiO_2) with catalyst clusters (Pt) applied to the its surface

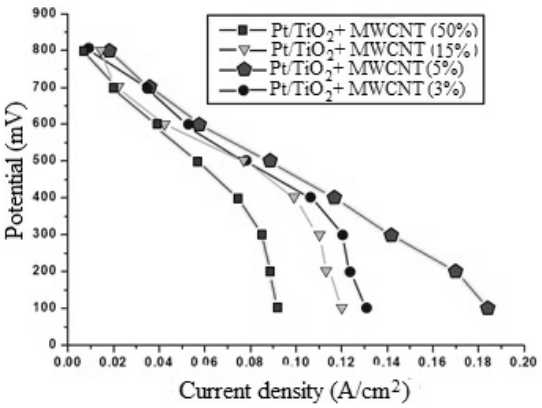

Fig. 8. Volt-ampere characteristics of the Pt / TiO_2-MWCNT system with different mass content of carbon nanotubes

CONCLUSIONS

Within the framework of work:

● A possibility of creating a mechanical mixture of TiO_2/CNS for 3D printing of CJP technology, which is used as a consumable raw material for the manufacturing of electrically conductive composite 3D products, has been found;

● A possibility of application of various carbon nanostructures (single- (SWCNT) and multi-walled carbon nanotubes (MWCNT) and carbon nanofibers (CNF)) in the creation of composite 3D products (TiO_2–CNS) by CJP 3D printing technology has been found;

● The mechanism for creating of electrically conductive mechanical mixtures for 3D printing of CJP technology has been elucidated;

● The optimal conditions for processing of mechanical mixtures (TiO_2/MWCNT) on a planetary ball mixer for composite 3D products (CJP) were justified, where the speed of rotation will be 100 rpm for 30 min;

● The dose of deformation effect on the mechanical mixture under optimal conditions of mechanochemical processing (76 J/g), which allows not to impair the electrical conductivity of the material, was found;

● The fact of creating a homogeneous mechanical mixture (TiO_2/CNS) with a specific surface from 55 to 80 m^2/g for its application in 3D printing technology (CJP) has been discovered;

● It was found that when creating electrically conductive ceramics using CJP 3D printing technology, carbon nanostructures (CNSs) require special processing, since damaged (defective) CNSs change their electrical conductivity;

● The dependence of the electrical conductivity of composite 3D products (CNS–TiO_2, where the content of CNS is 3 wt. %) on the type of carbon nanostructures (SWCNT, MWCNT and CNF) contained in ceramics (TiO_2) was found;

● It was found that composite 3D products (CJP) with multi-walled carbon nanotubes have the best electrical conductivity in contrast to other CNS;

● The exponential dependence of specific electrical conductivity (G) of composite 3D products (TiO_2–MWCNT) on the mass content of multi-walled carbon nanotubes was found. It was also recorded that with a content of 5 wt. % MWCNT the 3D product has the most effective electrical conductivity (2.2×10^{-2} S/cm). And when adding 1–2 wt. % MWCNT to the composite 3D product, the electrical conductivity of titanium oxide almost does not change (~5×10^{-6} S/cm);

● It was found that the Pt/TiO_2- MWCNT catalyst, which contains 5 wt. % of carbon nanotubes, has the best catalytic activity in oxygen reducing in the cathode electrode simulating fuel cell. At the same time, the average size of Pt particles is 5–10 nm, and the content of Pt in the samples, according to EDX data, is approximately ~10 wt. %;

● It was found, and in the Pt/TiO_2-MWCNT composite with the MWCNT content of 15 and 50 wt. %, the low efficiency of the Pt catalyst is shown, which may be associated with difficulties in contact with the reaction environment due to the large amount of carbon material;

● A fuel cell cathode based on a Pt/TiO_2-MWCNT composite was created using 3D printing of CJP technology.

But we believe that if composite 3D products obtained by synthesizing of carbon nanostructures directly on the surface of particles of oxide powders of the composite will have close contact between the composite components, and therefore will have better electrical conductivity.

Електропровідні композити на основі TiO_2 та вуглецевих наноструктур, виготовлені при використанні 3D друку технології CJP

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В роботі створено механічні суміші оксиду титану (TiO_2) з вуглецевими наноструктурами для 3D друку технології CJP, які використовують як витратну сировину для виготовлення електропровідних композитних 3D виробів. Використано різні вуглецеві наноструктури (одно- і багатостінні вуглецеві нанотрубки та вуглецеві нановолокна) у створенні композитних 3D виробів (TiO_2–ВНС) технологією 3D друку CJP.

Досліджено і запропоновано оптимальні умови обробки механічних сумішей (TiO_2/БВНТ) на планетарному кульовому змішувачі для композитних 3D виробів (CJP). Визначена доза деформаційного впливу на механічну суміш при оптимальних умовах механохімічної обробки (76 Дж/г), що дозволяє не погіршити електропровідність матеріалу.

Побудована залежність електропровідності композитних 3D виробів (ВНС/TiO_2, де вміст ВНС 3 мас. %) від типу вуглецевих наноструктур (ОВНТ, БВНТ та ВНВ), що містяться в кераміці (TiO_2). Також в роботі зафіксована експоненціальна залежність питомої електропровідності (G) композитних 3D виробів (TiO_2–БВНТ) від масового вмісту багатостінних вуглецевих нанотрубок.

В рамках дослідження електропровідності композитних 3D виробів (CJP) створено катод паливної комірки на основі композиту Pt/TiO_2–БВНТ. Встановлено, що каталізатор Pt/TiO_2–БВНТ, який містить 5 мас. % вуглецевих нанотрубок, має найкращу каталітичну активність у відновленні кисню. При цьому середній розмір частинок платини (Pt) складає 5–10 нм, а вміст Pt в зразках за даними EDX становить приблизно ~10 мас. %. Також проведені дослідження із створення композиту Pt/TiO_2–БВНТ із вмістом БВНТ 15 та 50 мас. %. Проведено аналіз зразків просвічуючою і скануючою електронною мікроскопією.

***Ключові слова**: вуглецеві наноструктури (ВНС), нанокомпозит (TiO_2–ВНС), оксид титану (TiO_2), електропровідність, каталітична активність, вуглецеві нанотрубки (ВНТ), Pt/TiO_2–ВНТ, 3D друк, адитивна технологія, CJP, паливна комірка, воднева енергетика*

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Received 19.09.2022, accepted 05.12.2022