Hydrogen generation by hydrolysis of metals and hydrides for portable energy supply

(An overview of the tasks and outcome of the NATO SPS Project G5233; NATO country: Norway; NATO Partner country: Ukraine)

V. Yartys, I. Zavaliy, Yu. Pirskyy, Yu. Solonin, V. Berezovets,
F. Manilevich, Yu. Verbovytskyy, A. Kytsya, A. Kutsyi

NATO project G 5233 “Portable energy supply” was executed by 4 teams (Institute for Energy Technology, Norway and 3 Institutes of the National Academy of Sciences of Ukraine). G5233 Project was focused on the development of hydrogen fueled portable energy supply systems integrating hydrogen generation and storage units based on use of light metals, metal and complex hydride materials and portable fuel cells. The weight efficient energy supply device was developed by using these selected materials and performance-optimised $NaBH_4$ *complex hydride. Besides, various new relevant units of equipment for the samples preparation and characterization were ordered and accommodated in the participants labs and the program of training of young scientists at IFE, Norway was accomplished.*

Different types of materials for hydrogen generation were synthesized and characterized (activated aluminium alloys, Mg-Al alloys, MgH_2 *and their composites,* $NaBH_4$ *with catalytic additives). The challenging objective of reaching a completeness of the hydrolysis of* MgH_2 *was achieved; the reaction conditions were optimized and the particular focus applications integrating efficient hydrogen generation systems were identified. The mechanism and the kinetics model of the hydrolysis process of* MgH_2 *in water solutions have been proposed which successfully describ the experimental data. In parallel with the hydrolysis reaction resulting in hydrogen generation and formation of* $Mg(OH)_2$*, the process involves passivation of the* MgH_2 *surface by the formed* $Mg(OH)_2$ *precipitate followed by its re-passivation with the rate constants of these processes being established. Increase of the concentration of* $MgCl_2$ *leads to just a minor increase in the rate constant of the interaction of* MgH_2 *with water but leads to a sharp increase of the rate constant of the re-passivation of* MgH_2 *surface.*

To achieve efficient hydrolysis of $NaBH_4$*, different types of catalysts (heterogeneous on the basis of Pt and "homogeneous" - salts of* Ni^{+2} *and* Co^{+2}*) were*

studied and optimized. Several systems were selected as candidates to provide the required hydrogen flow to operate a 30 W fuel cell over a given time exceeding 1 hour, based on a use of inexpensive and affordable hydrogen-containing materials and catalytic additives. 3 individual hydrolysis workstations (1 in Norway and 2 in Ukraine) were built, tested and optimized. The plan of the work to reach the objectives of the Project G5233 "Portable energy supply" is completely accomplished, all the milestones are successfully fulfilled and the overall goal of the Project is reached.

Keywords: *Portable energy systems; Hydrogen generation; Complex hydrides; Catalyst additives; Hydrolysis*

1. Motivation and project goals

In the development of renewable energy systems, hydrogen plays a central role because of its record-high specific energy density (120 MJ/kg), "green", i.e., pollution-free technology of its synthesis using the renewables, its easy and convenient conversion to electricity. Hydrogen can be stored, transported, and used in fuel cells driven energy systems allowing for a direct conversion of the chemical energy, through electrochemical oxidation, to electricity. Despite a reasonable efficiency of this process, its broad use is rather limited because of the necessity to have in the possession efficient hydrogen generation and storage technologies, particularly, when targeted demands for hydrogen use in portable applications should be implemented.

In contrast to the compressed H_2 gas and liquid hydrogen, an effective and safe way is to store H_2 in its chemical compounds, namely, in metal hydrides (MH). MH can store large amounts of hydrogen and reversibly release it following an increase in temperature and/or a decrease in pressure. The hydrogen storage tanks accommodating MH are extensively used for this purpose. However, for portable applications they should be optimized by reducing their weight and volume, while showing high hydrogen storage capacity. $LaNi_5$ intermetallic and many other alloys (TiFe, Ti_2Ni, Ti,Zr-based Laves phases, bcc Ti-V-based alloys) can absorb 1.5-4.0 wt.% H at ambient conditions (near room temperature and at pressures close to 1-2 bar H_2)

and reversibly release it following an increase in temperature or a decrease in pressure. Unfortunately, these values are insufficient to allow their efficient practical applications as hydrogen storage sources for the portable FC applications.

A promising group of H-storage materials is based on magnesium hydride. Magnesium metal can reversibly store large amounts of hydrogen - up to 7.6 wt.% H. However, there are principal challenges in utilizing Mg-based alloys. Indeed, due to a sluggish kinetics and unfavorable thermodynamics of hydrogen absorption-desorption processes, they require application of elevated operation temperatures (> 300 °C) while also investing a significant amount of heat because of high decomposition enthalpy of MgH_2 (74 kJ/Mol H_2). A great improvement in the hydrogen sorption kinetics by Mg was achieved by using suitable catalysts and adopting proper preparation methods [1, 2]. Mechanical alloying of Mg with different additives (and particularly its reactive ball milling in hydrogen gas) results in acceleration of the hydrogenation process and in a substantial decrease of the hydrogenation-dehydrogenation temperatures. However, the working temperatures (250-300 °C) are too high [3-5], thus a direct use of MgH_2 for the storage of gaseous H_2 should be ruled out meets practical limitations. At the same time, very intensive development of the complex hydrides, which are characterized by a high H-content (>10 wt.%), have not resulted in the development of the efficient hydrogen storage systems due to their low reversible capacity, limited cycle life and poor kinetics of hydrogen exchange [6,7]. Thus, the grand challenge of finding efficient, reversible at ambient temperatures solid hydrogen storage materials providing a high H storage capacity for use in portable FC applications remains to be solved [3,8].

An alternative and efficient way to generate hydrogen is in utilizing the hydrolysis reaction by using the metals, metal hydrides or complex hydrides. Such hydrolysis process takes place at relatively low temperatures and shows promising practical hydrogen supply efficiencies. The most frequently used hydrogen generation alloys include Al and Mg based materials [9,10]. The reason is in their light weight, high natural abundance, low cost, and environmental compatibility. However, there are practical challenges as aluminum forms a dense surface oxide layer which creates a barrier for the progression of the hydrogen evolution reaction, while, in turn, for Mg, the hydrolysis reaction is rapidly interrupted because of the formation of a blocking layer of magnesium hydroxide.

A great benefit of metal hydrides is in a fact that during the hydrolysis they generate a double amount of hydrogen as compared to the corresponding individual metals. A large number of metal hydrides have been studied as a portable source of hydrogen for fuel cell applications, including LiH, CaH_2, MgH_2, $NaBH_4$, $LiBH_4$, and $LiAlH_4$ [11]. Among them, LiH, CaH_2, and $LiAlH_4$ can react with water so violently that the uncontrollable reaction leads to a handicapped practicability. In turn, production of hydrogen using $NaBH_4$ is safe and well controllable, but the regeneration of $NaBH_4$ from the reaction product $NaBO_2$ is not simple and needs to apply an energy intensive catalytic process. In contrast, at room temperature MgH_2 can generate hydrogen in absence of a catalyst. However, the hydrolysis of MgH_2, even though it occurs immediately when MgH_2 comes in contact with water, is interrupted by the formation of a passive magnesium hydroxide layer covering the particles. Luckily, the use of aqueous acidic solutions and other “proton-containing compounds” results in a substantial increase of hydrogen yield.

Recent advances in a development of electronic equipment for soldiers at the battlefield witness an increased deployment of night-vision equipment, laptops, and communication devices to GPS and sensors. Due to the fact that these devices must operate autonomously, soldiers typically have to carry up to 17 kg of the batteries to power an individual device [12]. Therefore, necessity of the lightweight, reliable, portable and silent high-energy-density power sources for military use is in increased demand. Portable hydrogen-fueled fuel cells are considered as a prospective solution offering a number of advantages as compared to the battery systems.

The goal of the project G5233 PORTABLE ENERGY SUPPLY is in the development of the effective materials for hydrogen generation. The work is based on utilizing several innovative solutions allowing to enhance the efficiency of hydrogen generation process, to favorably affect the properties of the utilized materials thus providing an efficient solution to the task of the development of the technologies in the field of hydrogen storage and generation systems.

2. Consortium members

This project has been funded by NATO Science for Peace and Security Programme and joined forces of four institutions representing a NATO country – Norway (one participant), and a partner country – Ukraine (three participants). The project consortium included academic partners.

Coordinator: Institute for Energy Technology (IFE, Norway, *https://www.ife.no).*

IFE is an independent foundation and conducts research for a better future. Since its foundation in 1948, IFE has been a frontrunner in international energy research. IFE contributes to new solutions in renewable energy, petroleum and industry-oriented R&D. IFE develops zero-emission transport solutions based on novel batteries and hydrogen as an energy carrier, digital systems and ground-breaking cancer medicine. The Institute strives for a climate friendly energy supply. The annual turnover is approximately NOK 1 billion, with about 600 employees.

Coordinator of the project: Prof. V.A. Yartys (NATO Country Project Director).

Karpenko Physico-Mechanical Institute, NAS of Ukraine (PhMI-NASU, Lviv, Ukraine; *www.ipm.lviv.ua)****.***

PhMI-NASU was established in 1951 on the basis of the existing academic institutions. Scientific studies of the Institute in the field of fracture mechanics, materials strength and influence of hydrogen on materials properties provide the leading position in the world scientific community. PhMI-NASU is the biggest scientific institution of the Western Ukraine - it has about 400 employees (~180 researchers with PhD or DSci degrees).

Participants of the project: Prof. I. Zavaliy (Partner Country Project Director), Dr. A. Kytsia, young scientists: Dr. V. Berezovets, Dr. Yu. Verbovytskyy, Dr. P. Liutyy, Dr. I. Oshchapovskyy.

Frantsevich Institute for Problems of Materials Science, NAS of Ukraine (IPMS-NASU, Kyiv, Ukraine; *www.ipms.kiev.ua).*

IPMS-NASU was founded in 1952 (before 1964 it was named as the Institute of Metalloceramics and Special Alloys of Ukrainian Academy of Sciences). The institute has been involved in the investigations of high-temperature strength of metallic, nonmetallic and composite materials and development of new materials for high-temperature applications. Development of the theoretical principles and a variety of waste-free technologies to produce materials with predetermined properties is the current emphasis of the institute. IPMS-NASU is the leading institution in the field of materials science in Ukraine, it has 900 employees (~270 researchers with PhD or DSc degrees).

Participants of the project: Prof. Yu. Solonin (Partner Country Project Co-Director), young scientists: Dr. D. Korabliov, Dr. O. Bezdorozhev.

Vernadsky Institute of General and Inorganic Chemistry, NAS of Ukraine (IGIC-NASU, Kyiv), *www.ionc.kar.net***).**

The Institute was founded in 1918, when academician V. Vernadsky, the first President of the Academy of Sciences, set up a chemical laboratory within the Physical-and-Mathematical Department. It was transformed into the Institute of Chemistry in 1929-30. The institute consists of thirteen departments, and it has nearly 350 employees.

Participants of the project: D. Sc. Yu. Pirskyy (Partner Country Project Co-Director), Dr. F. Manilevich, young scientists: A. Kutsyi, T. Panchyshyn.

4. Project organization and communication

The overall management was carried out jointly by NPD, Prof. V. Yartys and PPD, Prof. I. Zavaliy. They defined the long-term project strategy, prepared and controlled the execution of the work plan, reaching the milestones and providing deliverables on time, and arranged regular joint project discussions (a kick-off meeting; an interim workshop, of- and on-line project meetings, the final workshop). Fig.1 shows project co-directors at the workshop 2019 (Lviv-Shepilske,Ukraine).

Fig. 1. Project co-directors at the workshop at Lviv-Shepilske, Ukraine on 6 September, 2019 (from left to right side: Prof’s Yu. Solonin, V. Yartys, Yu. Pirskyy and I. Zavaliy).

All research groups exchanged experimental samples and discussed the results on a monthly basis using E-mail communication, internet (Skype) or telephone calls. The minutes of the meetings and reports were disseminated between the participants of the project by NPD and PPD.

Young Ukrainian scientists from PhMI-NASU (Dr. Berezovets), from IPMS-NASU (Dr. Korablov. Dr. Bezdorozhev) and from IGAC-

NASU (Mr. Kutsyj) accomplished training visits to the partner institution – IFE, Norway. They participated in the development of the hydrolysis setup, preparation and testing of the new materials, testing of the hydrogen generation setup integrated with a FC device. They have successfully fulfilled the training programs.

5. Development of the dedicated equipment

According to the project plans, several units of equipment were purchased, and existing labs at the institutes were modernized. Description and photos of the selected equipment are given below (Table 1 and Fig. 2).

Table 1. Purchased materials and equipment.

Institute	Equipment
IFE	A flowmeter “SIERRA-100”, Horizon 30W PEM Fuel Cell. Laboratory modernization and equipment installation. Hydrolysis setup Turbopump vacuum station. Retsch planetary mill.
PhMI-NASU	Ball mill “Pulverisette 6 classic line”, 30W PEM Fuel Cell Stack, A flow-meter “SIERRA-100”, X-ray tube “BSV27-Cu”, Computer’s software, Vacuum pump and welding device, pH meter ADWA 1020, Magnetic stirrer MS-H280, SNOL resistance furnace, Laboratory scale PS600, Glove Box (individual order).
IPMS-NASU	High Pressure Milling Vial/Gas-Temperature-Monitoring system.
IGIC-NASU	A Potentiostat/Galvanostat model EC301, Power Booster model O200BS.A flow-meter “SIERRA-100”, Two Fuel Cell Stacks FCS-B30:H30 (B).

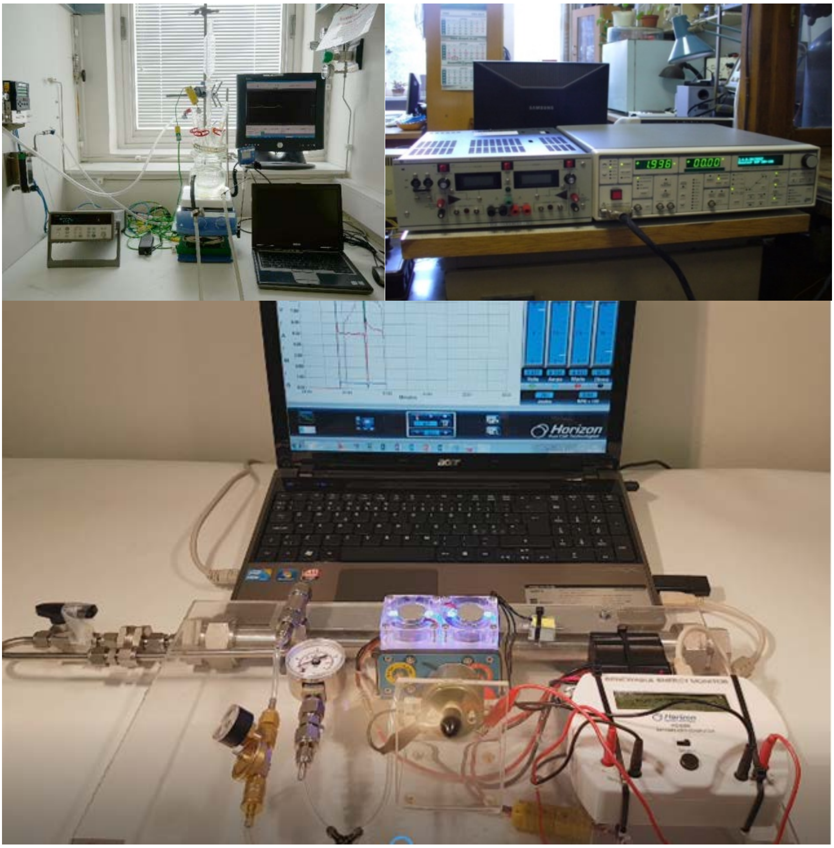


Fig. 2. Equipment for the testing of the materials for hydrolysis and hydrogen storage integrated with a FC unit

6. Results

6.1. Mg-based materials for hydrogen generation by hydrolysis

Materials preparation and characterization. Magnesium and MgAl commercial powders of a specific type: PAM-5, have been chosen as promising materials due to their low density, low cost, and as their components are locally available in Ukraine. They can be easily milled with different additivities (salts, metallic catalysts) as well as easily hydrogenated to produce nanoscale MgH_2. Pure MgH_2, Mg, MgAl or their composites with different additives were obtained by ball milling in hydrogen atmosphere using Fritsch Pulverisette P6 mill. Hydrogenation reaction studies were conducted for the following systems: MgH_2 + Al, MgH_2 + 5 wt.% $ZrCl_4$, MgH_2 + 5 wt.% $AlCl_3$, MgH_2 + 5 wt.% citric acid, MgH_2 + 5 wt.% EDTA, MgAl + KCl, MgH_2 + x $MgCl_2$, MgH_2 + +5 wt.% TiC-2TiB_2. From a practical point of view, the binary MgH_2 + $MgCl_2$ system was concluded to be the most promising. The above-mentioned system was studied in detail.

Hydrolysis reaction studies. The influence of $MgCl_2$ concentration on the kinetics of MgH_2 hydrolysis has been studied in a broad range of $MgCl_2/MgH_2$ relative ratios (between mole ratios of 0/100 and 19/100). Kinetic curves of hydrogen release show that the addition of $MgCl_2$ has a significant positive effect on the extent of MgH_2 conversion, when compared with pure MgH_2 without $MgCl_2$. The hydrolysis kinetics curves show, in each case, an exponentiality and consist of two parts: (a) Initial fast release of hydrogen for approximately 10 minutes, the H_2 generation rate reaching 800 $mL \cdot min^{-1} \cdot g^{-1}$ MgH_2 at maximum; (b) Slow ascending H_2-generation for up to 150 minutes, the amount of hydrogen produced increasing continuously and rates of hydrogen release decreasing. MgH_2 conversion peaked at 89 %. Efficiency should however also account for the overall mass of the system, including the $MgCl_2$. Therefore, in Fig. 3, we present the generation efficiency in terms of the unit of mass of MgH_2 and per 1 g of the "MgH_2 + $MgCl_2$" mixture. It can be concluded from the data in Figure 4*b* that the best "MgH_2 + $MgCl_2$" system performance was achieved at a $MgCl_2/MgH_2$ weight ratio of 12.75/100. This gave hydrogen yield of 1025 mL(H_2)/g per 1 g of the "MgH_2 + $MgCl_2$" system.

The addition of small amounts (17/100 wt. parts) of $MgCl_2$ leads to a factor of ~4 increase in the yield of the hydrolysis reaction, a factor of ~1 decrease in the pH of the working solution and an increase in the hydrolysis product - $Mg(OH)_2$ - precipitate crystallinity. pH of a working solution and conversion of the MgH_2 hydrolysis reaction linearly depend on the logarithm of $MgCl_2$ concentration. pH of the reaction mixture in presence of $MgCl_2$ is well described by considering a system "weak base and its salt with strong acid" type buffer solution. The mechanism of MgH_2 hydrolysis in $MgCl_2$ solutions includes the formation of the buffer solution that controls the pH of the reaction mixture. This leads to a decreasing supersaturation coefficient for the solution by $Mg(OH)_2$ and corresponding increase in the size of the critical nuclei and crystallinity of the precipitates. This is followed by the formation of an inhomogeneous passivation film on the surface of MgH_2.

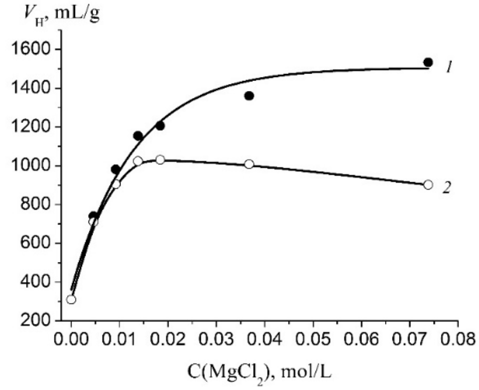


Fig. 3. Dependencies of the volume of H_2 generated per 1 g of MgH_2 and per 1 g of "MgH_2 + $MgCl_2$" system on the $MgCl_2$ weight fraction.

The MgH_2 hydrolysis process involves the hydrolysis reaction, resulting in the generation of hydrogen, and in the formation of $Mg(OH)_2$. It, however, also involves passivation of the MgH_2 surface by the $Mg(OH)_2$ precipitate, followed by its re-passivation. The rate constants for these processes were defined. An increase in $MgCl_2$ concentration leads to just a minor increase in the rate constant for MgH_2 interaction with water. This, however, also leads to a sharp increase in the rate constant of the re-passivation of the MgH_2 surface. Such behavior agrees well with XRD data for the precipitates, which show the formation of a well crystallized $Mg(OH)_2$, causing the formation of an inhomogeneous passivation film on the MgH_2 surface and improved water access to MgH_2.

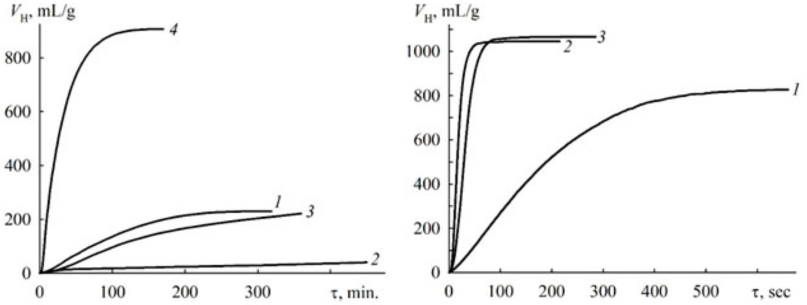
6.2. Al-based materials for hydrogen generation by hydrolysis

Materials preparation and characterization. Both home lab- prepared using the in-house laboratory facilities and commercial aluminum powders were used. Modifications of Al were performed by using low melting eutectic

Ga-based alloys. The following composite materials were studied for the hydrolysis reaction: Al + Ga-In-Sn (3, 5, 7 or 10 wt.%) at 25, 40, 55, 70 °C, PA-4 + 5 wt.% Ga-In-Sn + 0, 1, 3 wt.% C, PA-4 + 5 wt.% Ga-In-Sn-Zn + 3 wt.% C, ASD-1 + 5 wt.% Ga-In-Sn + 1, 3 wt.% C, ASD-1 + 5 wt.% Ga-In-Sn-Zn + 3 wt.% C at 5 and 25 °C.

Hydrolysis reaction studies. Unoxidized aluminum is one of the most promising metals for hydrogen generation from water by the hydrolysis process because it has a very negative value of the standard electrode potential ($E^0(Al^{3+}/Al^0) = -1.662$ V) and reacts with water at ambient temperature. Different methods can be used to activate aluminum by removing or cracking the protective oxide layer at its surface. Our studies showed that alloying of aluminum with low-melting (Ga, In, Sn, Zn) and electropositive (Bi, Sb) metals can be used to obtain active aluminum-based alloys that release hydrogen from water in a broad temperature range. Particularly, aluminum doped with 3, 5, 7 or 10 wt.% of the eutectic Ga-In-Sn alloy (68/22/10 wt.%, melting point 10.7 °C) reacts with water at the temperature of 25 °C, and the rate of the process increases for the higher content of ternary eutectic present in the aluminum alloy [13]. Alloying metals however do not participate in the hydrolysis reaction.

Bismuth and antimony, which have close and very positive values of standard electrode potentials ($E^0(Bi^{3+}/Bi^0) = 0.20$ V, $E^0(Sb^{3+}/Sb^0) = 0.24$ V) and form the corrosive galvanic couples with aluminum, were used as extra additives (3 wt.%) for the aluminum activated by the Ga-In-Sn eutectic (5 wt.%). We showed that the use of Bi and Sb led to a slowdown in the hydrolysis of activated aluminum, which was particularly considerable when Bi was added (Fig. 4*a*) [14]. However, the alloy of aluminum with Ga-In-Sn eutectic and Bi releases hydrogen from water with a practically constant rate for a long time, what is an important advantage when the hydrogen is used for feeding the fuel cells. On the other hand, the use of zinc as an extra additive (3 wt.%) to aluminum activated by the Ga-In-Sn eutectic led to a significant acceleration of the hydrolysis, particularly at lower temperatures (25 and 5 °C) (see Fig. 4*a*) [15]. Thus, the variation of the qualitative and quantitative compositions of aluminum-based alloys makes it possible to significantly change the rate of aluminum hydrolysis and hydrogen generation.



a b

Fig. 4. Time dependencies of the volume of the evolved hydrogen during the hydrolysis of aluminum from: *a* – aluminum alloys with 5 wt.% of eutectic Ga-In-Sn alloy (*1*) and 3 wt.% of Bi (*2*) or Sb (*3*) or Zn (*4*) at 25 °C; *b* – pellets from PA-4 powder activated by Ga–In–Sn eutectic (5 wt.%) (*1*) and graphite (3 wt.%) (*2*, *3*) at 25 °C (*1*, *2*) and 5 °C (*3*).

It is obvious that the high rate of hydrogen generation can be increased by using activated aluminum powders with a large surface area because the hydrolysis is a heterogeneous reaction. We used the aluminum powders PA-1 (grain size ≤ 100 μm) and ASD-1 (grain size <30 μm), which were mechanochemically activated by the Ga-In-Sn or Ga-In-Sn-Zn eutectic alloys (5 wt.%) and graphite (1 - 3 wt.%). Mechanochemical activation was carried out in the SPEX SamplePrep 8000D® Mixer/Mill in an argon atmosphere. Then the activated powders were compressed into the pellets with a mass of 0.2-0.3 g. It was shown that the use of graphite as an extra additive to the activated aluminum powders led to an increase in the rate of aluminum hydrolysis for more than an order of magnitude, and it easily proceeds at temperatures exceeding 5 °C (see Fig. 4*b*). The rate of hydrogen generation and its yield significantly increase with increasing graphite content in the pellets and duration of the mechanochemical treatment of the powders, as well as with decreasing the grain size of the aluminum powders and increasing the hydrolysis temperature [16].

6.3. Hydrogen generation by hydrolysis of $NaBH_4$

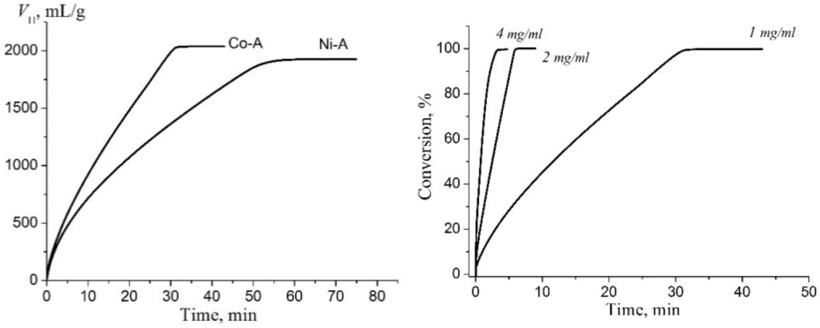
Materials preparation and characterization. Commercial $NaBH_4$ and NaOH were used for the hydrolysis reaction. A series of catalysts to enhance the hydrogen generation rate was prepared by chemical reduction processes. The catalysts were used in as-prepared form or when deposited on the supports (synthetic zeolite or cordierite). Single Co, Ni, Pt, and binary Co-B, Ni-B, (CoNi)-B, Ni-Cu, Ni-Ag catalysts systems were used. Effects of temperature and concentration of $NaBH_4$ and NaOH were studied to optimize the hydrolysis reaction.

Hydrolysis reaction studies. The Ni and Co powders and borides of these elements possess high catalytic activity in the reaction of $NaBH_4$ hydrolysis: $NaBH_4 + 2H_2O \rightarrow NaBO_2 + 4H_2$. We have studied the catalytic activity of the freshly prepared Ni and Co (marked as Ni-A and Co-A). To prevent a possible oxidation of Ni and Co borides, Ni-A and Co-A were synthesized in situ in the reaction mixture used for the hydrolysis experiment (concentration of $NaBH_4$ varied between 0.25…1 mol/L and pH was 12) via a reaction: $2M^{2+} + 4NaBH_4 + 9H_2O \rightarrow 4Na^+ + M_2B + B(OH)_3 + 12.5H_2$. Concentrations of Ni^{2+} and Co^{2+} varied from 0.017 to 0.067 mol/L which corresponds to 1 and 4 mg/mL of the formed catalysts, respectively. We found that (a) the kinetic curves of H_2 evolution are characterized by a presence of a prolonged near-linear section extending to the completion of the reaction which is very attractive for the practical utilization of such systems (Fig. 5); (b) Co-A is a more active catalyst as compared to Ni-A and the values of the specific rate of hydrogen evolution (the rates of hydrogen evolution per 1 g of $NaBH_4$) are equal to 26 and 54 mL/min for Ni-A and Co-A, respectively.

Synthesized zeolite supported samples (Ni-Z and Co-Z) were tested as catalysts of the hydrolysis of $NaBH_4$. It was found that both granulated and milled samples accelerate the hydrolysis reaction.

We have also studied the catalytic activity of zeolite-supported catalysts (Ni-Z and Co-Z). It was found that both granulated and milled samples accelerate the hydrolysis reaction.

A series of hydrolysis experiments was conducted by using two types of the reactors with an aqueous solutions of sodium borohydride and platinum-based catalysts.

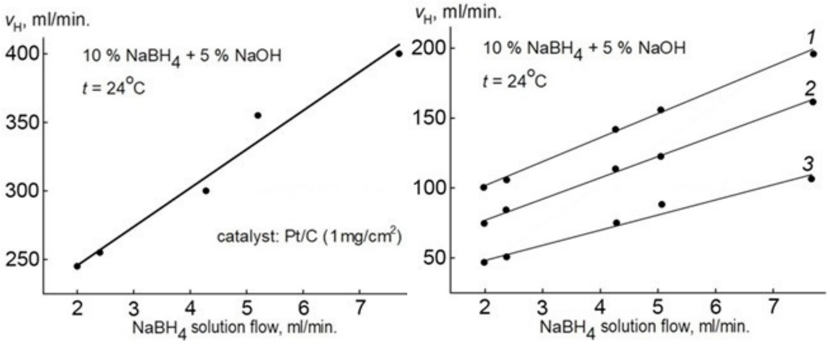


a b

Fig. 5. Dependencies of the volume of H_2 generated per 1 g of $NaBH_4$ as related to the type of the catalyst (*a*) and a conversion extent of $NaBH_4$ hydrolysis on the Co-A concentration (*b*).

The catalyst used in a flat reactor consisted of a nanodispersed platinum deposited on carbon black (XC-72), which, in turn, was immobilized on the surface of carbon cloth (1-2 mg/cm^2). The measured rate of hydrogen evolution in such a reactor at 24 °C was directly proportional to the solution pumping speed and reached 400 mL/min at a circulation rate of sodium borohydride solution of 7.8 mL/min, which is sufficient to provide a stable 30 W power of the hydrogen-oxygen FC with hydrogen used as a fuel. The progression of decomposition of sodium borohydride slows down with increasing rate of pumping the solution through the generator (see Fig. 6*a*).

For a cylindrical reactor, platinum catalysts were prepared by their deposition on various substrates. The regularities of hydrogen evolution in such a reactor are shown in Fig. 6*b*. It can be seen that platinized titanium is less active than the catalyst obtained by the polyol method. During the formation of a roll from the carbon cloth with applied platinum catalyst, the latter peeled off. That is why its activity was lower than in the flat reactor. From the reference data and from our experiments, it follows that it is promising to use a synthetic honeycomb cordierite as a substrate for platinum catalyst. Its use will allow creating a stable and highly efficient reactor for the decomposition of sodium borohydride solution.



a b

Fig. 6. Dependencies of the hydrogen evolution rate on the $NaBH_4$ solution flow rate: *a* – in the flat reactor (catalyst - 13 mg Pt/C on carbon cloth), *b* - in the cylindrical reactor (catalysts: *1* - 100 mg Pt/C on carbon cloth, *2* – 150 mg Pt on 2 g of active carbon (AG-3), *3* – 70 mg Pt on 5g of porous titanium).

6.4. Tests of a pilot hydrogen energy device

Apparatus and installation. Scheme of the fuel cell based hydrogen energy system consisting of a fuel cell stack and hydrogen generator is shown in Fig. 8. The setup for the monitoring of hydrogen generation efficiency during sodium borohydride hydrolysis when using released and supplied to the fuel cell hydrogen includes: a tank with a catalyst (hydrolysis reactor), electronic system for optimizing the performance; peristaltic pump; dc-dc converter; Li-ion battery pack; super-capacitor and a fuel cell connected to the hydrolysis reactor and control system.

Setup testing and technology verification. To ensure a stable operation of a fuel cell and reaching its required performance parameters, the following measures should be adopted: (1) Define the procedures for the system start-up; (2) Ensure start and termination of the operation; (3) Achieve stabilization of the output voltage and control over the hydrogen flow depending on the load (from idle to full power); (4) Monitor the performance parameters during the operation, perform data transfer using computerized recording and data analysis. H-30 Fuel Cell Stack was used as a FC. Output voltage and current depend on a hydrogen supply rate, while the other parameters can considerably vary. The payload is required to keep the voltage stable (12 V), and when the current (i.e., output power) changes, to control the fuel cell, hydrogen flow, and the water pump. For this purpose, a dedicated electronic system has being developed, which consists of a converter-stabilizer of the FC voltage, a battery, a supercapacitor, switches SW1-SW3 and a microcontroller.

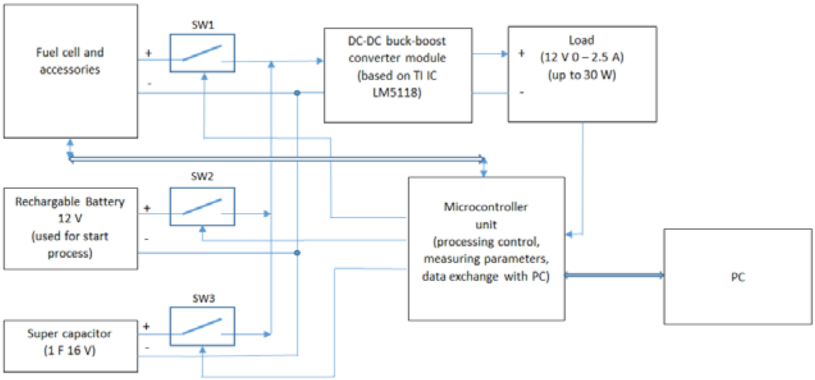


Fig. 7. Scheme of the fuel cell system consisting of a fuel cell stack and hydrogen generator.

The main function of the voltage stabilization is achieved by using a so-called buck-boost converter, which allows to keep a constant output voltage while the input can vary in a broad range (from lower than the output to higher than the output values) while providing a sufficiently high conversion efficiency. A module based on a commercial chip from a renowned supplier was used, which provides an output voltage of 12 V when changing the input from 5 to 16 V.

For initial start-up procedures it is necessary to have an external power supply – a 12 V battery is suitable. When entering the operating mode, the output voltage of the fuel cell may change, and the voltage instabilities are possible. To smoothen them, we use a super-capacitor (SC), which has certain advantages over the battery. The SC is capable of two or three orders of magnitude higher number of the charge-discharge cycles, with a smaller internal resistance as compared to a battery and, because of that a better stabilization efficiency is expected. For switching on-off the current as related to the voltage, the switches SW1-SW3 will be utilized, and the latter will be controlled by a microcontroller (MOSFET or diode, the best options EWMOVW will be selected).

The function of the overall control over the system, measurements of the current and voltage parameters will be performed by an electronic circuit based on a microcontroller (EFM8LB12F64 from Silicon Labs with a rather wide analog peripheral). It will also transfer the measurements data via USB port to a computer to analyze the system performance. The pilot device is shown in Fig. 8.

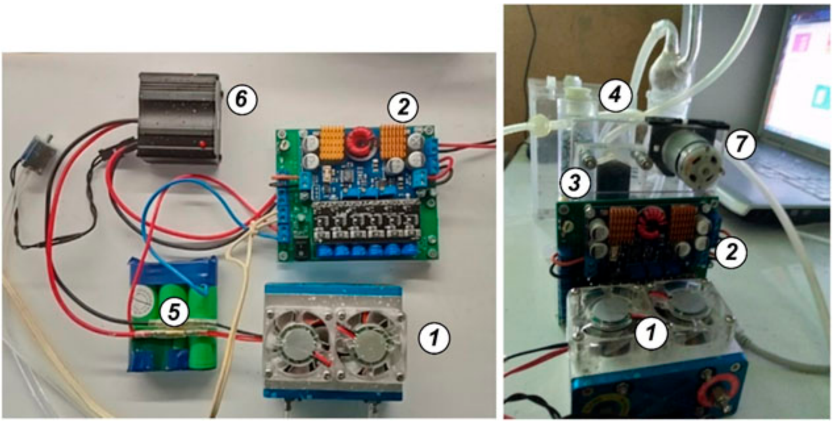


Fig. 8. The pilot device “H_2 generator – Fuel Cell”: 1 - Fuel Cell 30 W Horizon, 2 - voltage stabilizer and device control system, 3 - reactor, 4 - tank for a borohydride solution, 5 - Li-ion battery, 6 - fuel cell control unit, 7 - water pump RS385-635.

Conclusions

1. Portable power supply unit was built by using commercially available components together with parts constructed and manufactured in-house. Different types of hydrolysis reactors and catalytic systems were tested and obtained results show a feasibility of the proposed technology in achieving the goals of the project. We found that PtNPs immobilized on cordierite of honeycomb structure when applied in a cylindrical flow reactor provide

sufficient flow of hydrogen gas used as a fuel to achieve operation of a 30 W stack of fuel cells for 9-10 hours with the weight of the portable setup not exceeding 7 kg. Hydrogen is generated by the hydrolysis of 1.1 L of the $NaBH_4$ solution.

2. Hydrolysis is an expedient and convenient method for hydrogen generation, which allows to conveniently obtain the required amounts of H_2 with controlled rate. Studied in the project catalyzed aluminum powders, magnesium hydride, and sodium borohydride are all efficient materials for hydrogen generation from water for portable power supply.

3. The optimal conditions for the hydrolysis for aluminum are in use of its catalyzed by additives powders. MgH_2 is best hydrolyzed in the solutions of magnesium chloride providing hydrogen generation rate of 80 mL/min per 1 g of MgH_2. For the efficient hydrolysis of sodium borohydride the choice and efficiency of the catalyst is a decisive factor. Due to a low cost combined with the high efficiency (providing the rate of H_2 evolution up to 6000 mL/min per 1g of $NaBH_4$) and reliability, cobalt-based catalysts are considered particularly promising.

4. The work resulted in a publication of 7 papers in the peer-reviewed scientific journals and in 15 conference presentations.

Acknowledgment

This work was supported by the NATO Programme "Science for Peace and Security" (Project G5233 "Portable Energy Supply").

References

[1] Sakintuna B., Lamari-Darkrim F., Hirscher M. Metal hydride materials for solid hydrogen storage: A review. *Int. J. Hydrogen Energy*, 2007, vol.32, pp. 1121-1140.

[2] Huot J., Ravnsbæk D.B., Zhang J., *et al*. Mechanochemical synthesis of hydrogen storage materials, *Prog. Mater. Sci.*, 2013, vol.58, pp.30–75.

[3] Ross D.K. Hydrogen storage: The major technological barrier to the development of hydrogen fuel cell cars, *Vacuum*, 2006, vol.80, pp. 1084-1089.

[4] Gandía Luis M., Arzamendi Gurutze, Diéguez Pedro M. (Eds.). Renewable Hydrogen Technologies. Production, Purification, Storage, Applications and Safety, Elsevier, Amsterdam, 2013, 472 pp.

[5] Yartys V. A., Lototsky M. V. An overview of hydrogen storage methods, *Hydrogen Mat. Sci. Chem. of Carbon Nanomat. (Proceed. ICHMS’2003),* 2004, pp. 75-104.

[6] Jain I.P., Jain P., Jain A. Novel hydrogen storage materials: A review of lightweight complex hydrides, *J. Alloys Compd.,* 2010, vol. 503, pp. 303-339.

[7] Ley M.B., Jepsen L.H., Lee Y.-S. *et al*. Complex hydrides for hydrogen storage – new perspectives, *Mat. Today,* 2014, vol.17, pp. 122-128.

[8] Rango P., Marty P., Fruchart D. Hydrogen storage systems based on magnesium hydride: from laboratory tests to fuel cell integration, *Appl. Phys. A,* 2016, vol.122, 126 (1-20 pp.).

[9] Wang H.Z., Leung D.Y.C., Leung M.K.H., Ni M. A review on hydrogen production using aluminum and aluminum alloys, *Renew. Sustain. Energy Reviews,* 2009, vol.13, pp. 845-853.

[10] Grosjean M.-H., Zidoune M., Roué L., Huot J.-Y. Hydrogen production via hydrolysis reaction from ball-milled Mg-based materials, *Int. J. Hydrogen Energy,* 2006, vol.31, pp. 109-119.

[11] Ouyang L., Ma M., Huang M. *et.al.* Enhanced Hydrogen Generation Properties of MgH_2-Based Hydrides by Breaking the Magnesium Hydroxide Passivation Layer, *Energies,* 2015, vol.8, pp. 4237-4252.

[12] Lewis N.S., Abarbanel H., Bildsten L., et al. JASON report JSR-02-135, The MITRE Corp., McLean, Virginia, June, 2003.

[13] Manilevich F.D., Kozin L.Kh., Danil'tsev B.I., Kutsyi A.V., Pirskyy Yu. K. Regularities of the hydrolysis of aluminum activated with the eutectic alloy of gallium, indium, and tin. *Ukr. Khim. Zh.,* 2017, vol. 83, pp. 51-59.

[14] Manilevich F.D., Pirskyy Yu.K., Kutsyi A.V., Danil'tsev B.I. Regularities of hydrolysis of aluminum activated by Ga-In-Sn eutectic alloy and zinc. *Ukr. Khim. Zh.,* 2020, vol. 86, pp. 63-77.

[15] Manilevich F.D., Pirskyy Yu.K., Danil'tsev B.I., Kutsyi A.V., and Yartys V.A. Studies of the hydrolysis of aluminum activated by additions of Ga–In–Sn eutectic alloy, bismuth or antimony. *Mater. Sci.,* 2020, vol. 55, pp. 536–547.

[16] Manilevich F.D., Pirskyy Yu.K., Kutsyi A.V., Berezovets V.V., Yartys V.A. Studies of mechanochemically activated aluminum powders for hydrogen generation from water. *Powder Metallurgy,* 2021, No. 5/6. pp. 14-24. (in Ukrainian)

List of project publications

Journal articles:

1. F.D. Manilevich, Yu.K Pirskyy, B.I. Danil'tsev, A. Kutsyi, V.A.Yartys. Studies of the Hydrolysis of Aluminum Activated by Additions of Ga–In–Sn Eutectic Alloy, Bismuth, or Antimony. *Materials Science*, 2020, vol. 55 , pp. 536–547.
https://doi.org/10.1007/s11003-020-00336-x

2. Yu.V. Verbovytskyy, V.V. Berezovets, A.R. Kytsya, I.Yu. Zavaliy, V.A. Yartys. Hydrogen generation by hydrolysis of MgH_2. *Materials Science*, 2020, vol. 56, pp. 1–14. *https://doi.org/10.1007/s11003-020-00390-5*

3. D.S. Korablov, O.V. Bezdorozhev, S. Gierlotka, V.A. Yartys, Yu.M. Solonin. Effect of various additives on the hydrolysis performance of nanostructured MgH_2 synthesized by high-energy ball milling in hydrogen. *Powder Metallurgy*. 2020. № 9/10. pp. 3–12. (in Ukrainian)

4. F.D. Manilevich, Yu.K. Pirskyy, A.V. Kutsyi, V.V. Berezovets, V.A. Yartys Studies of mechanochemically activated aluminum powders for hydrogen generation from water. *Powder Metallurgy*, 2021, No. 5/6. pp. 14-24. (in Ukrainian)

5. A.Kytsya, V.Berezovets, Yu.Verbovytskyy, L. Bazylyak, I. Zavaliy, V. Yartys'. Zeolite Supported Ni and Co Catalysts for Hydrogen Generation via Hydrolysis of $NaBH_4$. *Proceedings of the Intern Conf. "Nanomaterials: application and properties"* (NAP-2021), 5-11 Sept., Odesa - Ukraine), *submitted.*

6. V. Berezovets, A. Kytsya, I. Zavaliy, V. Yartys. Kinetics and mechanism of hydrolysis of MgH_2 in $MgCl_2$ solutions. *Int. J. Hydrogen Energy*, 2021, vol. 46, pp. 40278-40293.
http//doi.org/10.1016/j.ijhydene.2021.09.249.

7. A. Kytsya, V. Berezovets, Yu.Verbovytskyy, L. Bazylyak, V. Kordan, I. Zavaliy, V. Yartys. Hydrogen generation by hydrolysis of sodium borohydride catalyzed by bimetallic Ni-Co nanoparticles. *J. Alloys and Comp.*, 2021, *in preparation.*

Selected Conference presentations and public lectures:

1. V. Berezovets, Yu. Verbovytskyy, I. Zavaliy, D. Korablov, Yu. Solonin, R. Denys, F. Manilevich, A. Kutsyi, V. Yartys. Mg and Al based hydrides for the efficient hydrogen generation by hydrolysis process. Col. Abstr. of Int. Symp. on Metal-Hydrogen Systems: Fundamentals and Applications. MH-2018, October 28-November 2, 2018 – Guangzhou (China), 2018. – P.286.

2. V. Berezovets, Yu. Verbovytskyy, D. Korablov, Yu. Solonin, I. Zavaliy, V. Yartys. Mg-based hydrides as a source of hydrogen for autonomous energy devices. Proceedings of the XX International Scientific Conference on Renewable Energy and Energy Efficiency in the 21st Century, May 15-16, 2019, Kyiv, Ukraine. P.198-201.

4. V. Berezovets, Yu. Verbovytskyy, I. Zavaliy, V. Yartys. Mg-based materials for application hydrogen supply systems. 6th Intern. conf. «HighMathTech–2019», 28–30 October, 2019, Kyiv, Ukraine, - P.143.

5. A.Kytsya, V. Berezovets, Yu. Verbovytskyy, I. Zavaliy, V. Yartys Modeling of kinetics of MgH_2 hydrolysis. XVII Scient. Conf. « Lviv Chemical Readings-2019», 02–05 June, 2019 p., Lviv, Ukraine, - M3.

6. V. Berezovets, I. Zavaliy, O. Pavlovska, L Vasylechko., Yu. Kosarchyn. Composites of magnesium hydride with catalytic nanoadditives. Intern. research and practice conference «Nanotechnology and nanomaterials (Nano-2019)», August 27-30, – 2019, Lviv, Ukraine. -P.208.

7. F. Manilevich, Yu. Pirskyy, B. Danil'tsev, A. Kutsyi Activation of aluminum by doping with low-melting metals and regularities of its hydrolysis. Proc. of Ukrainian Conf. with International Participation "Chemistry, Physics and Technology of Surface" and Workshop "Metal-based biocompatible nanoparticles: synthesis and applications". – Kyiv, 2019. – P. 116.

8. Yu. Pirskyy, F. Manilevich, T. Panchyshyn, Ya Kolosovskiy. Bifunctional iridium electrocatalysts for modifying surface of fuel cell proton-conducting membranes. Proc. of Ukrainian Conf. with International Participation "Chemistry, Physics and Technology of Surface" and Workshop "Metal-based biocompatible nanoparticles: synthesis and applications". – Kyiv, 2019. – P. 144.

9. A. Kutsyi, F. Manilevich, B. Danil'tsev, Yu. Pirskyy. Effect of magnesium additions on hydrogen generation in the hydrolysis of

aluminum activated with Ga-In-Sn alloy. Proc. of XVI Intern. Conf."Hydrogen Materials Science and Chemistry of Carbon Nanomaterials". – Kiev, 2019. – P. 28-29.

10. D.S. Korablov, O.V. Bezdorozhev, Yu.M. Solonin. Nanostructured materials based on refractory compounds for hydrogen energy technologies, Abstract book of 7th International conference "Nanotechnology and Nanomaterials" (NANO-2019) 27 - 30 August 2019, Lviv, Ukraine, 173.

11. D.S. Korablov, O.V. Bezdorozhev, Yu.M. Solonin. Effect of 2D titanium carbide (MXene) on hydrogen storage properties of magnesium, Abstract book of VI conference NANSYS-2019, 4-6 December 2019, Kyiv, Ukraine, 78.

12. A. Kytsya, V. Berezovets, L. Bazylyak, Yu. Verbovytskyy, O. Kos Ni-based nanopowders as catalysts of $NaBH_4$ hydrolysis . Book of abstracts Ist International research and practice conference «Nanoobjects & Nanostructuring» (N&N–2020) September 20–23, 2020, Lviv, Ukraine.

13. F.D. Manilevich, Yu.K. Pirskyy, A.V. Kutsyi, V.V. Bereszovets. Mechanical activation of the surface of aluminium powders and regularities of their hydrolysis. Proceedings of Ukrainian Conference with International participation "Chemistry, Physics and Technology of Surface" dedicated to the 90th birthday of Aleksey Chuiko, Academician of NAS of Ukraine. 21-23 October 2020. – Kyiv, 2020. – P. 117. poster

14. A. Kutsyi, F. Manilevich, Yu. Pirskyy, T. Panchyshyn. Obtaining hydrogen by hydrolysis of sodium borohydride to power fuel cells. IV Ukrainian scientific conference "Actual problems of chemistry: research and prospects". (Zhytomyr, April 29, 2020). - Proceedings of the conference. – P. 145-147.

15. F. Manilevich, Yu. Pirskyy, A. Kutsyi, B. Danil'tsev. Influence of zinc on hydrolysis of aluminum activated by Ga-In-Sn eutectic alloy. Proceedings of XXI International Scientific-Practical Conference "Renewable Energy and Energy Efficiency in the XXI Century". (Kyiv, May 14-15, 2020). – P. 239-242.