TARGET COMPLEX PROGRAMME FOR RESEARCH OF NAS OF UKRAINE

Development of scientific bases for hydrogen production, storage and use in autonomous energy supply systems

AUTONOMOUS POWER SOURCE BASED ON FUEL CELLS AND HYDROLYSIS TYPE HYDROGEN GENERATOR

project No 16-20
3rd Milestone

Project leader: head of lab., DrSc. Pirsky Yu.K.
The project team : senior researcher Manilevich F.D., eng. Panchyshyn T.M., eng. Kutsiy A.V., eng. Daniltsev B.I. eng. Bogdanova A.K.
V.I.Vernadsky Institute of General and Inorganic Chemistry NAS of Ukraine

November 2021

Project purpose

The aim of the project is to develop and manufacture an autonomous power source, which will consist of fuel cells and an aluminum-hydrogen generator, using new technical solutions to create a battery of fuel cells and promising energy-storing substances.

Project tasks

- Development of hydrogen-air fuel cells (HAFC) based on high-efficiency membrane-electrode blocks of the new generation.

- Increase of reliability and capacity of HAFC and their batteries by using new technical solutions in the manufacture of advanced membrane-electrode blocks.

- Creation of hydrogen generator with using aluminum based energy-storage substances (ESS) capable to release hydrogen from water at room temperature.

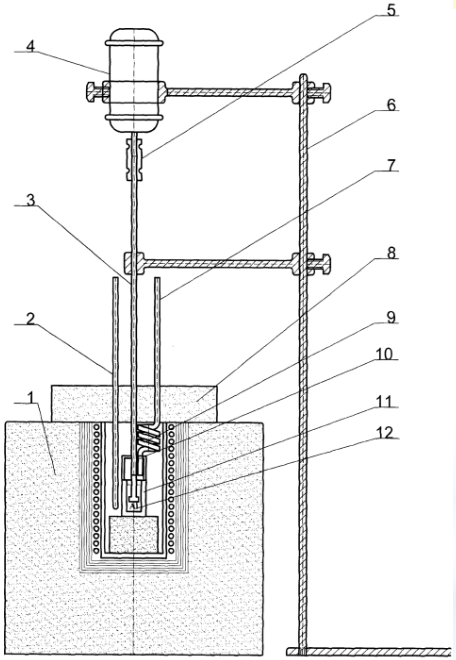
- Use of obtained hydrogen to power the fuel cells of autonomous power source. It is assumed that the use of promising developments will increase the ratio of electricity to the mass of its source.

Aluminum alloys and their hydrolysis

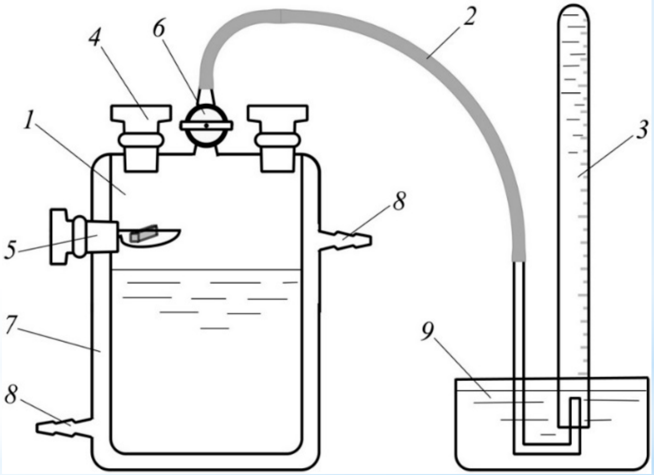
Methods for preparing samples of activated aluminum and volumetric measurements of hydrogen during their hydrolysis

- melting in a mine electric furnace: 900 ºC, 30 min, argon atmosphere, mechanical stirring;
- Pouring out the melt into a flat rectangular graphite or aluminum mold: the thickness of the alloy is about 5 mm.

- sample weight 1 g, volume of distilled water 100 ml, temperature 25-70 ºC.



1 - electric furnace, 2 - thermocouple, 3 - stirrer, 4 - electric motor, 5 - coupling, 6 - rack, 7 - argon supply tube, 8 - lid, 9 - furnace working chamber, 10 - protective cap, 11 - crucible, 12 - melt.



1 - thermostated glass, 2 - tube, 3 - eudiometer, 4 - hole for filling water, 5 - ground glass stopper with a spatula, 6 - faucet, 7 - thermostatted shell, 8 - fittings for connecting a thermostat, 9 - crystallizer.

The use of aluminum-based ESS in hydrolysis-type hydrogen generators

- an effective way of producing hydrogen directly at the place of its use and eliminating problems associated with its accumulation, storage and transportation.

In the absence of a protective film, Al reacts with water with the release of pure H_2:

$$2Al + 3H_2O = Al_2O_3 \text{ (oxide)} + 3H_2,$$

$$2Al + 4H_2O = 2AlOOH \text{ (boehmite)} + 3H_2,$$

$$2Al + 6H_2O = 2Al(OH)_3 \text{ (baerite)} + 3H_2.$$

As a result of hydrolysis of 1 kg of Al, 1245 liters or 0.111 kg of hydrogen are released.

The chosen method for activating aluminum and obtaining Al based ESS capable of releasing hydrogen from water under ambient conditions is alloying with low-melting metals and alloys.

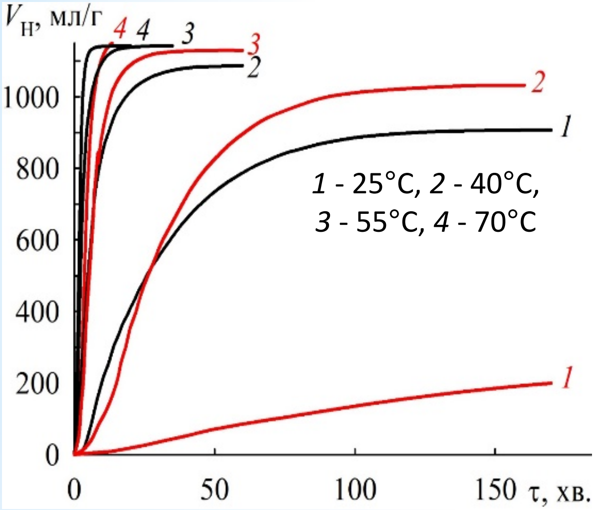
The temperature of the onset of stable interaction of aluminum activated in this way with water is determined by the temperature at which the alloying metals become liquid.

ESS based on the aluminum activated by eutectic alloy Ga-In-Sn and zinc were obtained , and the regularities of their hydrolysis were investigated.

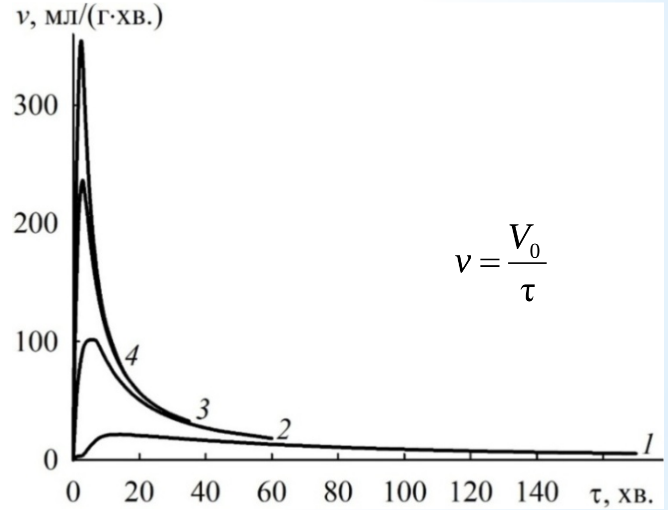
T_{mel} (eutectic Ga-In-Sn) = 10.7 ± 0.3°C; T_{mel} (eutectic Ga-In-Sn-Zn) ~3°C

Regularities of hydrolysis of activated aluminum

Dependences of the volume of released hydrogen on the duration of hydrolysis



Dependences of the average rate of hydrogen evolution on the duration of hydrolysis



Сплави:

Al + Ga-In-Sn (5 wt.%) (—) та Al + Ga-In-Sn (5 wt.%) + Zn (3 wt.%) (—)

- ***The introduction in the alloy Al + 5 wt.% of eutectic alloy Ga-In-Sn of additive zinc (3 wt.%) leads to a significant increase in the amount of released hydrogen, especially at low hydrolysis temperatures (25, 40°C).***
- ***During hydrolysis, the samples of the investigated ESS based on aluminum are quickly cracked and destroyed, resulting in the maximum values of the average rate of hydrogen evolution which are reached in the first minutes of hydrolysis.***
- ***The increase in temperature causes a sharp increase in the rate of hydrogen evolution during the hydrolysis of the studied ESS.***

Comparison of hydrogen yields in the hydrolysis of aluminum activated only by an alloy of Ga-In-Sn (5 wt.%) and with the addition of Zn (3 wt.%)

$$\eta(\%) = V_0/V_{theor} \cdot 100$$

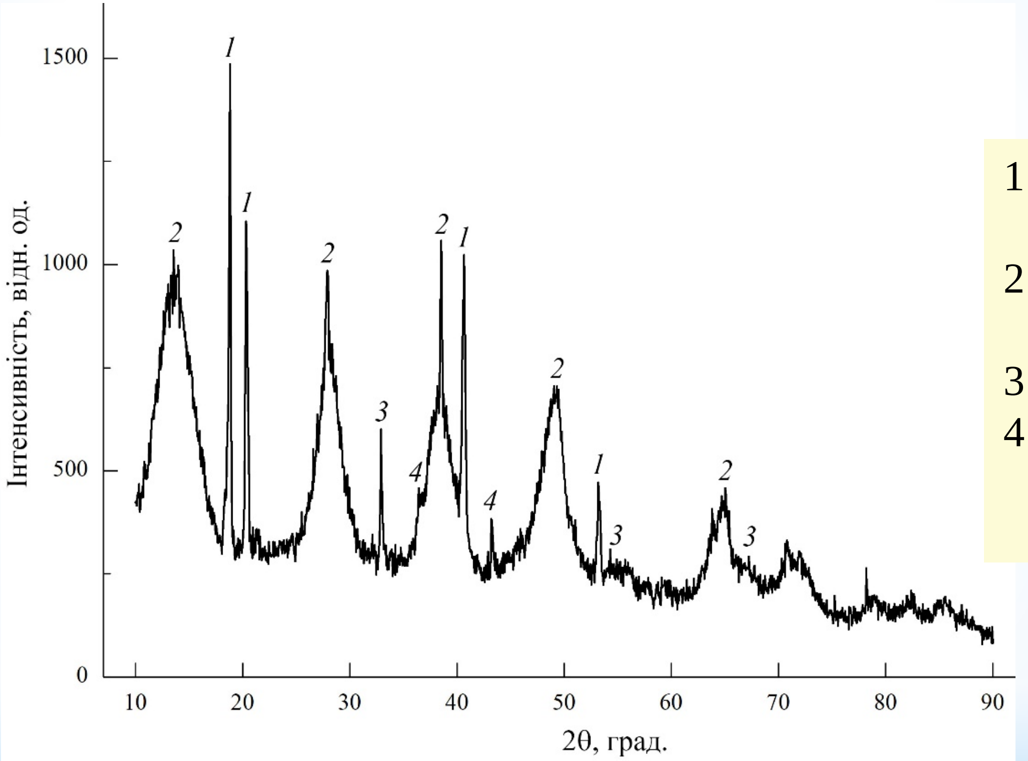
Temperature, °C	25	40	55	70
ESS	Hydrogen yield, % / duration, min.			
Al + 5 wt.% Ga-In-Sn	19.5 % / 320 min.	87.3 % / 147 min.	95.6 % / 50 min.	98.8 % / 23 min.
Al + 5 wt.% Ga-In-Sn + 3 wt.% Zn	79.3 % / 170 min.	95.0 % / 60 min.	99.8 % / 35 min.	99.8 % / 20 min.

- *An increase in the temperature of hydrolysis from 25 to 70°C leads to a significant increase in the yield of hydrogen and a decrease in the time until its maximum values are reached during the hydrolysis of both ESS.*
- *The maximum values of the hydrogen yield are close to 100%, their achievement indicates the completion of the hydrolysis of aluminum.*
- *During the hydrolysis of aluminum activated by the Ga-In-Sn eutectic alloy and Zn, high values of the hydrogen yield were achieved and in a shorter time than during the hydrolysis of aluminum activated only by the Ga-In-Sn eutectic, especially at low temperatures (25 and 40°C) .*
- *The introduction of a zinc (3 wt%) into the Al + 5 wt% Ga-In-Sn eutectic alloy leads to a significant increase in the rate of hydrolysis and the yield of hydrogen at temperatures of 25 and 40°C.*

Investigation of the phase composition of hydrolysis products of aluminum activated by the eutectic Ga-In-Sn alloy (5 wt.%) and Zn (3 wt.%)

The hydrolysis was performed at 55 °C.

The products were dried and ground in a porcelain mortar



1 - bayerite $Al(OH)_3$ (14.7 wt.%);
2 - boehmite AlOOH (84.9 wt.%);
3 - indium (0.2 wt.%);
4 - zinc (0.2 wt.%)

X-ray phase analysis on the Ultima IV diffractometer (Rigaku, Japan)

- ***The main component of the hydrolysis products of the studied ESS at a temperature of 55°C is boehmite.***
- ***In addition, the products include bayerite and small amounts of alloying metals, which do not enter the hydrolysis reaction. Wide peaks on the diffraction pattern indicate nanoscale (10-20 nm) crystallites of hydrolysis products.***

Mechanochemical activation of the surface of aluminum powders

Aluminum powders:

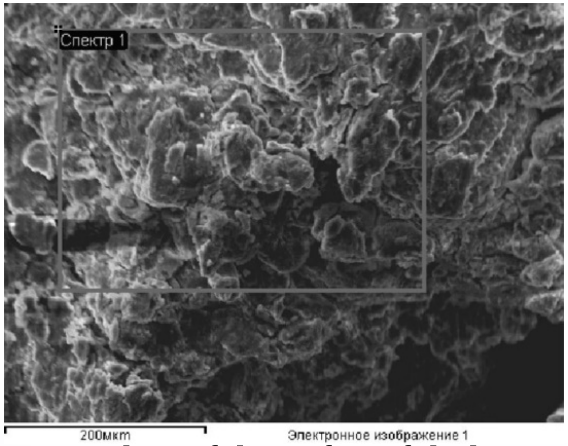
PA-4: non-spherical particle size <100 µm; ASD-1: spherical particle size <30 µm.

Eutectic alloy GaInSn:

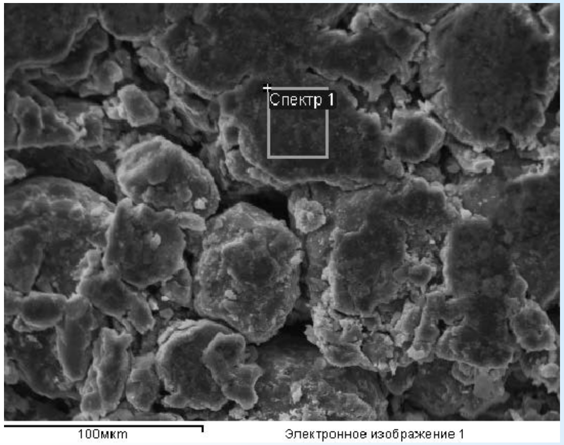
Eutectic Ga-In-Sn alloy: composition (wt%): Ga - 67, In - 22, Sn - 11. Melting point: 10.7 ± 0.3 ° C. Content in the starting mixture: 5 wt%

Aluminum powders were ground together with the GaInSn eutectic in a planetary ball mill (Fritsch Pulverisette P6) with steel balls for 1 hour. at 400 rpm. (PA-4) or 4 years. (ASD-1) and in a ceramic mortar by hand.

Photo of a lump formed in a mill by activated aluminum powder.



SEM photo of the surface of the lump formed by the activated powder PA-4: Al - 89.5, Ga - 4.8, In - 3.4, Sn - 2.3 мас.%.

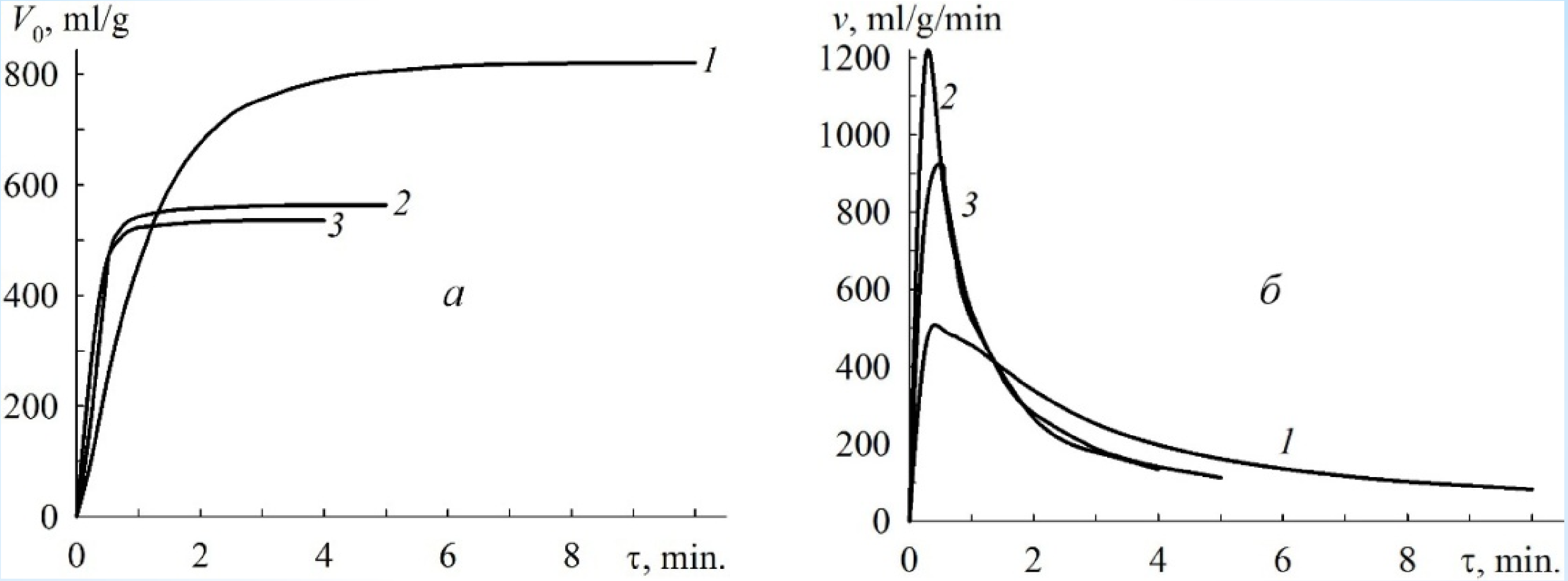


SEM photo of the surface of the lump formed by the activated powder ASD-1: Al – 83.5, Ga – 8.9, In – 4.9, Sn – 2.7 %.

In the planetary mill, a part of the powder enriched with Ga-In-Sn eutectic stuck to the chamber wall. The content of the eutectic alloy in the lump on the wall was much higher and, consequently, the content of aluminum was lower than in the rest of the aluminum powder.

At the ceramic hub, the breasts of aluminum powder with eutectic were not approved.

Investigation of the kinetics of hydrolysis of mechanochemically activated aluminum powders



Dependences of the volume of released hydrogen (a) and the average rate of its release (b) on the duration of hydrolysis at 25°C of the following powders: *1* - PA-4, activated in the mortar; *2* - ASD-1, activated in the mill; *3* - PA-4, activated in the mill.

Mechanochemical activation of aluminum powders by Ga-In-Sn eutectic (5 wt.%) in a planetary ball mill and in a ceramic mortar allows to obtain materials capable of releasing hydrogen from water with high speed at a temperature of 25°C.

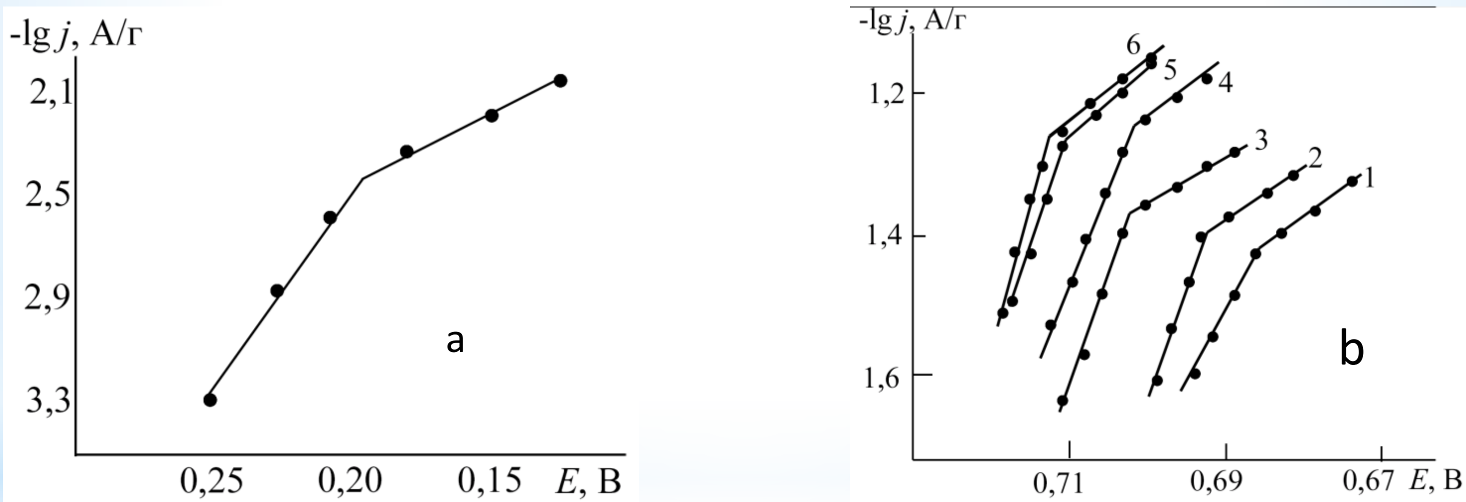
The aluminum powders that formed lumps in the mill reacted with water faster than the powder ground in a mortar, but the yield of hydrogen in the hydrolysis of the latter powder was higher than in the hydrolysis of powders ground in the mill.

Preparation of cathode and anode electrocatalysts

Effect of polyvinylpyrrolidone on the synthesis and catalytic properties of platinum-containing electrocatalysts Pt (40%) / XC-72 for oxygen reduction in fuel cells

Synthesis conditions for Pt (40%) / XC-72 electrocatalysts:

Hexachloroplatinic acid solution H_2PtCl_6, oxidized carbon black Vulcan XC-72, 1 M KOH solution to create the necessary medium (*pH* = 9-12), ethylene glycol, deionized water, polyvinylpyrrolidone (PVP) (C - 100 mg, D - 300 mg and F - 300 mg PVP) and 60 ml 30% formaldehyde (for samples E, F). Heating mode - 130 ° C for A, 160 ° C for sample B, 140 ° C for C and D, 75 ° C for E, F.



Pic. 1. Potentiostatic polarization curves of oxygen reduction on a carbon black + 30% PTFE (a) and Pt on carbon black XC-72 in a 0.5 M solution of H_2SO_4 for electrocatalysts (b): 1 - A; 2 - C (100 mg PVP, 140 ° C); 3 - B; 4 - D (300 mg PVP, 140 ° C); 5 - E; 6 - F (300 mg PVP, 75°C).

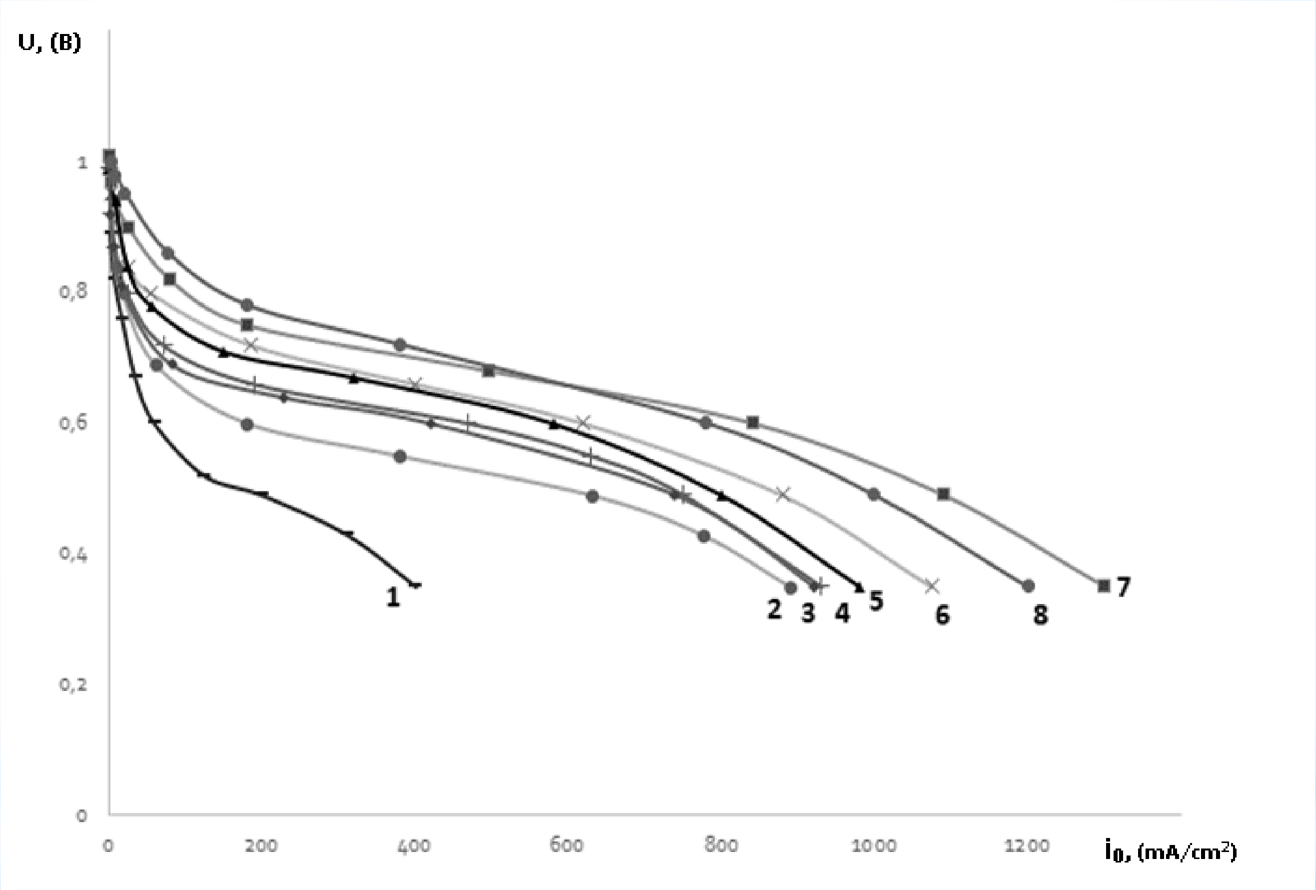
Activity of Pt (40%)/XC-72 electrocatalysts in the reaction of OR:

F (300 mg PVP, 75 ° C)> E (75 ° C)> D (300 mg PVP, 140 ° C)> B (160 ° C)> C (100 mg PVP, 140 ° C)> A (130 ° C).

Kinetic parameters of electrocatalytic oxygen reduction on platinum catalysts in 0.5 M H_2SO_4 solution

№	Catalyst	E_{st}, B	*dE/dlgj*, B		j_o, A/g
			b_1	b_2	
1	Carbon black +30% PTFE	0,264	0,064	0,147	$6{,}53 \cdot 10^{-5}$
2	Synthesis E, 75 °C	0,696	0,050	0,122	0,0216
3	Synthesis D, 300 мг PVP, 140 °C	0,703	0,030	0,130	0,0141
4	Synthesis B, 160°C	0,716	0,033	0,140	0,0164
5	Synthesis C, 100 мг PVP, 140°C	0,700	0,045	0,121	0,0603
6	Synthesis A, 160°C	0,725	0,032	0,110	0,0182
7	Synthesis F, 300 мг PVP, 75°C Controlling the pH of the reaction	0,725	0,028	0,120	0,0188

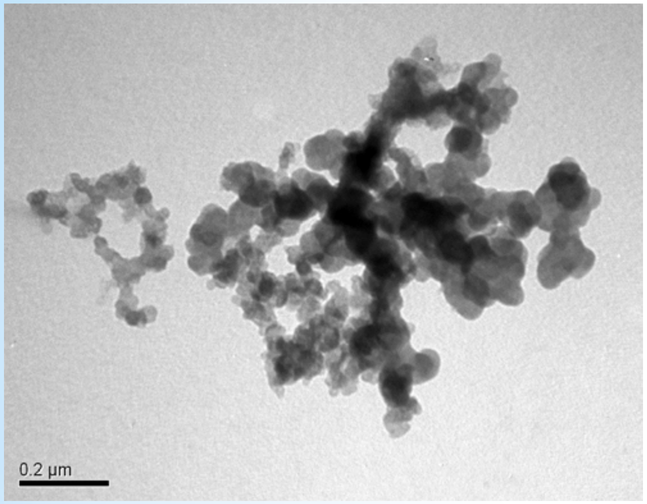
Study of catalysts in a mock-up of a hydrogen-oxygen fuel cell as part of an MEA



Comparison of current-voltage characteristics for using platinum catalysts:
1 - synthesis A (130 ° C); 2 - synthesis E (75 ° C); 3 - synthesis D (300 mg PVP, 140 ° C); 4 synthesis B (160 ° C); 5 - synthesis C (100 mg PVP, 140 ° C); 6 - synthesis G (100 mg PVP, 140 ° C) without control of the pH of the reaction; 7 - synthesis F (100 mg PVP, 75 ° C) with control of the pH of the reaction; 8 - industrial design E-TEK

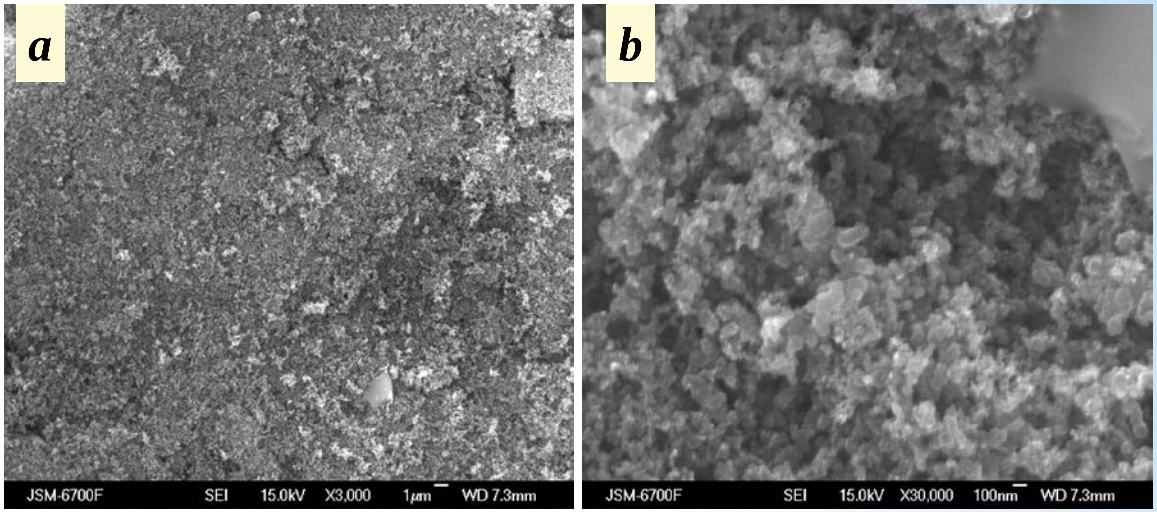
High-resolution photographs of catalysts and SEM photographs of catalyst morphology

TEM micrograph



Leo Supra 50 VP[6] at an increased voltage of 5 kV

Raster photomicrographs



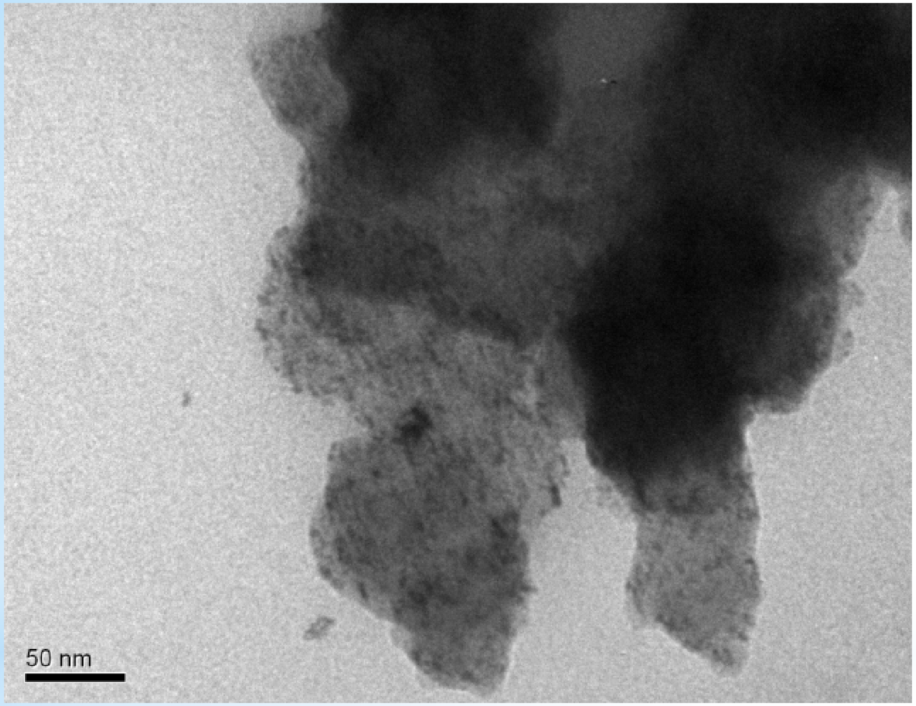
JSM 6700F, increase x 3000 and 30000

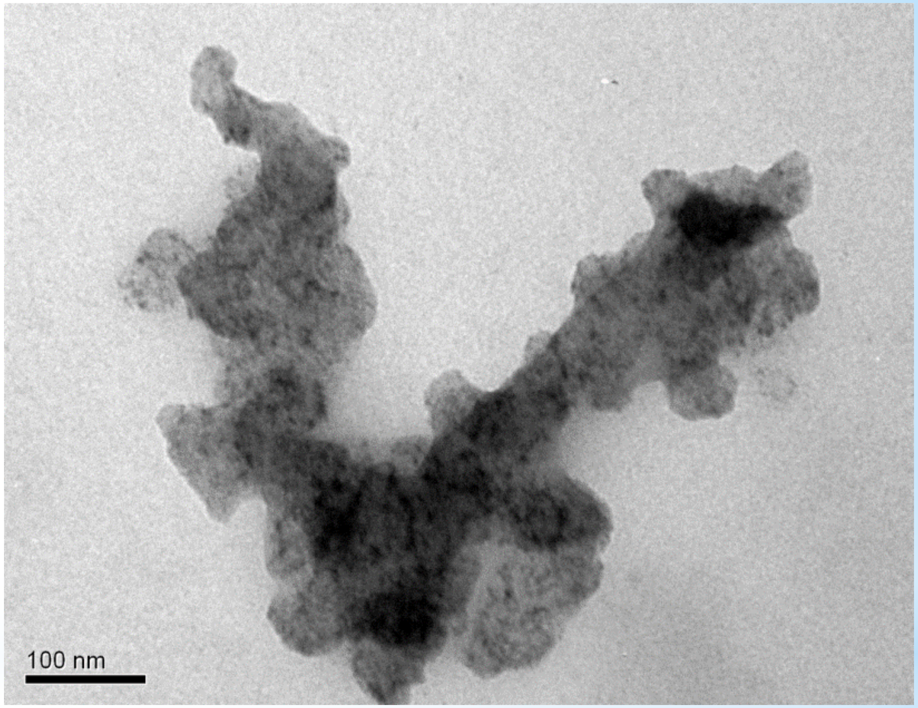
Micrographs of carbon nanoparticles obtained using a transmission electron microscope

Micrographs of carbon nanoparticles obtained with using a scanning electron microscope (resolution: *a* - 1 μm; *b* - 0.1 micron).

Micrographs of platinum nanoparticles of catalysts on a carbon black Vulcan °XC-72, obtained with using a transmission electron microscope

TEM micrographs

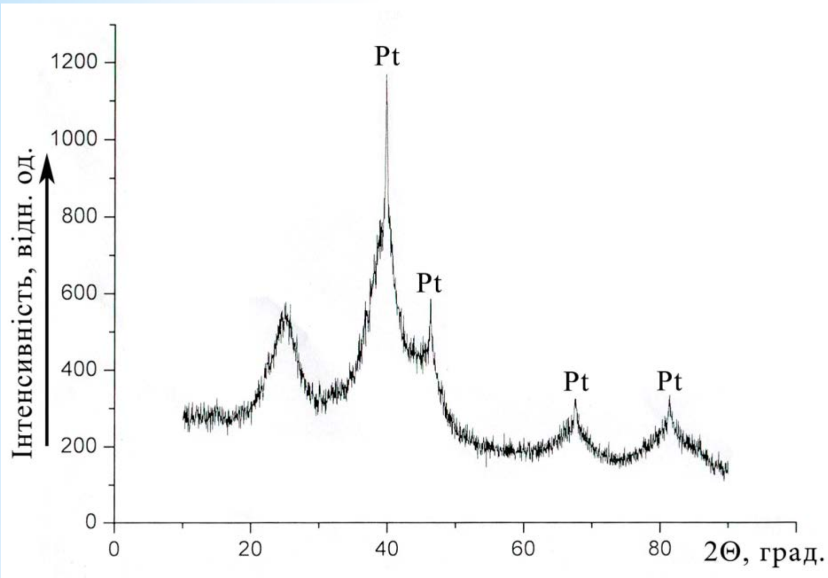




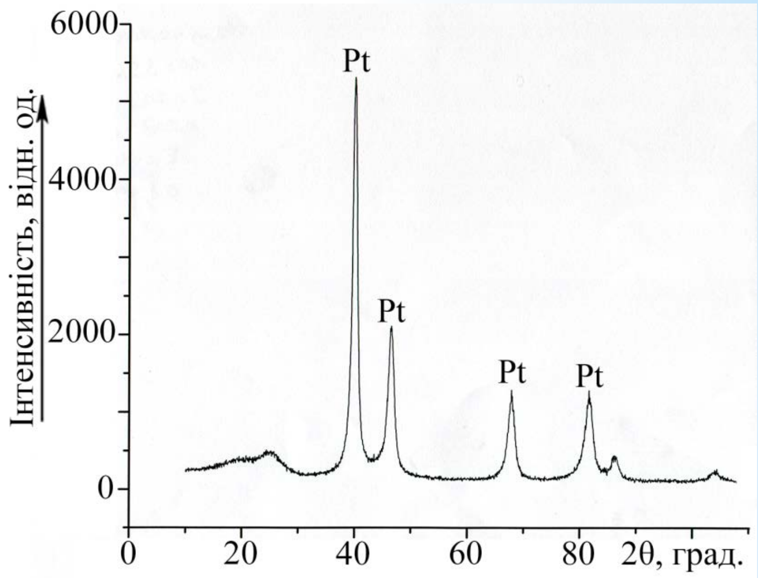
Leo Supra 50 VP[6] at an increased voltage of 5 kV

PEM micrograph of Pt (40%) / XC-72 for samples F (300 mg PVP, 75 ° C), grain size of Pt nanoparticles 2-5 nm.

Diffraction patterns of Pt-composite materials with XC-72



Diffraction pattern of the cathode electrocatalyst Pt10/Vulcan XC-72

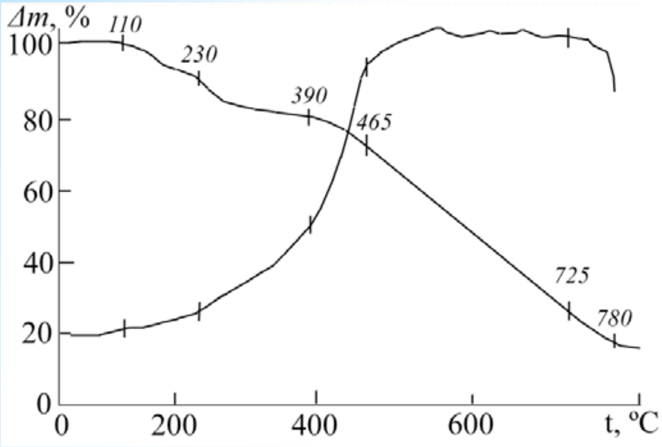


Diffraction pattern of the cathode electrocatalyst Pt40/Vulcan XC-72

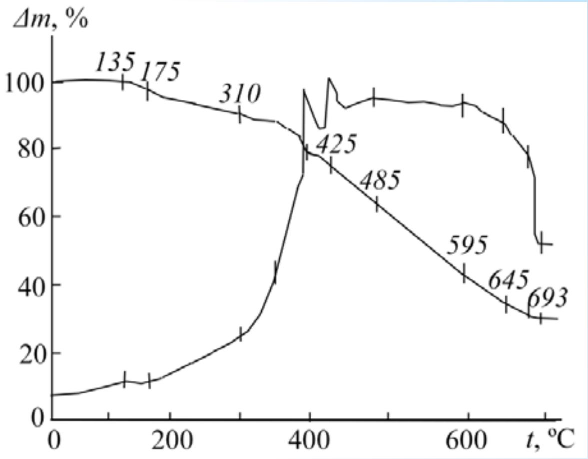
Scherrer Particle Size Chart

D = K · λ / (β · cosθ) = 0,97 · 0,154184 / (0,0349 · cos 0,69464) = 0,1496 / 0,04023 = 5,5 (nm)
The sizes of the nanoparticles were 4.3; 3.7; 2.1; 1.7 nm.

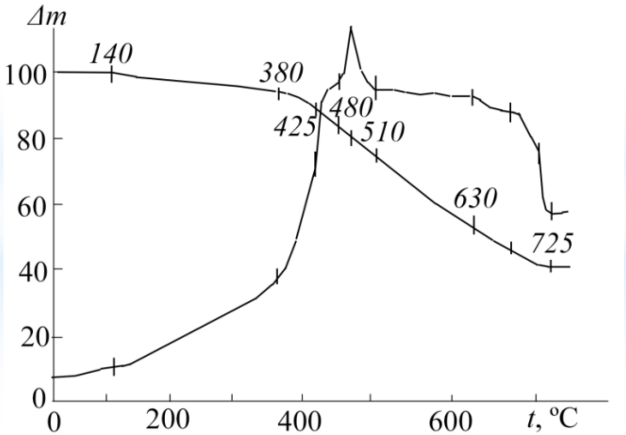
Thermogravimetric analysis of Pt 0/XC-72 electrocatalysts for O_2 reduction and H_2 oxidation versus synthesis parameters



Thermogram for a Pt cathode catalyst on Vulcan XC-72 carbon black after heat treatment and washing for 1 h from impurities

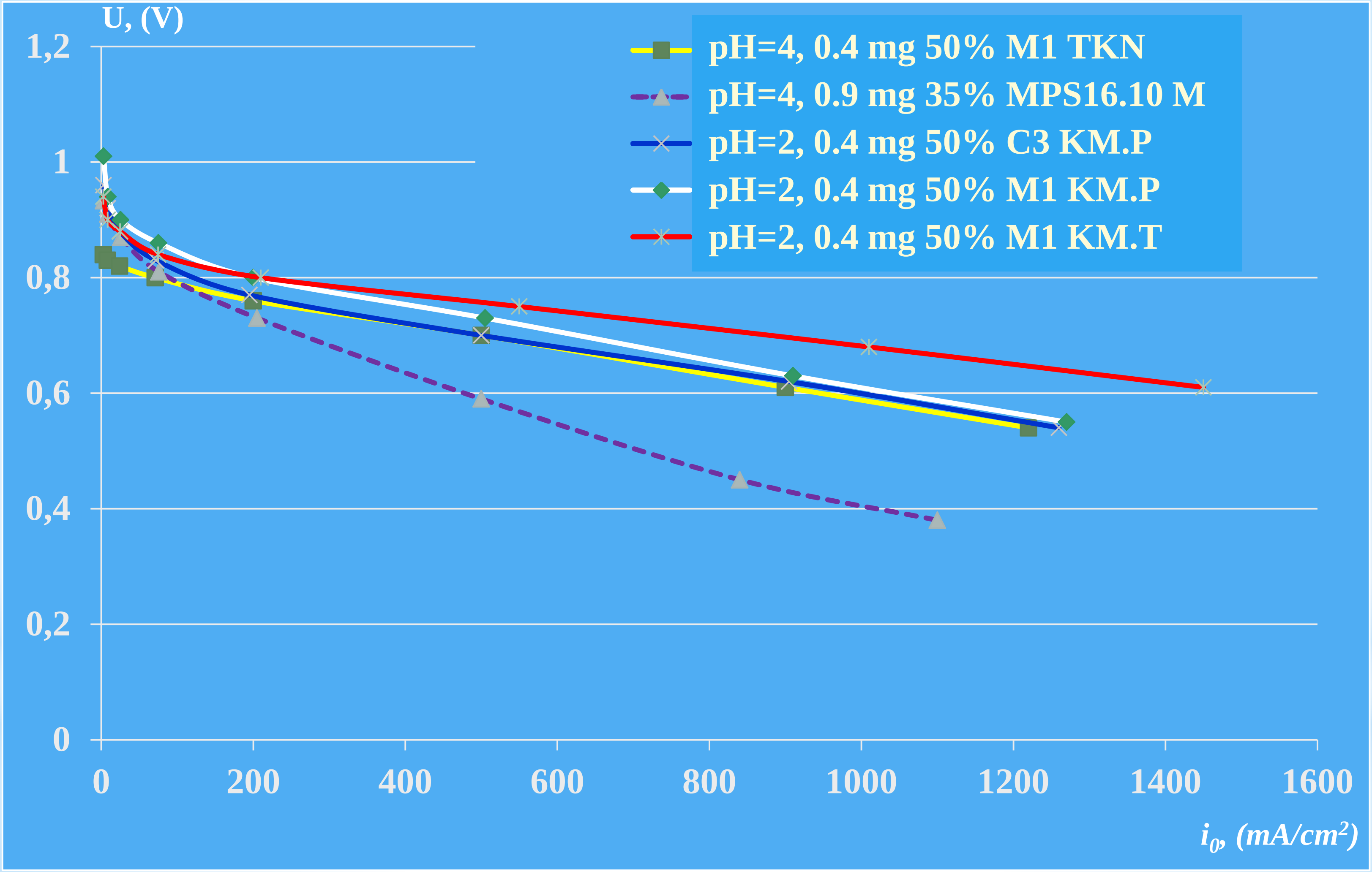


Thermogram for a Pt cathode catalyst on Vulcan XC-72 carbon black after heat treatment and washing for 4 h from impurities



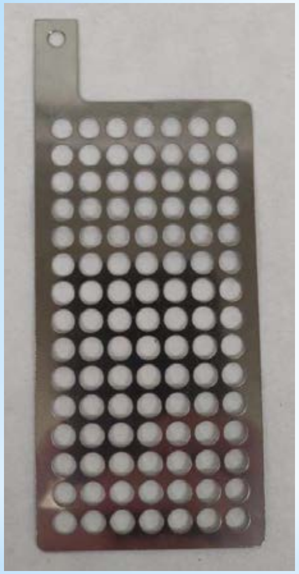
Thermogram for a Pt cathode catalyst on Vulcan XC-72 carbon black after heat treatment and washing for 12 h from impurities

Results of work on the development of catalytic ink for application on gas diffusion layers

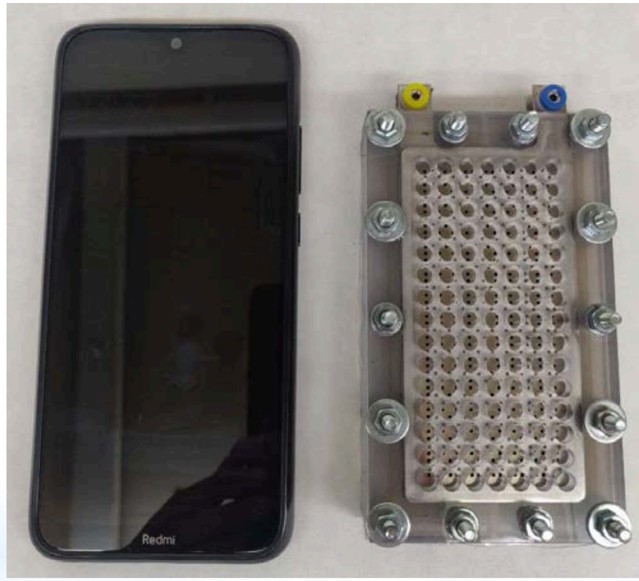


Charger based on fuel cells and an aluminum-hydrogen generator

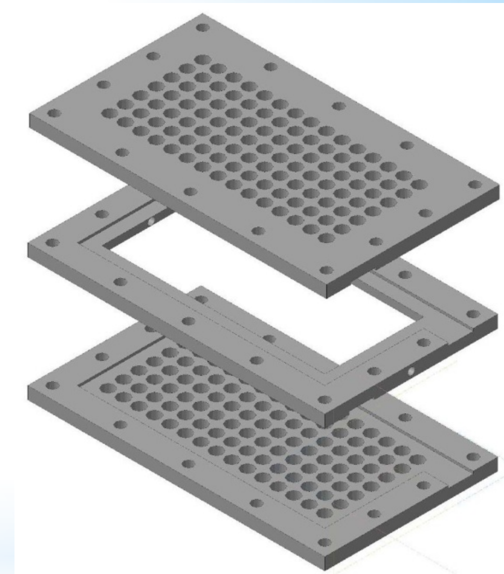
Components of combined fuel cell



Current supplyfor the combined fuel cell



Combined fuel cell for charger with energy-storage materials (aluminum-based)



Details of the combined fuel cell

Combined fuel cell assembly

Necessary components and components (combined fuel cell body parts, sealed diaphragm-electrode unit gaskets) for experimental samples of hydrogen-air cells and their batteries have been developed and manufactured.

Scheme of a stand-alone charger based on fuel cells and an aluminum-hydrogen generator

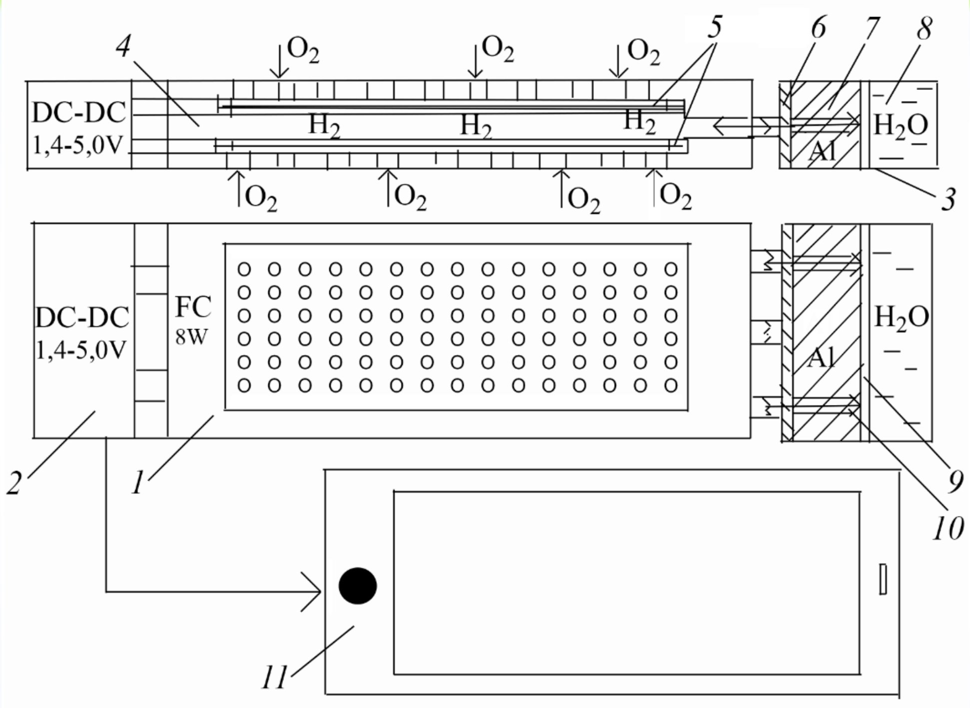


Fig. 3. Scheme of an autonomous charger based on fuel cells and an alumohydrogen generator: combined fuel cell (*1*); DC-DC voltage converter (*2*); hydrolysis-type hydrogen generator (*3*); hydrogen cell (*4*); membrane-electrode blocks (*5*); water-retaining separator (*6*); activated aluminum powder (*7*); container with water (*8*); porous membrane (*9*); activating needle (*10*); energy consumption device, e.g., smartphone (*11*)

The hydrogen-air fuel cell will be powered by hydrogen from a hydrolysis-type hydrogen generator, in which activated aluminum in powder form will be used as an energy storage substance. During the hydrolysis of activated aluminum powders at room temperature, hydrogen will be generated from the water in an amount sufficient to power the fuel cells or their batteries and ensure the operation of an autonomous power source. As a result of activation on the surface of the grains of powders of activated aluminum, its alloys with alloying elements are formed, which makes it possible for aluminum to interact with water.

Conclusions

1. It was shown that as a result of activation on the surface of grains of powders of activated aluminum, alloys with alloying elements are formed, which makes possible the interaction of aluminum with water. The introduction of a zinc additive (3 wt%) into the Al + 5 wt% Ga-In-Sn eutectic alloy leads to a significant increase in the rate of hydrolysis and the yield of hydrogen at temperatures of 25 and 40 ° C.

2. The activation of aluminum powders of grades PA-4 and ASD-1 with the eutectic alloy Ga-In-Sn (5 wt.%) By grinding in a planetary ball mill with steel balls for 1 hour (PA-4) or for 4 hours (ASD -1) at a rotation speed of 400 rpm. or in a ceramic mortar by hand. It was found that some of the powders activated in the mill formed lumps, which, according to the data obtained using an EVO 40XVP scanning electron microscope with an INCA Energy microanalysis system, are enriched in the Ga-In-Sn eutectic (≫5 wt%) localized on the grain surface aluminum. Powder grains, which were not included in the composition of lumps, had an insignificant amount of eutectic alloy (5 wt%) on their surface.

3. The regularities of hydrolysis of the obtained powders at 25 C were investigated by periodically determining the volume of hydrogen released during hydrolysis in a volumetric installation. It was found that the mechanochemical activation of aluminum powders with the GaInSn eutectic (5 wt%) in a planetary ball mill and in a ceramic mortar makes it possible to obtain materials capable of releasing hydrogen from water at a high rate at a temperature of 25 ° C, but the distribution of the eutectic alloy in the materials of the mill is very uneven.

3. New methods for the synthesis of platinum-containing nanodispersed electrocatalysts immobilized on Vulcan XC-72 carbon black for hydrogen-ear fuel cells were developed, and anodic and cathodic Pt(40 %)/XC72 electrocatalysts were synthesized. The efficient catalytic inks were developed for applying catalysts onto gas diffusion layers formed on a proton-exchange membrane.

4. The autonomous power supply has been developed based on the hydrogen generator of hydrolysis type and portable battery of hydrogen-air fuel cells. As a result of the combination of fuel cells and a hydrogen generator of a hydrolysis type, an autonomous power supply was created in which hydrogen, produced in the generator as a result of the interaction of Al-based ESSs with water, feeds the fuel cells.

5. The results of this work can find application in the creation of energy storage substances for use in highly efficient hydrolysis-type hydrogen generators for various purposes, including supplying hydrogen to fuel cells. The closest analogues of the developed autonomous charger based on an alumohydrogen generator and fuel cells with a power of 5-10 W are: MiniPAK/Horizon Fuel Cell (2.5 W, fuel – hydrogen, cartridge), Dynario™ Toshiba (5 W, fuel – methanol, cartridge), HandyPower (10 W, fuel – hydrogen obtained as a result of hydrolysis of activated aluminum, cartridge). The level of technological readiness of the development is IRL3, TRL4. The development is ready for the customer to issue a specific performance specification.

Intellectual property: Vernadsky Institute of General and Inorganic Chemistry, NAS of Ukraine, Palladina Prospekt, 32/34, Kyiv, Ukraine, 03142.

Main publications on the project 2019-2021

1. **F.D. Manilevich, Yu.K. Pirskyy, A.V. Kutsyi, B.I. Danil'tsev. Regularities of hydrolysis of aluminum activated by Ga-In-Sn eutectic alloy and zinc. *Ukrainian Chemistry Journal,* 2020, vol.86(2), pp. 63-77. https://doi.org/10.33609/0041-6045.86.2.2020.63-77 (in Ukrainian).**
2. **F.D. Manilevich, Yu.K. Pirskyy, B.I. Danil'tsev, A.V. 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.**
3. **Yu.K. Pirskyy, F.D. Manilevich, T.M. Panchyshyn, Ya.V. Kolosovskiy, O.G. Alabut. Effect of polyvinylpyrrolidone on the synthesis and catalytic properties of platinum-containing oxygen electroreduction catalysts. *Ukrainian Chemistry Journal,* 2020, vol.86(7), pp. 53-64. https://doi.org/10.33609/2708-129X.86.7.2020.53-64 (in Ukrainian).**
4. **F.D. Manilevich, Yu.K. Pirskyy, A.V. Kutsyi. Promising hydrolytic methods of hydrogen generation for fuel cells // In: *Electrochemistry of today: achievements, problems and prospects*. - Kyiv: MPBP "Gordon", 2021, pp. 167-168. https://doi.org/10.33609/978-966-8398-64-3.01.2021.1-191 (in Ukrainian).**
5. **Yu.K. Pirskyy, F.D. Manilevich, A.V. Kutsyi. Autonomous power supply based on fuel cell battery and hydrolysis type hydrogen generator // In: *Electrochemistry of today: achievements, problems and prospects*. - Kyiv: MPBP "Gordon", 2021, pp. 70-71. https://doi.org/10.33609/978-966-8398-64-3.01.2021.1-191 (in Ukrainian).**

Vernadsky Institute of general and inorganic chemistry of the Ukrainian National Academy of Sciences

prospekt Akademika Palladina, 32/34, 03142-Kiev, Ukraine