TARGET COMPREHENSIVE PROGRAM
OF THE SCIENTIFIC RESEARCHES
OF NAS OF UKRAINE

Developing the scientific principles of hydrogen generation, storage and use in the autonomous power supply systems

RESEARCH OF THE PROCESSES AND IMPROVEMENT OF THE DESIGN AND TECHNOLOGICAL PARAMETERS OF HIGH PRESSURE ELECTROLYSIS SYSTEMS INTENDED FOR THE AUTOMOMOUS HELIO-HYDROGEN POWER SUPPLY PLANTS

Project № 2
Term of implementation: 03.06.19 – 31.12.21.

Scientific Leader: V.V. Solovey, Dr. of Techn. Science
Performers: M.M.Zipunnikov, Ph.D, senior research officer, I.O.Vorobjova, head technologist,
V.M. Semikin, head engineer, L.I.Golubtnko, engineer.
A.M.Pidhorny Institute of Mechanical Engineering Problems of NAS of Ukraine

Project Aim:

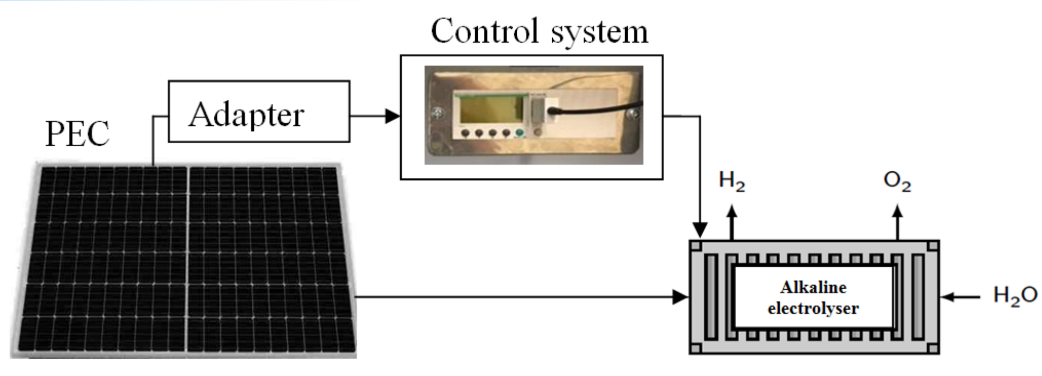
research of the processes of hydrogen (oxygen) production and improvement of the design and technological parameters of the hydrogen membrane-less high pressure electrolysis systems operating in composition with the photoelectric converters.

Project Tasks:

- **developing the schemes for connecting a photoelectric converter to a high-pressure cell and determining the potential possibility for hydrogen production, taking into account volatility of solar power generation;**
- **studying the hydrogen generation electrochemical process that provides minimal electricity consumption and can be realized in the autonomous energy complex using power of the renewable energy source (sun)**;
- **creating a mock-up of a power plant with a photoelectric converter and a high-pressure electrolyzer, experimental studies of its operation depending on changes in solar insolation and testing the effective modes of maximum gas evolution;**
- **developing a method for calculating the parameters of feed water replenishment to ensure the optimal concentrations of alkali in the electrolyte during electrolysis.**

A mock-up of the autonomous helio-hydrogen power plant with PEC and membrane-less HPE

Structural lay-out of a power plant mock-up with PEC and HPE

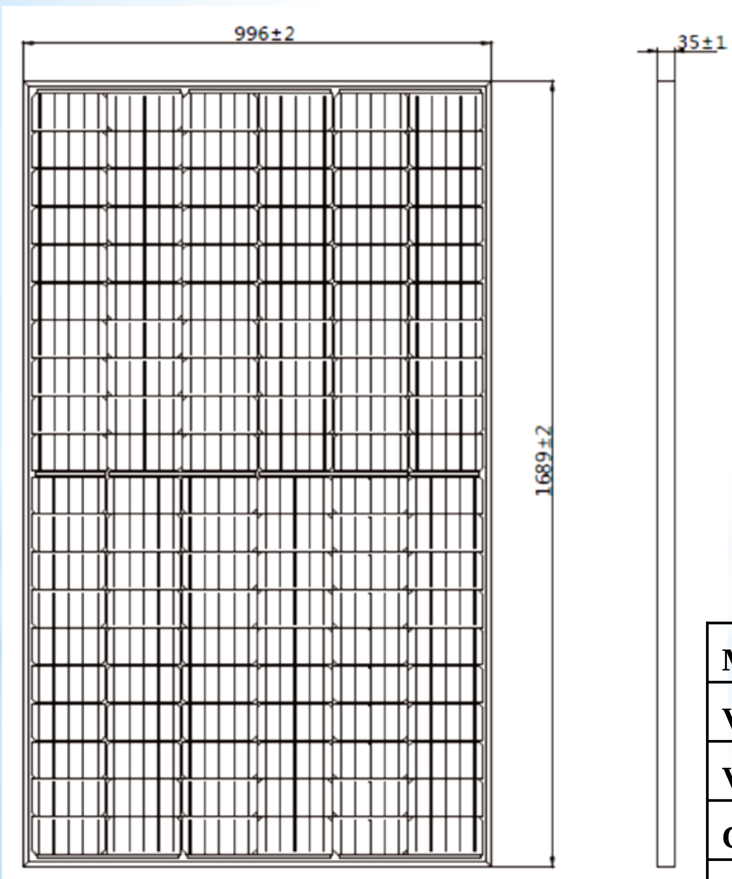


DM-0.002-3 deemonstration membrane-less electrolyzer

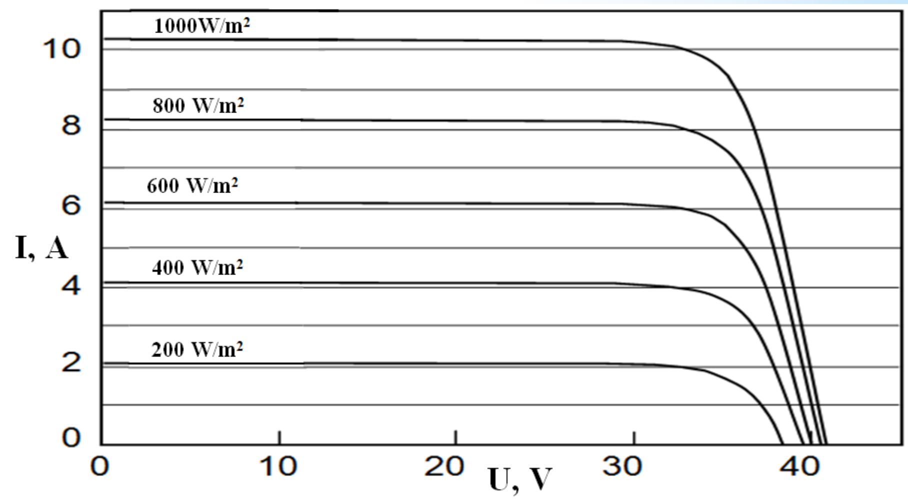
JAM60S10-330/PR sun photoelctrical module of "JA SOLAR Technology" Company in the nature condition

Parameters of the sun photoelectrical converter of the “SOLAR Technology” Company

Design lay-out of the JAM60S10-330/PR PEC



JAM60S10-330/PR PEC volt-ampere characteristics under various insolation



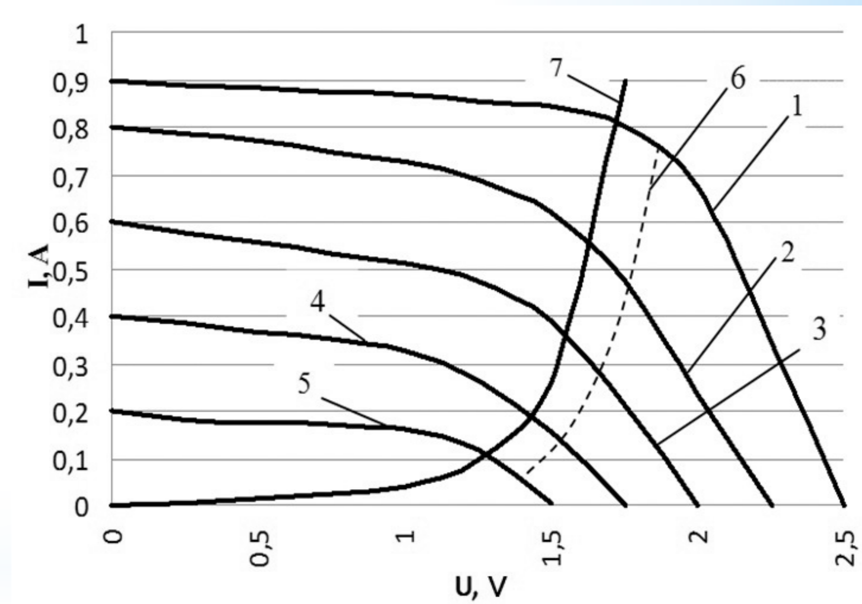
JAM60S10-330/PR PRC electrical parameters under insolation of 800 W/m², environment temperature of 25 °C, wind velocity of 1 м/s

Maximal Power (P_{max}), W	244
Voltage of the unlocked circuit (U_{oc}), V	37,65
Voltage at the maximal power point (U_{mp}), V	33,82
Current of short circuit (I_{sc}), A	8,25
Current of maximal power point (I_{mp}), A	7,22

Experimental research of joint operation of an electrolysis cell with a sun PEC

Experimental laboratory plant with PEC in nature condition

Volt ampere characteristics of the alkali electrolyzer and PEC (under various levels of the sun insolation)



PEC is of the TOPRAY SOLAR Company:

– short circuit current $I_{кз}$ = 1.07 A;

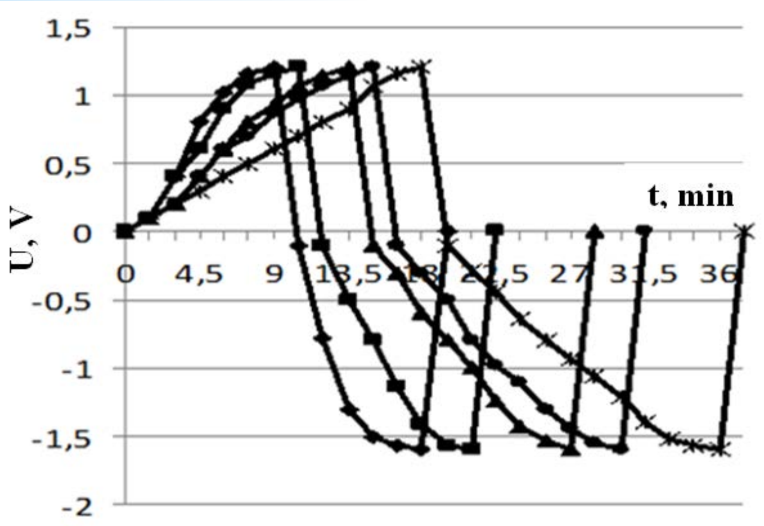
– idling voltage U_{xx} = 22.4 V;

– total surface area S = 0.288 m^2.

1 – June (47.2 kW·h); 2 – September (30.2 kW·h);
3 – March (26.35 kW·h); 4 – November (10.28 kW·h);
5 – December (7.77 kW·h);
6 – maximal power of the solar panel;
7 – electrolyzer volt ampere characteristic

Results of experimental research of the electrode twin electrochemical activity depending on the insolation level (current density)

Voltage change during whole cycle of hydrogen and oxygen generation when 08X18H10T - Fe_p twin is used under electrolysis for various levels of solar insolation



♦ – June (5.46 кW·h/(m²·day));
■ – September (3.49 кW·h/(m²·day));
▲ – March (3.05 кW·h/(m²·day));
● – November (1.19 кW·h/(m²·day));
× – December (0.9 кW·h/(m²·day)).

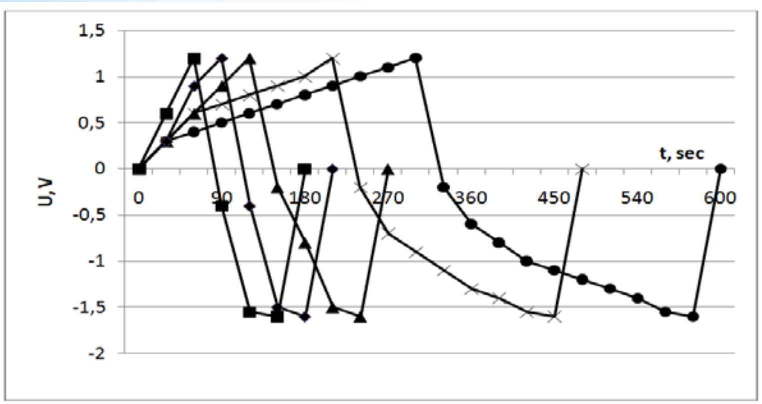
08X18H10T - Fe_p twin electrochemical activity depending on current density

Electrode material	Current density, A/cm²	Duration of H_2 evolution half cycle, min	Volume of generated hydrogen, ml	Volume of Generated oxygen, ml	Active electrodemass, g
08X18H10T–Fe_p	0.0255	9	30	15.0	13.6
	0.0227	11	27	13.5	
	0.0170	14	24	12.0	
	0.0110	16	22	11.0	
	0.0057	18	16	8.0	

The electrolysis cell was connected directly to the TOPRAY SOLAR PEC during experiments

Results of experimental reseach of joint operating the PEC and membrane-less HPE under various insolation levels (current density)

Voltage change during whole cycle of hydrogen and oxygen generation under various insolation levels



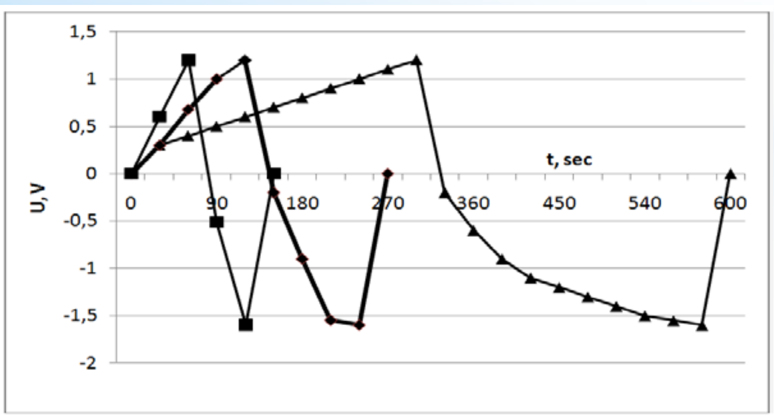
■ – 136 A/m²; ♦ – 106 A/m²; ▲ – 91 A/m²; × – 60 A/m²; ● – 45 A/m²

$08X18H10T\text{-}Fe_p$ twin electrochemical activity depending on current density (various insolation)

Electrode material	Current density, A/m^2	The electrolyzer specific capacity for hydrogen, $m^3/(m^2 \cdot h)$	Specific electricity consumption, $kW \cdot h/m^3$	Active electrode area, m^2
$08X18H10T\text{-}Fe_p$	45	5.1×10^{-3}	4.70	0.066
	60	7.7×10^{-3}	4.10	
	91	16.2×10^{-3}	4.02	
	106	21.4×10^{-3}	3.96	
	136	25.8×10^{-3}	4.00	

The electrolysis cell was connected to JAM60S10-330/PR PEC of JA SOLAR Technology Company directly during experiments

Voltage change during whole cycle of hydrogen and oxygen generation when electrolyzer is fed from the electrical network



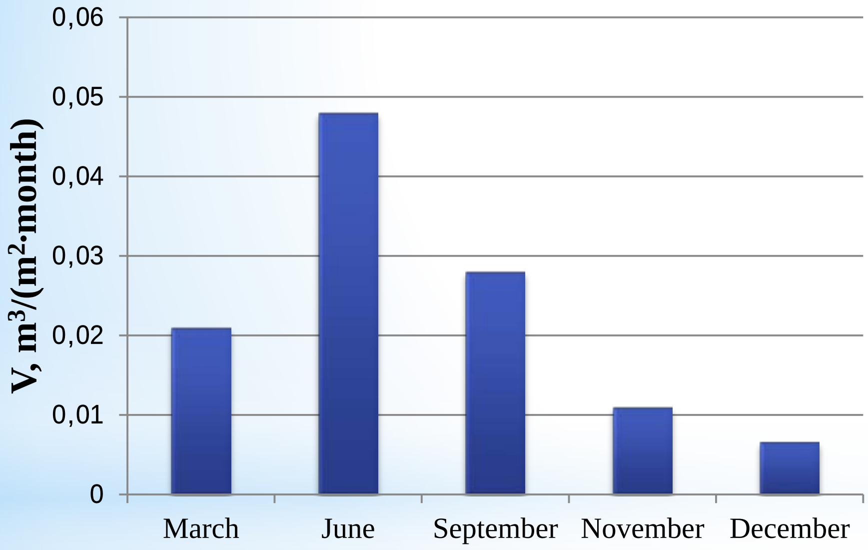
■ – 136 A/m²; ♦ – 91 A/m²; ▲ – 45 A/m²

$08X18H10T\text{-}Fe_p$ twin electrochemical activity depending on current density (feeding from the electrical network)

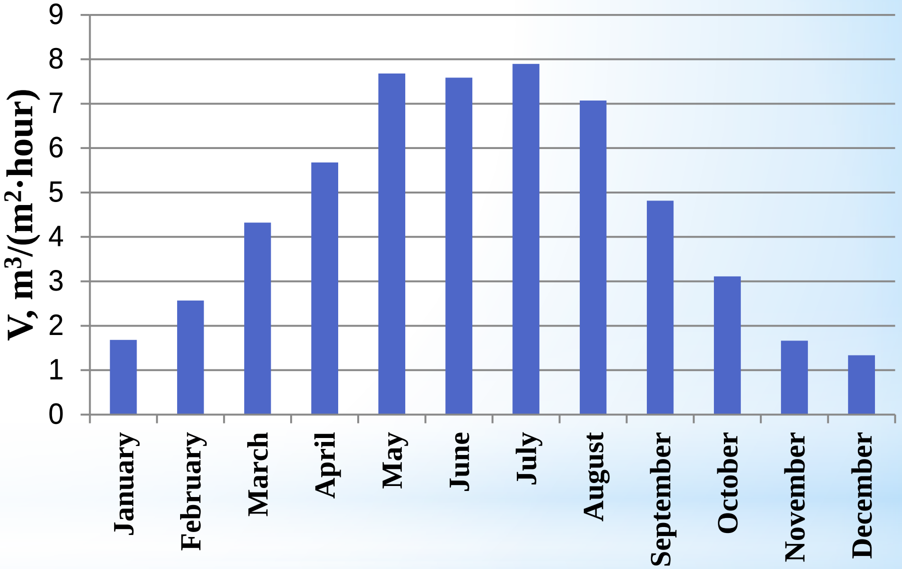
Electrode material	Current density, A/m^2	The electrolyzer specific capacity for hydrogen, $m^3/(m^2 \cdot h)$	Specific electricity consumption, $kW \cdot h/m^3$	Active electrode area, m^2
$08X18H10T\text{-}Fe_p$	45	4.9×10^{-3}	4.20	0.066
	91	16.2×10^{-3}	4.02	
	136	29.8×10^{-3}	4.00	

Capacity of the electrolysis cell by hydrogen generation taking into account insolation

Month hydrogen generated volume when the electrolysis cell is fed from PEC (S = 0,288 m^2) in various seasons (various insolation levels)



HPE month specific capacity by hydrogen taking into account insolation (on 1 m^2 of PEC surface)



M-lHPE specific capacity by hydrogen

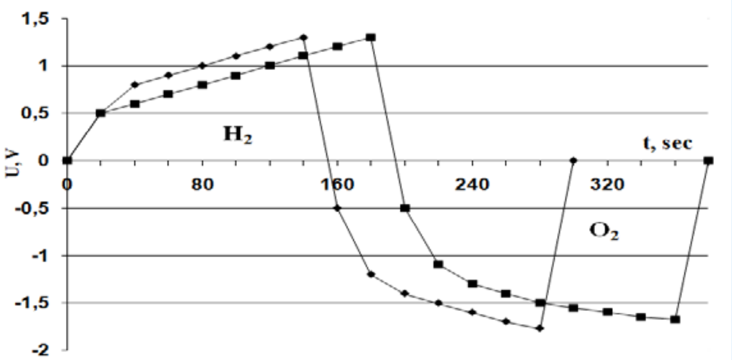
Current density, A/m^2	45	91	150	250	350	450
The electrolyzer specific capacity for hydrogen, $m^3/(m^2 \cdot h)$	5.1×10^{-3}	16.2×10^{-3}	30.4×10^{-3}	54.6×10^{-3}	78.7×10^{-3}	102.8×10^{-3}

Influence of the constructive elements of the electrode twin on its electrochemical ativity under water electrolisis

Pt - Fe_p twin electrochemical activity

Active electrode area (Fe_p), cm^2	Current, A	Passive electrode area (Pt), cm^2	Current density, A/cm^2	Volume of hydrogen released, m^3/h	Volume of oxygen released, m^3/h	Specific electricity consumption, $kW \cdot h/m^3$
31	0.48	12.57	0.015	0.34×10^{-3}	0.17×10^{-3}	3.72
	0.96	12.57	0.030	0.44×10^{-3}	0.22×10^{-3}	3.85

Voltage change during whole cycle of hydrogen (oxygen) genertion when the Pt – Fe_p cathode-anode twin is used



1 – 0.015 A/m^2; 2 – 0.03 A/m^2

Influence of the distance between electrodes on electrochemical parameters of Pt - Fe_p twin

Active electrode area, cm^2	Current, A	Current density, A/cm^2	Distance between electrodes, mm	Gas evolution voltage, V		Change in standard Gibbs energy, –G, kJ/kg	
				H_2	O_2	H_2	O_2
31	0.47	0.015	2.0	0.30	–1.2	4.846×10^6	19.384×10^6
			3.0-4.0	0.10	–0.8	1.615×10^6	12.923×10^6
			6.0	0.25	–1.1	4.038×10^6	17.769×10^6

Method for calculating the support of given alkali concentration range in the electrolyte under water electrolysis

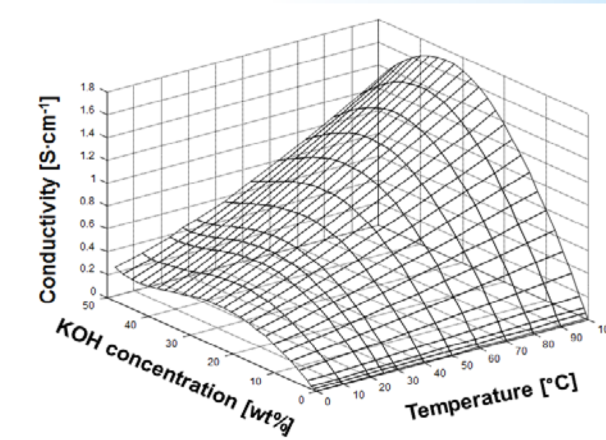
Maximal specific electrical conductivity of electrolyte under KOH concentration of 28 - 33 %.

Under electrolysis process of hydrogen (oxygen) generation, water is consumed from the electrolyte and alkali, being in the solution, provides the ions transfer.

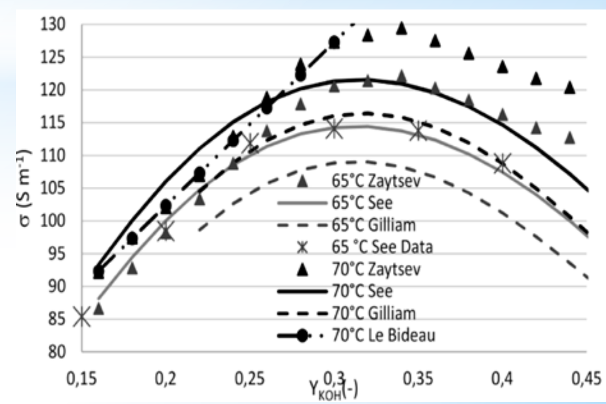
So, it needs to add some water periodically. It is done when the limit minimal electrolyte volume is achieved.

In this case the electrolysis process take place undert changeable alkali concentration in tj\he electrolyte. It leads to change the electrolyte specific electrical conductivity and causes additional energy consumption.

Specific electrical conductivity of KOH water solutions



Dependence of specific electrical conductivity of KOH water solutions on alkali oncentration



Method for calculating the support of given alkali concentration range in the electrolyte under water electrolysis

The water mass in the electrolyte is

$$m_w = m_{wt} + m_{wcons} ,$$

where m_{wt} is the mass of the technological water volume in the electrolyte;
m_{wcons} is the mass of the consumable water volume in the electrolyte.

When the alkali is dissolved in water, the volume of the electrolyte is equal to water volume

$$V_{el} = V_{wt} + V_{wcons}$$

The mass of the consumable part of water in the electrolyte composition

$$m_{wcons} = m_{wt} \cdot K_{\Delta C} ,$$

where $K_{\Delta C} = \dfrac{1 + \frac{C_{max}}{1 - C_{max}} - \frac{1}{1 - C_{min}}}{\frac{1}{1 - C_{min}} - 1}$ is the coefficient taking into account the change of the alkali concentration in the electrolyte during electrolysis;

C_{min} is the alkali concentration in the electrolyte at the initial moment after water adding;
C_{max} is the alkali concentration in the electrolyte after entire consumption of the consumable part of water.

The volume of the electrolyte

$$V_{el} = V_{wt} (1 + K_{\Delta C})$$

The time of consuming the consumable part of the water in the electrolyte

$$\tau_{cons} = \frac{m_{wcons}}{P_{H2} \cdot \gamma_{cons}} ,$$

where P_{H2} is the electrolyzer hydrogen productivity;
γ_{cons} is the consumption of feed water to obtain 1 m^3 of hydrogen.

Electrolyte parameters under exploatation of the developed at IPMash electrolyzers

Electrolyzer	P_{H2}, m^3/h	V_{el}, *l*	m_{wt}, kg	m_{wcons}, kg	C_{min}	C_{max}	γ_{cons}, kg/m^3	τ_{wcons}, h
EHP 1.0-150	1.0	182.6	142.0	40.6	0.25	0.30	0.82	49.5
EHP 0.5-150	0.5	91.3	71.0	20.3				49.5
EHP 0.02-150	0.02	12.9	10.0	2.9				176.8

$K_{\Delta C} = 0.286$

The module design of the membrane-less high pressure electrolyzers provides the possibility for increasing the electrolyzer capacity due to increasing the module number with identity of electrolysis process. Such condition provides the same duration of consumption of the consumable part of water τ_{wcons} in the EHP 1.0-150 and EHP 0.5-150 electrolyzers.

Method for calculating the alkali current concentration in electrolyte under electrolysis

The current concentration of alkali in the electrolyte during the production of consumable water by electrolysis

$$C_i = \frac{1}{\frac{m_{wt}}{(m_{wt} + V_{Hi} \cdot \gamma_{ccons}) \cdot \left(\frac{1}{1 - C_{init}} - 1\right)} + 1},$$

where C_i is the current concentration of alkali in the electrolyte during the water electrolysis;
C_{init} is the concentration of alkali in the electrolyte at the initial moment of operation of the electrolyzer or after replenishment of feed water;
V_{Hi} is the volume of hydrogen produced after replenishment of feed water, or the volume of hydrogen calculated by the formula

$$V_{Hi} = \tau_i \cdot P_{H2} ,$$

where τ_i is the current duration of the electrolyzer operation without replenishment of feed water.

The change of the current concentration of KOH in electrolyzers EHP 1.0-150, EHP 0.5-150 and DM-0.002-3

Electrolyzer	V_{Hi}, m^3	C_i, %
EHP 1.0-150	1.3	25.14
	2.1	25.27
	5.4	25.58
	11.9	26.27
	18.2	26.92
EHP 0.5-150	0.6	25.13
	2.4	25.52
	7.3	26.55
	9.8	27.06
	12.3	27.57
DM-0.002-3	0.0007	25.006
	0.0016	25.014
	0.0029	25.261

Conclusions

- **The efficiency of the membrane-less HPE was confirmed when its connecting directly to the PEC (without secondary transducers). There is no need for inverter equipment and special settings.**
- **It was determined that at direct connection the solar panel provides power supply for electrolyzer completely in all range of solar insolation change. An important component of reliable and efficient operation of solar helio-hydrogen plants is the coordination of the PEC and gas generation system operation.**
- **It was experimentally determined that when the Pt – Fe_p electrode stack is used for hydrogen generation, the optimal distance between the electrodes is in the range from 3 mm to 4 mm, which corresponds to the hydrogen evolution minimum initial voltage of 0.1 V and oxygen evolution of 0.8 V.**
- **It is investigated that electro-generation by PEC (i.e. current density at electrolysis) depends on insolation. At the same time, the specific electricity consumption at all modes of HPE operation practically does not change (3.96 - 4.1 kW·h/m^3), which confirms the efficiency of the electrolysis process in the whole range of insolation changes. The HPE hydrogen performance and the specific energy consumption when HPE is powered by PEC are almost no different from the similar parameters when HPE is powered by the mains. Therefore, there is no need in special settings.**

Conclusions

- **It was developed a method to calculate the parameters of feed water replenishment and to determine the current alkali concentration during electrolysis, which gives the possibility for:**
  - to reduce energy consumption during electrolysis, providing the optimal range of changes in the electrolyte specific conductivity by selecting of the limit concentration values of alkali in the electrolyte by optimizing the water supply to the electrolysis cell;
  - to analyze the efficiency of the applied electrolytes at a variable alkali concentration, taking into account the specific electrolyte conductivity.

- **The use of renewable energy for production of epy environmentally friendly green hydrogen by the alkaline water electrolysis is an important step towards the decarbonization of industrial processes and the transport sector. It ensures the sustainable hydrogen production without carbon dioxide emissions.**

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**A. Podgorny Institute of Mechanical Engineering Problems, NASU,
2/10 Pozharsky St., Kharkiv, 61046, Ukraine**

Thank you for attention

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