

Alkaline matrix water electrolyzers and regenerative systems

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Introduction

It is known that NPP and HPP have excessive capacity at night-time because of non-uniform power consumption. As noted in [1], Leningrad NPP can generate along about 400 mln. kW·h/year in such hours of load reduction, allowing the generation of approx. 8,000 t of hydrogen per year by modern electrolyzers. The situation seems to be the same and at another plants. The resultant hydrogen would be more economically used in Fuel Cell (FC) power plants. Also it would be attractive to use electroextracted oxygen in the same FC, because, as shown in [2, 3], substitution of oxygen for air at FC cathodes results in the power increase of these power plants by a factor of 3 to 4 with unchanged mass and dimensions parameters. The consumption of precious metals is reduced by the same factor, and pneumatic-hydraulic circuits of power plants can be simplified noteworthy.

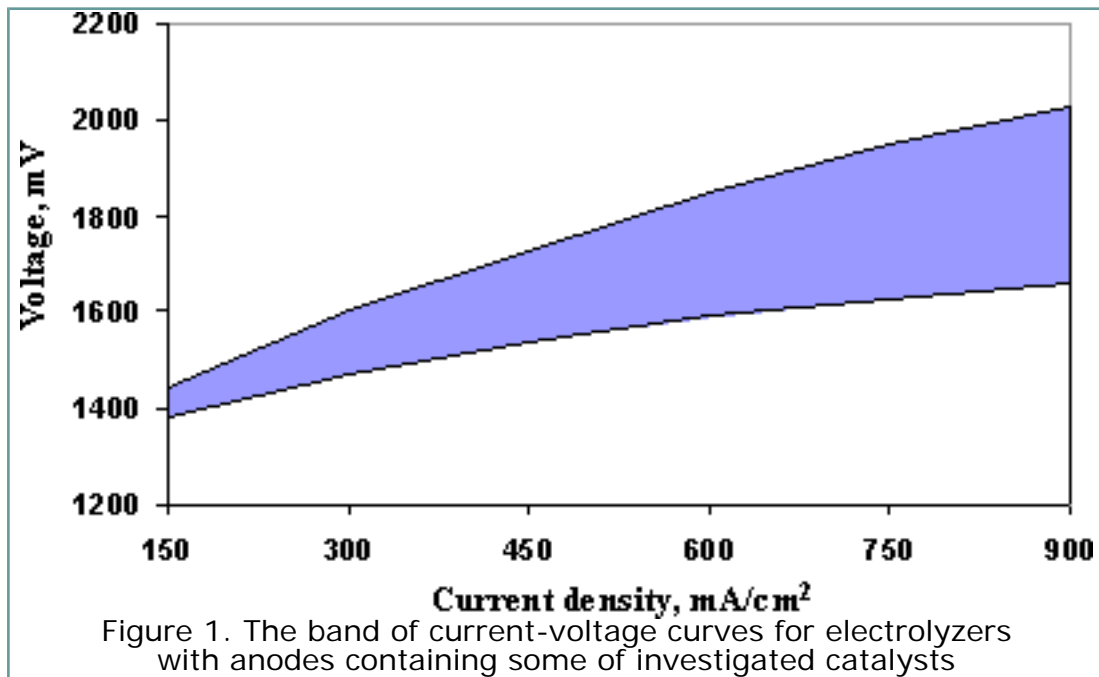
When transporting electrolytic gases to the areas of consumption, it is necessary either to condense or compress them. Compressing appears to be the simplest for wide employment. To get rid of compressors and additional energy consumption required for these purposes, it is necessary to produce gases in high-pressure electrolyzers.

Furthermore, in view of outlined tendencies for creation of alternative distributed power with application of renewed energy sources (solar, wind, tide, biofuel), the creation of regenerative systems is gaining a significant importance, in which hydrogen and oxygen are produced by electrolysis under the influence of natural factors, and at the absence thereof, the electric energy is generated in fuel cells through the use of product gases.

Alkaline Matrix Water Electrolyzers

In parallel with Alkaline Matrix Fuel Cell Generators, UEIP was engaged in the development of electrochemical energy storage units of matrix type and laid a scientific and technological groundwork that can be used for the development of hydrogen and oxygen generators in a broad range of capacity and pressure:

1. The stacks containing multicell assemblies of matrix water electrolyzers and fuel cells combined in one module between two end plates and having common gas and heat carrier loop were developed, manufactured and tested. Different versions of electrolyzer anode catalysts made of platinum-group metals were tested being included in these stacks. Figure 1 shows the band of current-voltage curves for electrolyzers with anodes containing some of investigated catalysts. They were determined at a temperature of 95°C and pressure of 0,4 MPa. Based on the test results, the catalyst content was optimized for anode oxygen evolution. A total absence of electrolyte removal from electrolyzers was shown, and opportunity of long-term operation for multicell stacks of water electrolyzers was confirmed.



2. Electrolyte transfer in multicell stack was experimentally investigated. As a result, a total absence of electrolyte transfer in gaseous phase as well as negligible rate of electrochemical transfer by ultrafine films in multicell stack collector was shown. (Leakage currents in multicell stacks associated with electrolyte migration amount to $5 \mu\text{A}$ at a lifetime of more than 1,500 h).
3. Multicell stacks for nickel-hydrogen storage batteries with common gas collector in one solid vessel were developed, manufactured and tested. The components of singular nickel-hydrogen storage battery are similar to those of a fuel cell, and stack design is based on the main engineering solutions developed for the fuel cell stacks. Hydrogen pressure in the stack vessel of nickel-hydrogen storage batteries varies between 0 and 12 MPa in the process of charge-discharge cycle. Continuous operation time of stacks in space achieved more than 8 years. The investigation of electrodes after long-term stack operation demonstrated their practical invariance.
4. UEIP has a pilot production of fuel cells of TЭ-176 type (with active area of 176 cm^2), fuel cell stacks and fuel cell generators on the basis of this standard size. About 300 FC stacks were produced, each of which had 128 fuel cells. The production can be renewed, if necessary.
5. The manufacture of pilot samples was prepared for TЭ-700 fuel cells (with active area of 700 cm^2) and fuel cell stacks on the basis of this standard size.
6. Equipment was developed for pneumatic-hydraulic circuits of FC generators providing heat- mass-exchange processes (water separator-humidifier (evaporator), temperature regulators, pressure regulator, etc.), which can be used as analogues when creating key devices for operation of water electrolyzer stacks.

Based on these developments, the electrolyzers in a wide range of capacity and pressure can be created, as well as regenerative systems that will provide both the water electrolysis and product hydrogen and oxygen consumption in fuel cells, which will convert these gases in water with simultaneous generation of heat and electricity.

High Pressure Electrolyzers

UEIP has developed a mathematical model of High Pressure Electrolyzer and made calculations. A preliminary engineering study was performed.

The design of such Water Electrolyzer Stack (WES) will consist of series-connected Electrolysis Cells (EC) in an amount corresponding to specified voltage and hydrogen

and oxygen capacity. Figure 2 shows a section of assembly made of a number of FC. All these elements are identical with electrolysis cell components. The stack assembly is comprised of a porous matrix and bipolar electrode. The later contains a frame with a heat carrier channel. Collector plates as well as cathode and anode are securely fixed to the frame. An external view of above-listed components is shown in Figure 3.

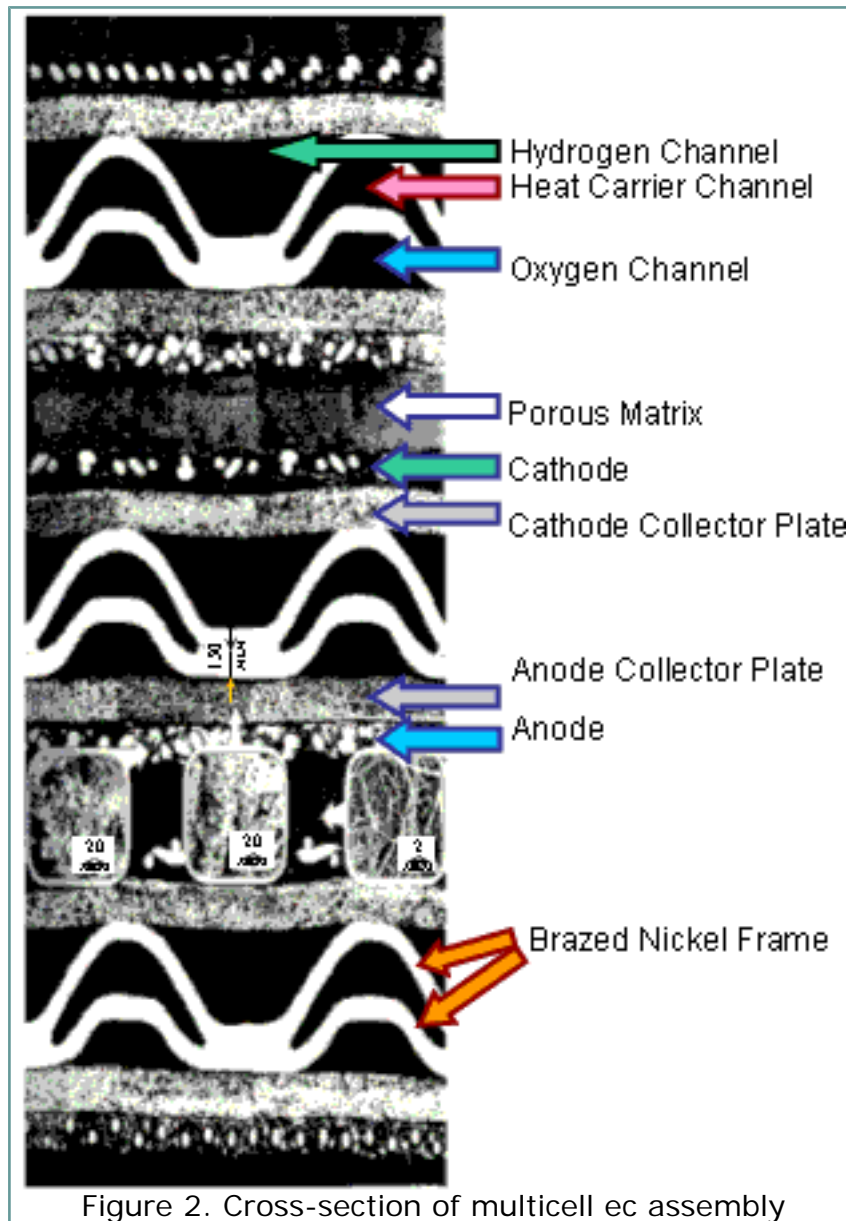


Figure 2. Cross-section of multicell assembly

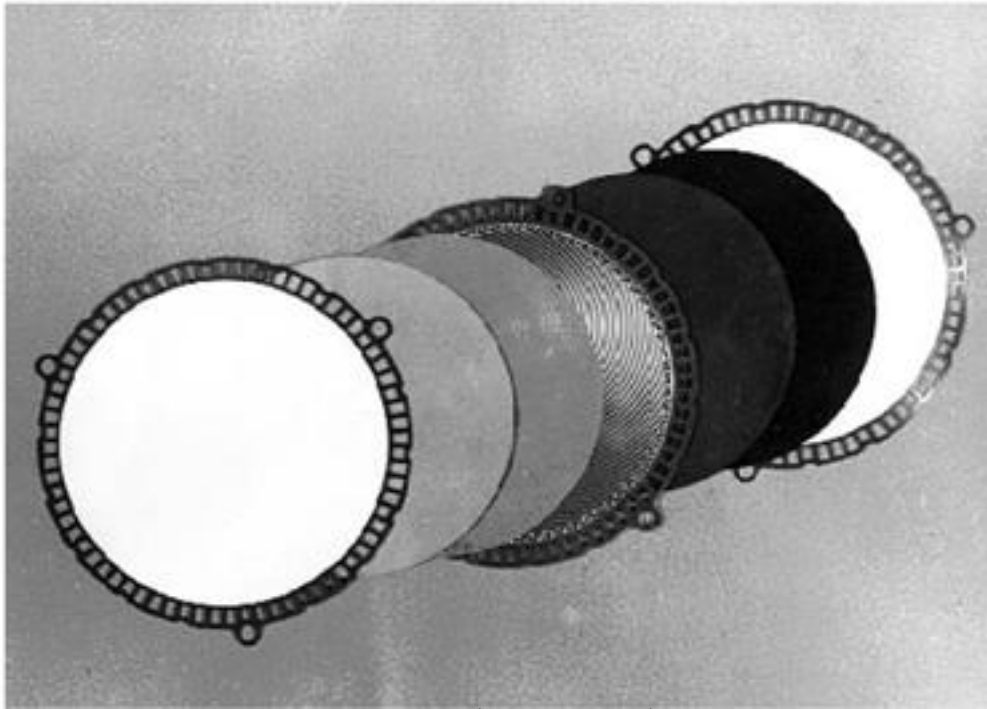


Figure 3. EC components (left to right): matrix, anode, collector plate, frame, collector plate, cathode, matrix

Water for electrolysis is delivered to stack in dynamic way by means of induced circulation of steam-hydrogen mixture through evaporator and WES. Due to the difference in electrolyte temperatures and concentrations, the water steam, when condensed in WES, replenishes the water spent for electrolysis. Under pressure altering in a wide range (0 to 35 MPA), the circulation inducer provides the required volumetric flow rate of steam-hydrogen mixture depending on external load. As water is supplied to WES in steam form, there is no strict cleanliness requirement imposed on it.

Estimates for 35MPa pressure were obtained by computing method and showed that equivalent leakage currents at the expense of gas interdiffusion through 0.3 mm porous membrane (porosity of approx. 60%) filled with electrolyte amounted to 0.4 A or less than 1% of operating current.

The development of WES for hydrogen-oxygen generator with a large capacity range is feasible on the basis of two EC sizes with an active area of 176 cm² and 700 cm² (Table 1).

Table 1

EC Number, pc.	Data for EC size, cm ²			
	176		700	
	Power Consumption, kW	Generated Hydrogen Amount, nm ³ /h	Power Consumption, kW	Generated Hydrogen Amount, nm ³ /h
10	0.87	0.235	3.47	0.936
20	1.75	0.47	6.95	1.87
30	2.62	0.706	10.43	2.81
40	3.49	0.94	13.90	3.74
50	4.40	1.78	17.38	4.68
100	8.74	2.35	34.75	9.36

150	13.11	3.53	52.13	14.04
200	17.48	4.70	69.51	18.72
250	21.84	5.88	86.88	23.40
300	26.10	7.06	104.30	28.08
350	30.58	8.24	121.60	32.76
400	34.95	9.41	139.00	37.44

Note:

1. Hydrogen capacity of WES is nominal for a long-term operating mode. Maximum capacity for short runs (to 15 minutes) can be doubled.
2. Anode with chosen catalyst provides the current-voltage curve in Fig. 1, contains 400 cells operating at a current density of 320 mA/cm², temperature of 98°C, pressure of 35 MPa.
3. Rated energy consumption per 1 m³ of hydrogen in normal conditions is 3,7 kW·h/nm³.

Regenerative System

UEIP has performed an engineering study of two versions of regenerative system.

The first one represents a Separate Regenerative Stack (referred as SRS) consisting of two assemblies: fuel cells and water electrolyzer combined in one module with common end plates. One of this stack assemblies is made up of series-connected electrolysis cells (EC), another one is made up of series-connected fuel cells (FC). EC assembly (ECA) and FC assembly (FCA) have common hydrogen, oxygen and heat carrier loops. The number of EC and FC in assemblies is defined by requirements for water electrolysis capacity and electric power in power generating mode, correspondingly. Individual EC and FC are similar except for porous structure of electrodes and catalysts used for their activation. In both cases, the identical porous membrane is in use as electrolyte carrier.

When generating power, ECA is in no-current condition, while FCA operates as electrochemical generator.

The second version of regenerative system implies that one and the same cells operate by turns in the mode of electrolysis or current generation and make up a Unified Regenerative Stack (referred as reverse URS). It favorably differs from the first version stack, since it has higher specific power and smaller materials consumption due to essential reduction of cell number.

However, the main complexity for the development of regenerative stack of the second (unified) type consists in creation of bifunctional catalyst for oxygen electrode and non-corrosive coating for bipolar frame, which will operate in a wide range of potentials (0,8 V to 1,7 V).

UEIP has a definite groundwork for solving these issues. The catalyst developed provides both the oxygen electrolytic reduction and oxygen evolution in electrolysis mode. However, at FC oxygen electrode operation, the catalyst efficiency is considerably inferior to conventional platinum catalyst. Of even greater complexity is the problem of protective covering, and, as experiments showed, even gold is not sufficiently resistant to corrosion in these conditions. Thus, up to the present, it is not evident that unified version of regenerative stack will be essentially more effective than the separate one. The final decision on the problem can be made after carrying out appropriate research and development activities.

References

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