High-pressure alkaline water electrolyser of coaxial configuration

V N Kuleshov, S V Kurochkin, N V Kuleshov and E Ya Udris

National Research University "MPEI", Russia, 111250 Moscow, Krasnokazarmennaya, 14

KuleshovNV@mpei.ru

Abstract. At present, hydrogen is increasingly being used in various industries. Moreover, among all technologies for producing hydrogen, the proportion of electrolytic hydrogen is constantly increasing. The most widely used technology is industrial water alkaline electrolyzers of various capacities. In parallel, the direction associated with the development of high-pressure water alkaline electrolyzers begins to develop. This paper considers the issue of creating and testing a high-pressure water alkaline electrolyser of coaxial configuration. Possible problems are considered during the operation of its components under high pressures, and ways to solve these problems. The proposed type of coaxial configuration and the changes made to the composition of the diaphragm material made it possible to reach a pressure of 100 bar.

1. Introduction

At present, hydrogen is considered as a promising secondary energy carrier. It is actively used in modern energy, which in turn is due to the rapid development of renewable energy sources [1, 2]. The indisputable advantage of the electrolytic method for the production of hydrogen is its high purity without expensive and technically sophisticated cleaning systems, the possibility of quick start and quick stop, smooth control of productivity without significant loss of efficiency of direct conversion of electrical energy into chemical energy. However, the use of hydrogen is not limited solely to the needs of the energy sector, where water electrolyzers with a sufficiently high hydrogen productivity are required. There is a separate large group of consumers, for example, research laboratories, the defense industry, and the space industry, which constantly require small amounts of hydrogen under high pressure. Most often, hydrogen is delivered to consumer in compressed form. Therefore, the use of small-performance electrolyzers for the hydrogen production under pressure already in place can serve as an alternative to centralized hydrogen production, excluding the stage of its transportation and storage.

Currently, two types of low-temperature water electrolysis are known: with proton exchange membrane (PEM) and alkaline water electrolyzers (AWE). The advantages of PEM electrolyzers include the high purity of the generated gases and the possibility of generating hydrogen under high pressures. But their main disadvantage is high cost, since expensive platinum group metals are used as the anode and cathode catalysts, the only producer of proton exchange membrane, and high technical requirements to maintenance and operation of the electrolyzers.

The advantages of alkaline water electrolyzers are the absence of expensive catalysts, various diaphragm materials, a simpler design, the ability to work at low temperatures (up to -40 °C) [3]. At the same time, alkaline electrolyzers operating at high pressures (up to 100-300 bar) are known only in...
the space industry. This work describes a new design electrolysis battery with an alkaline electrolyte, designed for the production of hydrogen under a pressure of up to 100 bar.

2. Design of electrolysis battery

Traditionally planar design of electrolysis modules with PEM and alkaline electrolyte is used, i.e. the flat electrodes of each cell are parallel to each other, and between them with or without a gap is a membrane or diaphragm. From these cells mounted assembly - electrolytic battery. To create a pressure at the output of the electrolysis battery up to 30 bar, it is necessary to use massive thick-walled diaphragm and electrode frames, and end plates that hold the assembly. Increasing pressure to 100 bar requires to put stack into a massive steel pressure vessel.

To solve the problem of increasing pressure directly at the outlet of the electrolysis module without a significant increase in weight and size characteristics can be proposed an alternative layout option — a coaxial design. According to an coaxial design, the cathode and anode are a cylinder in the cylinder, and a cylindrical diaphragm is located between them.

MPEI together with RSC Energia created and tested an alkaline water electrolyser with wick water supply in zero gravity based on a modern elemental base [4]. The results of comprehensive tests of the experimental sample confirmed the high efficiency and reliability of the electrochemical group created at the chair of Chemistry and Electrochemical Energy of MPEI. Based on this installation, experimental design work was carried out with the active use of digital design to create an energy-efficient small-sized coaxial alkaline water electrolyser of high pressure with low hydrogen productivity.

In the USA, alkaline water electrolyzers of coaxial configuration were also used to create an autonomous hydrogen refueling complex based on renewable energy sources. Cells of high-pressure alkaline water electrolyzers are capable of producing hydrogen under high pressure for a storage system without the use of a hydrogen compressor [5-7]. The membrane material Zirfon from Agfa Pearl was used as a gas separation element. The anode was made of a metal rod, and the role of the cathode was played by a cylindrical shell, which simultaneously serves as an outer containment shell. The electrolysis cell is made with an interelectrode gap, simultaneously playing the role of a cathode and anode chamber.

The electrolysis cell of coaxial configuration presented in this work has a key feature - it is a coaxial design with zero gap between electrodes. The cell consists of two cylindrical pipes of stainless steel. The diameters are selected so that the internal volume of the cathode (external) chamber is two times larger than the volume of the anode (internal).

Figure 1 shows a sectional view of the internal layout of the developed electrolysis cell. The inner electrode (1) is a stainless steel tube with perforation in the reaction zone. A nickel mesh (2) with a porous nickel coating modified by an anode process catalyst is welded to the outer surface of the anode. A polymer diaphragm is applied to the anode (3). Further around the diaphragm is the cathode (4). The cathode is welded to the outer tube (5) - the outer containment shell of the electrolysis cell. The current supply is provided by connecting a positive polarity to the inner electrode at the outlet of the electrolysis cell and a negative one directly to the outer shell. The generated oxygen is removed from the inside of the anode (2) through the perforation of the inner electrode (1) and enters the line. Hydrogen is removed from the outside of the cathode (4) into the space between the cathode and the outer containment shell (5). In this work, we used commercially available fittings and pipes certified by the manufacturer for working with chemically aggressive media at pressures up to 300 bar. In the standard set of fittings made the only change - steel conical seals were replaced with polymer ones to exclude direct electrical contact between the cathode and anode.

The proposed coaxial electrolysis cells can be combined into an electrolysis battery, Figure 2. This arrangement allows to change the performance of the cell over a wide range, not only by changing the current density, but also by disconnecting single cells.
The diaphragm obtained by the method of phase inversion [8–10], which is a porous polysulfone matrix with a hydrophilic filler (TiO₂), is used in the electrolysis battery. In contrast to previous research works, a pore former, polyvinylpyrrolidone, was not added to the polymer solution. As a result, the total porosity of the diaphragm significantly decreased, and increased voltage on the cell. However, a decrease in porosity made it possible to reduce the gas permeability of the diaphragm material (to increase the purity of the generated gases), which is especially important working at high pressures.

To reduce energy consumption, electrodes that can significantly reduce the overvoltage of oxygen and hydrogen evolution [11, 12] were used. The electrodes used in this work were obtained by method of electrodeposition. In a standard Watts bath micron-sized particles of nickel powder were electrodeposited onto an expanded nickel mesh. Subsequently, to reduce the overvoltage of hydrogen evolution, the electrode was modified with phosphorus. On the surface of nickel powder the nickel was chemically reduced from a solution of sodium hypophosphite to obtain NiPₓ [13]. The overvoltage
of oxygen evolution was reduced by obtaining the NiCo$_2$O$_4$ spinel structure on the surface of nickel particles.

3. Results and discussion

The assembled coaxial electrolysis cell (Figure 3) was connected to separators, a distilled water supply system and an electrolyte circulation. To control the temperature of the electrolyte, resistance thermometers were installed inside the unit, and pressure sensors were placed on the separators. Before taking the current-voltage curves, the electrolyser smoothly reached the set temperature mode of 80°C, and the pressure increase was achieved by closing the check valves on the hydrogen and oxygen circuits. An alkaline electrolysis battery of water was tested at pressures of 1, 15, 30, 50, 80, and 100 bar. The obtained dependence of the current-voltage curves on pressure are shown in Figure 4.

![Figure 4](image)

Figure 4. Mean cell voltage versus current density measured on the alkaline water electrolyser of coaxial configuration at 80°C and different operating pressures.

From the above data it can be seen that with increasing pressure from 1 to 30 bar, the voltage on the battery decreases, which contradicts thermodynamics. This can be explained by the intensified process of depolarization of the electrodes, as well as a decrease in gas filling in the internal volume of the shells. Another possible explanation is the rapid replacement of the generated gases in the porous structure of the electrode with an electrolyte, significantly improving the access of the electrolyte to the entire inner electrode surface. With a further increase of pressure from 30 to 100 bar, the voltage begins to rise again. Thus, the maximum energy consumption of an alkaline electrolyser shows at a pressure of 100 bar.
4. Conclusions
In the presented work it was demonstrated the possibility of creating high-pressure water alkaline electrolyser of coaxial configuration. This type of construct is completely different from the planar design of electrolysis batteries traditionally used today. It was developed and tested a coaxial battery originally designed to generate pure oxygen and hydrogen under high pressure. An existing electrochemical elemental base was adapted and tested for it, and it used commercially available structural elements certified for working with chemically aggressive media at pressures up to 300 bar. The obtained results indicate great prospects for using this type of design when creating alkaline electrolyzers of small and medium capacity with high output pressure of the generated gases without the use of any compressors.

5. References
[1] Grigoriev S A, Grigoriev A S, Kuleshov N V, Kuleshov V N and Fateev V N 2015 Power installations with co-generation of electricity and heat based on renewable power sources and electrochemical hydrogen systems Thermal Engineering 62 (2) 82
[2] Kuleshov N V, Kuleshov V N, Dovbysh S A, Kurochkin S V and Slavnov Yu A 2018 High-pressure alkaline water electrolyzer for renewable energy storage systems (Conference Paper). Proc. of 3rd Renewable Energies, Power Systems & Green Inclusive Economy (REPS-GIE) Conf., 23-24 April 2018, IEEE, Casablanca, Morocco
[3] Kuleshov N V, Kuleshov V N, Dovbysh S A, Grigoriev A S, Kurochkin S V and Millet P 2019 Development and performances of a 0.5 kW high-pressure alkaline water electrolyser Int. J. Hydrogen Energy 44 (56) 29441
[4] Korolev S P, Kuleshov N V and Kuleshov N V 2019 High Pressure Water Electrolyzer for Ungravity Space Proceedings of the Russian Academy of Sciences 2 68
[5] Nelson A Kelly, Thomas L Gibson and David B Ouwerkerk 2008 A solar-powered high-efficiency hydrogen fueling system using high-pressure electrolysis of water: Design and initial results Int. J. Hydrogen Energy 33 (11) 2747
[6] Nelson A Kelly, Thomas L Gibson and David B Ouwerkerk 2011 Generation of high-pressure hydrogen for fuel cell electric vehicles using photovoltaic-powered water electrolysis Int. J. Hydrogen Energy 36 15803
[7] Shimko MA, Verma S, Jackson T, Kamlani JS, Moss DK Electrolyzer apparatus and method for hydrogen and oxygen production U.S. patent 7,510,633; March 31, 2009
[8] Patent RU 2322460. Kuleshov N.V., Kuleshov V.N., Terentiev A.A. A method of manufacturing a membrane for electrolytic decomposition of water
[9] Kuleshov N V, Kuleshov V N, Dovbysh S A and Udris E Ya 2016 Polymeric composite diaphragms for water electrolysis with alkaline electrolyte Russ. J. Appl. Chem. 89 (4) 600
[10] Kuleshov N V, Kuleshov V N, Dovbysh S A, Kurochkin S V, Udris E Ya and Slavnov Yu A 2018 Polysulfone-based polymeric diaphragms for electrochemical devices with alkaline electrolyte Russ. J. Appl. Chem. 91 (6) 928
[11] Patent RU 2534014. Kuleshov N.V., Kuleshov V.N., Udris E.Ya. A method of manufacturing electrodes with a porous nickel coating for water alkaline electrolyzers
[12] Kuleshov N V, Kuleshov V N, Grigoriev S A, Udris E Ya, Millet P, and Grigoriev A S 2016 Development and characterization of new nickel coatings for application in alkaline water electrolysis Int. J. Hydrogen Energy 41 (1) 36
[13] Kuleshov N V, Kuleshov V N, Dovbysh S A and Udris E Ya 2017 High-performance composite cathodes for alkaline electrolysis of water Russ. J. Appl. Chem. 90 (3) 389