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RESEARCH, DESIGN, CALCULATIONS, AND OPERATING EXPERIENCE

PROCESSES AND EQUIPMENT FOR CHEMICAL AND OIL-GAS PRODUCTION

ELECTROCHEMICAL SYSTEMS WITH A SOLID POLYMER ELECTROLYTE.

PART II. WATER ELECTROLYZERS, BIFUNCTIONAL ELEMENTS, AND HYDROGEN CONCENTRATORS*

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Information is provided about water electrolyzers, bifunctional systems, and hydrogen concentrators/ compressors with a solid polymer electrolyte, and fields of application are considered. Membrane, electrode, and catalytic materials used within them are described.

Keywords: *electrochemical system, solid polymer electrolyte, water electrolyzer, bifunctional element, hydrogen concentrator/compressor.*

Water Electrolyzers with a Solid Polymer Electrolyte. Electrolysis in systems with a solid polymer electrolyte (SPE) are the safest and most effective method for producing hydrogen from water. Development of electrolyzers with SPE is historically connected with development of perfluorinated ion exchange membrane grade Nafion® from DuPont. The first electrodes with an SPE were created in 1966 by General Electric and were intended for space craft, underwater equipment, etc.

Oxygen is liberated at an anode (positive electrode) of a water electrolyzer with an SPE:

$$H_2O \rightarrow 1/2O_2 + 2e^- + 2H^+.$$

Hydrogen ions are transferred through an ion-exchange membrane (SPE), and hydrogen is liberated at a cathode (negative electrode): $H^+ + 2e^- \rightarrow H_2$.

The overall reaction is in contrast to that in a fuel element: $H_2O \rightarrow H_2 + 1/2O_2$.

In order to accomplish this reaction, it is necessary to supply electrical energy, and also thermal energy with a voltage of less than 1.48 V (value of the thermally neutral potential at 25°C).

A finely dispersed catalyst based on platinum group metals is used in electrolyzers with SPE. Unfortunately ruthenium, exhibiting the maximum catalytic activity in the oxygen electrical liberation reaction under anodic conditions, is unstable (potential more than 1.23 V in an acid medium), and therefore currently iridium or its oxide (Fig. 1) are used most

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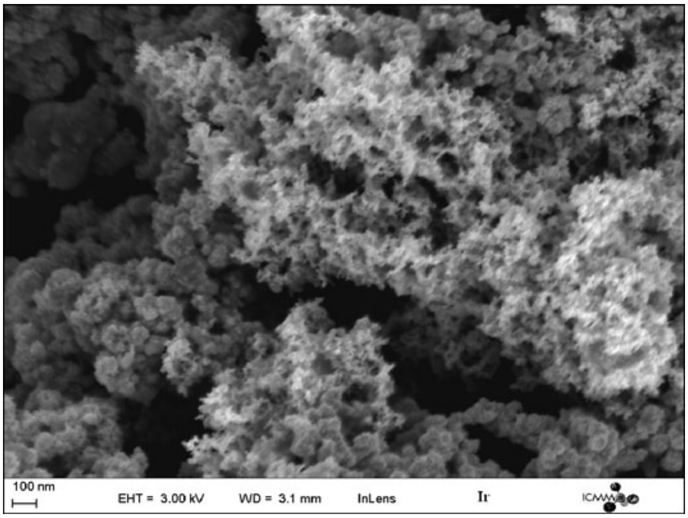

Fig. 1. Microphotograph of iridium black obtained using a scanning electron microscope.

extensively, and also mixed oxide compositions such as $Ru_xIr_ySn_{1-x-y}O_2$ with catalyst consumption of about 1.5 mg/cm^3. Finely dispersed platinum may also be used as an anodic catalyst, although in this case the electrolysis cell voltage is higher by 100–200 mV. Platinum and/or palladium, including on a carbon support [1], may be used at the cathode.

Plates of porous titanium with a thickness of about 1 mm are used as current collectors for electrolyzers providing passage of an electric current, reagent supply, and product removal to/from the reaction zone. It is noted that in order to protect current collectors from oxidation there is also use of platinum group metals (for example, a platinum film is applied with a consumption up to 1 mg/cm^2).

Currently, the main foreign developers and producers of commercial water electrolyzers with SPEs are Hamilton Sundstrand (USA), Hydrogenics Corporation (Canada), Teledyne Technologies Incorporated (USA), Proton OnSite (USA), NEL Hydrogen (Norway), CETH S.A. (France), and some other companies. The German firm H-TEC Wasserstoff-Energie-Systeme GmbH manufactures small demonstration examples of water electrolyzers with an SPE for development purposes. Research and development of electrolyzers with SPE is carried out in many countries, in particular, Greece, Italy, Germany, France, and USA. The possibility of marked progress in this field has been demonstrated within the scope of a WE-NET (Japan) program. An electrolysis model was created consisting of five electrochemical elements with an area of 2500 cm^2 each, making it possible with a current density of 1 A/cm^2 and at 80°C to realize a voltage in an element of 1.563 V, and this corresponds to an energy conversion efficiency of about 95%.

Development of improved electrolysis systems with SPEs at increased (up to 13 MPa) pressure is carried out successfully at the Kurchatov Institute (development of electrolyzers for the 30 MPa). At these pressures, direct filling of standard gas cylinders is possible, and also metal hydride hydrogen storage systems. An important feature of high-pressure electrolysis is the fact that in creating pressure it is not necessary to expend additional energy, apart from that expended in the electrolysis process itself. For example, an electrolyzer developed at the Kurchatov Institute consumes about 4 kW·h for productivity of 1 nm^3 of hydrogen both at atmospheric pressure and at a pressure of 13 MPa. Just for compressing 1 m^3 of hydrogen to 13 MPa in traditional or mechanical membrane compressors it is possible to use up to 2 kW·h of electrical energy [2]. Thus, the saving in electrical energy using a high-pressure electrolyzer may be up to 50% and higher. An advantage of electrolyzed gas production under pressure is also simple purification from water vapor.

In order to reduce energy expenditure in hydrogen production, it is possible to use depolarization of an anode by sulfurous anhydride [3] or methanol. In the first case, a considerable reduction in electrolysis voltage is possible (up to 50%), although commercial introduction of this process is hindered in particular by the impossibility of realizing electrolysis high current density due to diffusion limitations for supply of SO_2 to an anodic catalytic layer.

Recently, electrolyzers with SPEs have been created with productivity for hydrogen from several ml/h to several of m^3/h for various purposes [4]. Alongside demonstration projects for hydrogen power (production of reagents for fuel elements), water electrolyzers with SPEs are used in a different class for special purposes (space, underwater fleet, etc.), and in fields where high quality of the hydrogen produced is required: metallurgy for especially pure metals and alloys, production of semiconductors for the electronic industry, analytical chemistry (gas chromatography equipment, provision of laboratory hydrogen), systems for correction of the water-chemical regimes of atomic reactors, hydrogen welding, cutting, etc.

With certain anodic electrocatalysts (PbO_2, SnO_2 [5]) electrolyzed oxygen may contain up to several volume percent of ozone. In particular, use at an electrolyzer anode of a composite based on PbO_2 makes it possible to implement preparation of ozone with a current efficiency up to 8% with a current density of 1 A/cm^2, voltage of 3.2–3.4 V, and temperature of 15–25°C [5]. Electrolyzed ozone is an effective bactericide and may be used for sterilizing drinking and waster water, disinfecting water in pools, in chemical synthesis, and in medicine. Ozone is used extensively instead of chlorination in some cities for water treatment. Due to the high oxidizing capacity of ozone, it is capable of neutralizing a considerable number of organic and inorganic compounds.

Bifunctional Elements with a Solid Polymer Electrolyte. In a number of areas for use of electrochemical systems with SPEs (decentralized power supply, balancing a nonuniform load for an electric power station, transport, aerospace objects, etc.), there is a requirement for operation of a fuel element and a water electrolyzer in different time periods. In order to reduce the cost and size of power plant characteristics, it is expedient to combine a fuel element and a water electrolyzer in a bifunctional (reversible) electrochemical device, operating alternately in an electrolyzer regime (manufacturing oxygen and hydrogen), and then in a fuel element regime (manufacturing electric power and heat).

The idea of creating a bifunctional element based on an ion exchange membrane was realized in practice for the first time at the start of the 1960s [6]. However, in view of problem with a membrane and complexity, catalytic layer preparation for a catalytic element it was extremely low. Significant success in developing bifunctional systems with SPEs was achieved by General Electric, who in 1972 created a prototype for a reversible element for a power system of a space satellite [7]. In 1991, work for creating bifunctional elements was continued by Lawrence Livermore National Laboratory (LLNL) and AeroVironment of Monrovia [7], as a result of which a reversible system was created with a specific power capacity from 450 W·h/kg for a Pathfinder pilotless high-altitude aircraft. Subsequently, LLNL together with Hamilton Standard (division of United Technologies) carried out a research program for creating an automobile based on bifunctional elements.

Commercially available Unigen bifunctional modules and systems based on them were created by Proton Energy Systems. Unigen modules, using up to 15 kW in an electrolyzer regime and manufacturing up to 5 kW of electric power in a fuel element regime, were used in particular for experimental systems of the decentralized power supply at flying equipment heights (up to 20–30 km), and also for the needs of a naval airbase in California. In Russia, development of electrochemical system with SPE is the concern of the Kurchatov Institute [8].

Since electrocatalytic layers and gas diffusion electrodes of a reversible element should satisfy the specifications of bifunctionality, during their development it is desirable to consider experience of creating electrolyzers and fuel elements. It should be noted that in creating a bifunctional system the basis may be two possible schemes for organizing its operation (Fig. 2).

The majority of research groups have confined themselves to schemes of a bifunctional element whose electrodes change their oxidation-reduction function during switching of an element operating regime (see Fig. 2*a*) [7]. These electrodes are called hydrogen and oxygen electrodes, depending on which gas is liberated or used at a given electrode. An achievement of this scheme is the ease of changing a system operating regime, since a change in gases (reagents and electrode reaction products) is not required; a disadvantage is the impossibility of using carbon materials (gas diffusion substrate, catalyst support) at an oxygen electrode, since carbon oxidizes rapidly under the action of oxygen and its radicals, liberated in a reaction zone with anodic electrolysis. Another scheme of organization of a bifunctional element [8] (see Fig. 2*b*) does not have this disadvantage, although during its use it is necessary to change the gas composition of the electrode chambers during switching an element operating regime, and this may be practically implemented by flushing with an inert gas or extraction of gases with water followed by discharge. In particular, for an anodic (oxidizing) element of this electrode it is desirable to use an electrocatalytic composition based on finely dispersed platinum or iridium black (or a mixture of oxide composites).

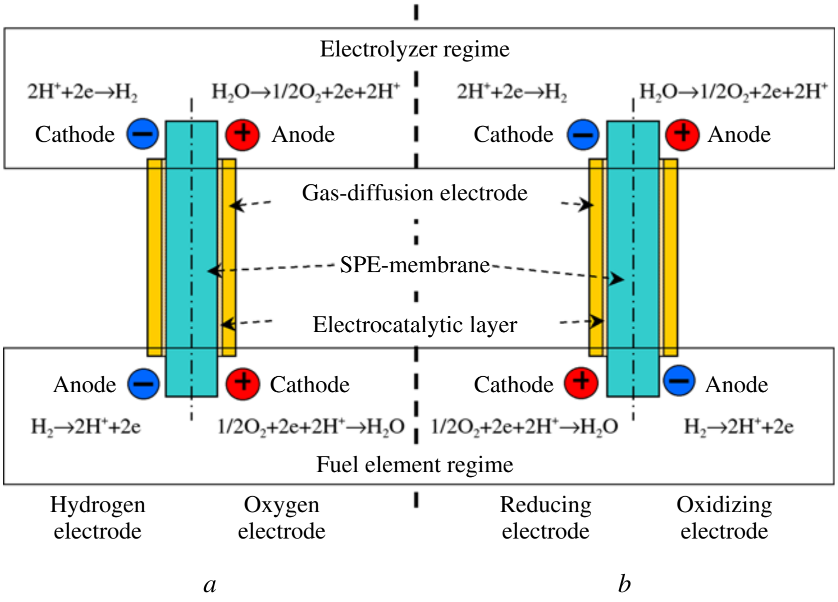

Fig. 2. Possible organization schemes for operation of a reversible element and electrochemical reactions occurring at electrodes: *a*) chemically reversible electrodes; *b*) electrodes not changing their oxidation-reduction functions during a working element switching regime.

Hydrogen Concentrators/Compressors with a Solid Polymer Electrolyte. For production processes connected with simultaneous hydrogen purification and compression, there is specific potential for electrochemical hydrogen concentrators/compressors. They may be used for cleaning (regeneration) and maintenance of a required hydrogen pressure, used in cooling steam and gas turbines, and generators, separation of compressed hydrogen from organic fuel conversion products, and from fuel element waste gases, regulation of the water-chemical regime for atomic power station circuits, and liberation of hydrogen (including under pressure) from its mixture with natural gas (so-called hitane) in the case of hydrogen transportation along gas pipelines. It is desirable to combine a hydrogen concentrator/compressor with an electrolysis device with the aim of additional purification and compaction of electrolyzed hydrogen for objects of the hydrogen infrastructure (in particular, filling stations).

Hydrogen compression by means of traditional mechanical compressors has a number of disadvantages: low efficiency of the process, high energy consumption, wear and hydrogenation of compressor elements, noise, cumbersome nature, and contamination of hydrogen with lubricating materials. Electrochemical hydrogen compressors with SPEs are free from these disadvantages. In particular, electrochemical hydrogen compressors are more effective than traditional compressors (membrane and piston) in the low capacity region [2]. High purity hydrogen is obtained at the outlet (water vapor is a possible impurity).

There is also a potential need for “oxygen pumps,” which may be used in fields where high purity oxygen is required (medicine, industry, etc.).

Study of electrochemical transport of hydrogen in a system with SPE has been carried out since the second half of the twentieth century. In Russia, research has been performed at the Kurchatov Institute for study of electrochemical compression/liberation of hydrogen in a system with SPE [9].

As in other electrochemical systems with SPE, in a hydrogen compressor membrane grade Nafion® or its analogs, electrocatalysts based on platinum group metals, gas diffusion electrodes in the form of a porous titanium plate or carbon cloth or paper, are used. In the case when at an anode a mixture is supplied containing apart from hydrogen, CO, H_2S, and other gases, contaminating a platinum electrocatalyst, it is necessary to use a catalyst in the form of a PtRu alloy on a carbon support.

The overall reaction in an electrochemical hydrogen concentrator/compressor with an SPE has the form:

$$H_2(P_a) \rightarrow H_2(P_c),$$

where P_a is the hydrogen pressure in a the anodic chamber, and P_c is the pressure in the cathodic chamber.

A pressure drop between electrode chambers is determined by the mechanical strength and gas permeability of an SPE membrane, and with the use of traditional membranes of grade Nafion® it is not more than several atmospheres. In order to achieve high pressure, it is possible to use a so-called cascade scheme, according to which individual electrochemical elements are joined into a battery successively with respect to gas. In this case, in the first element of a battery a hydrogen-containing mixture is supplied at low (for example, atmospheric) pressure p_0, and the element gives hydrogen at the outlet under pressure p_1. Then gas under pressure p_1 is fed to the next element, which compresses it to pressure p_2, etc. As a result of this, use of battery consisting of n elements makes it possible to raise hydrogen pressure from p_0 to np_1. In particular, the authors of a patent [10] have used this scheme for achieving a hydrogen pressure of 12000 psi (≈82 MPa), and this corresponds to the specifications laid down for automobile filling systems into fuel elements.

Conclusion. Electrochemical systems with SPEs, making it possible with high efficiency to accomplish conversion of forms of energy without damage to the environment have been used more extensively in various branches of industry, in transport, in power generation, and for specific purposes. In spite of the considerable amount of research and development in the field of electrochemical systems with SPEs, the high cost of electrocatalysts and membranes restrains their commercialization. In the event of successful solution of membrane-catalytic system cost reduction due to development of new nanomaterials and technology, the market for electrochemical systems may become almost unlimited.

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