LLC «MEVODENA»

(membranes for hydrogen energetics)

New membrane technologies for direct conversion of organic fuel chemical energy in an electricity

Business offer/proposal:

LLC "MEVODENA" (the participant of Skolkovo innovation Center) has prepared the project on grant of Skolkovo. The project will be submitted on «sowing» stage with the grant sum/size up to 30 million rbl. Co-investment of the project is required at a rate of 25 % of grant size.

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1. Direct conversion of organic fuel chemical energy in an electricity – energy efficiency technology of the near future

Chemical energy of organic fuels (natural gas, diesel fuel, a methanol, biofuel, etc.) can be converted directly to an electricity by means of fuel cells. As the electric power is generated in this case, passing a thermal cycle, there are no **efficiency** restrictions under the theorem of Karno and the **efficiency** of chemical energy conversion in the electricity can far surpass **efficiency** of traditional electrogenerators. Electrochemical generators (ECG) on fuel cells have no moving parts, are noise-free and harmless. Due to these advantages ECG have the enormous potential market: from power supplies for portable computers and mobile communication facilities to ship engines and generating stations. Application of these power-saving-up technologies in municipal electro- and a heat- supply is a special perspective direction.

2. A role of membrane technologies

Fuel, which is consumed directly by fuel cells, including the most developed solid polymer fuel cells, is hydrogen of 99.99 % purity. Accordingly, the electric power is generated from organic fuel under the following scheme (fig. 1). Organic fuel converts to a gas mixture in the chemical reactor (reformer). Next, hydrogen of 99.99 % purity is separated from this mixture, and finally electricity is generated by means of fuel cells. Membrane technologies allow separating hydrogen of 99.99 % purity from gas mixture most simply and efficiently.

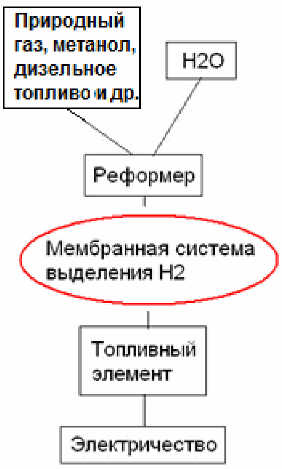

Fig. 1. Direct conversion of organic fuel chemical energy in electricity

3. Problems of existing technology

Usually, membranes of palladium alloys are used for this purpose. Still the price of such membrane system is extremely high, for example, the membrane system of electric capacity of 60 kW (typical capacity of the automobile engine) costs about $170 000 (Power and Energy Co, USA).

4. Prospects and market

Certainly, such high price is unacceptable for the most applications, and essentially hampers the development of the given direction of power engineering, including current state of affair in Russia. It concerns such key industries as shipbuilding, gas industry, *etc*. Development of a highly effective membrane at the comprehensible price will essentially lower a cost of direct conversion of organic fuel energy in an electricity that will not only allow to solve a problem specified above, but also will expand a field of application of this power-effective and non-polluting way of electricity generation on such spheres as municipal electro- and a heat- supply and transport.

Note that according to experts, the investment into development of hydrogen power will be up to 10 trillion US dollars over the next 30-50 years [1].

5. Innovation

Contrary to an opinion that hydrogen has an unique ability to pass trough palladium, it turned out that the transport of hydrogen through the lattice of group V metals (V, Nb, Ta) is faster by orders of magnitude [2, 3]. However, because of dense oxide layers, blocking dissociative absorption of H_2 molecules, membranes from V, Nb and Ta are almost impermeable to hydrogen [4].

To use the record speed of transcrystalline transport of hydrogen, typical for 5 group metals, it is necessary to cover the input and output membrane surfaces of these metals (or their alloys) with thin palladium layer, which (1) will provide catalytic absorption of hydrogen molecules, (2) will protect a membrane from corrosion at high temperatures under operation with chemically active gas mixtures, but (3) will not lower considerably the hydrogen permeation which metals of 5 groups and their alloys capable to provide. It is possible, if palladium covering has a thickness of 1 micron or less.

6. Experimental testing, a current state of the project

For experimental testing Competitor have been made a few laboratory samples of flat membranes of vanadium, covered with palladium on both membrane sides by plasma (magnetron) sputtering method. Testing results presented in fig. 2 demonstrate that these membranes pass hydrogen through more than on an order faster, than palladium membranes of the same thickness at the same 100 % selectivity on hydrogen [5, 6]. In addition, palladium consumption is two order of magnitude lower in case of composit membranes Pd-V-Pd, than that for purely palladium membranes. Membrane testing performed in the gas mixture (synthesis-gas) obtained at steam conversion of diesel fuel, have shown the same high speed of hydrogen extraction at hydrogen purity isn't worse then 99.9 %.

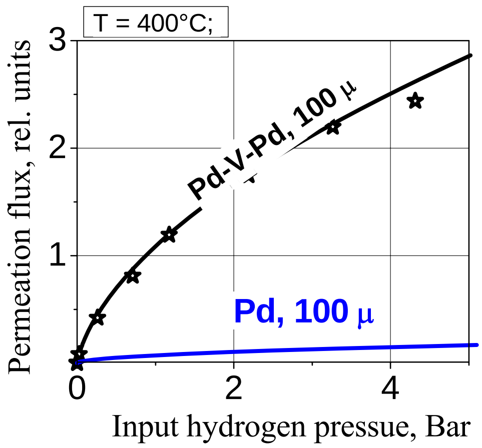

Fig. 2. Permeation hydrogen flux through the composit membrane Pd-V-Pd in comparison with permeation flux through palladium membrane of the same thickness

Technology of chemical deposition of palladium onto vanadium surface was developed. This technology is more economical than plasma deposition method and permits to cover internal surfaces (for example, internal surfaces of tube membranes) – fig. 3 [6]. It is shown experimentally, that the membrane with a chemical covering doesn't yield to a membrane with a plasma covering as regarding hydrogen permeation, and concerning protective properties of cover at operation in the gas mixtures [6].

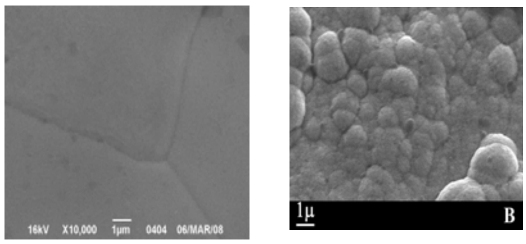

Fig. 3. Electronic – microscopical images of palladium coatings deposited onto vanadium surface with plasma method (on the left) and with chemical covering (on the right)

For optimization of composit membrane properties it is important to have possibility to produce the membranes not only of pure 5 group metals (for example, vanadium), but also of their alloys of various structure/composition. However it is rather problematically because of the alloys are usually less plastic, than the pure metals, and it is difficult (and even often impossible) to produce thin metal-rolling (sheets, tubes) from them. Competitors of the grant found and experimentally testing a method of transformation of ready metal-rolling from pure 5 group metals of into alloys of required structure (for example, in V-Ni alloy, fig. 4). The application on inventory on this technology (№ 2011126061) was submitted.

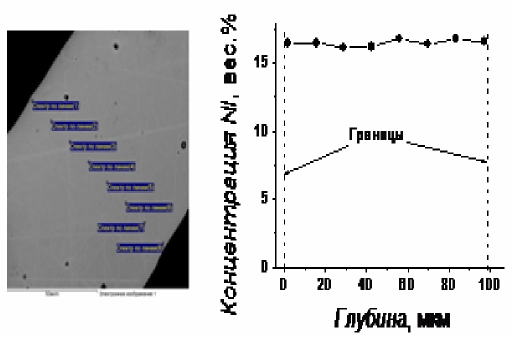

Fig. 4. Distribution of nickel over a cross-section of V-Ni foil of 0,1 mm thickness (on the right). First, foil was rolled from vanadium ingot and after that converted into V16Ni alloy by mean of solid-phase mixing. Data presented was obtained with X-ray microanalysis of cross-section of the sample.

Thus, R&D project phase is mainly finished at present, and the principal idea of the project is experimentally confirmed and the basic technologies are tested.

7. Products/technologies created on current and the subsequent stages of the project

At the current stage (years 2012 – 2013) the following products and technologies will be created.

(1) ***Composit materials*** on the base of 5 group metals (for example, Pd-V-Pd) and of their alloys with other metals, possessing ability to pass hydrogen selectively through with a essentially higher (at least, in times) speed than that of palladium alloys.

(2) ***Selective membranes*** from composite materials pointed out above in item (1). Their specific productivity will be; at least, several times higher, and content of precious metals will be two orders of magnitude lower, than in the case of membranes from palladium alloys of the same thickness. Accordingly, the membranes required to produce the given amount of pure hydrogen (or for generation of the given amount of electric power) become considerably cheaper at its industrial production. simultaneously, such composite membranes will possess 100% selectivity in relation to hydrogen and any other gases (as well as existing membranes from palladium alloys) and can operate at pressure difference of 15–20 Bar (on which membranes from alloys Pd is also rated usually). Such the membrane will be the finished product (presumably, the tubular form), having the stainless steel transition allowing to carry out routine installation of membranes in any constructions (for example, to mount membrane system in the case specially designed for this purpose).

(3) ***Technologies***

(A) composite materials (item 1),
(B) selective membranes from these materials (item 2)

(4) ***Patents and knowhow*** on products developed under item (1) – (3)

At the next stage of the project (years 2014–2015) the following products and technologies will be created.

(5) ***Set of membrane modules***. Each module in this number will represent assembly from the membranes specified in item (2) above, and, depending on number of such membranes, will have various productivity. The membrane module will be the finished product which the user can build in the standard energy power installation (or any system where it is necessary to separate pure hydrogen from a gas mixture), and also its multiplication to obtained demanded productivity/power will be very simple. A concrete set of module values will be chosen according to market requirements. For example, the membrane modules of 10 W, 50 W, 1 kW and 10 kW of electrical power, could satisfy the market requirements regarding electrochemical generators/power supply from portable means for informatics and communication to ship power and generating stations.

(6) ***Technology of industrial production***

(A) composite materials of item (1),
(B) selective membranes of item (2),
(C) membrane modules, item (5).

It is planned that at the stage of years 2014–2015 samples and the intellectual property, created over the period of 2012–2013, will lay a basis for attraction of private and state budget investments to create the prototypes of membrane systems and their small series for various market segments, for instance:

- rather large electrochemical generators for ship power,
- average electrical supplies for the country house-building,
- portable electrical supplies for mobile communication facilities and computer science.

At this stage marketing researches and product advancement on the market are planned, including product producing under individual orders.

8. Project team

Project team has own unique decisions of the present problem based on specific experience of its previous work in the given direction, confirmed with the concrete experimental results partially published in special international magazines, partially patented or in process of patenting or preparation for patenting.

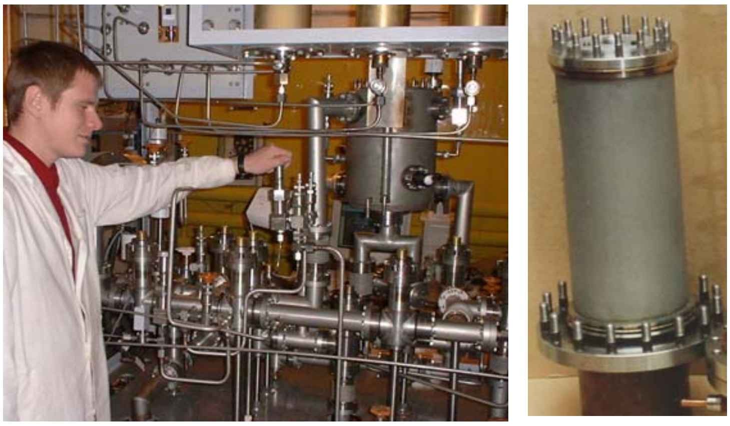

Fig. 5. Stand for tritium superpermeability research, created under the direction of and with participation in of the Competitor in the Federal Nuclear Center (Sarov) in the framework of ISTC project [11]. On the right: niobium cylindrical membrane.

The main executors of the project are:

Prof. Alexander I. Livshits, president of LLC MEVODENA, project head; Mikhail E. Notkin, vice-president of LLC MEVODENA, Vasily N. Alimov, the director for scientific research of LLC MEVODENA, Andrey O. Busnjuk, leading research assistant of LLC MEVODENA, Prof. Yury E. Gorbachev, the head of research department of LLC Geolink Technologies, Prof. Yuji Hatano, Hydrogen Isotope Research Center (Japan), Rune Bredeson, PhD, Research Director, SINTEF (Norway).

Participants of the project, the founder of LLC MEVODENA A.I. Livshits, M.E.Notkin, A.O.Busnjuk and V.N.Alimov are the professional physicists specializing in area of physical-chemical properties of a surface and membrane-hydrogen technologies. Current project has resulted from their research activity in laboratories of Europe and Japan as the invited scientists[1]. The subject of these researches was the phenomenon of superpermeability of metals on energetic hydrogen particles [7, 8] discovered by them. In these works hydrogen transport through 5 group metals has been thoroughly investigated, the first samples of V, Ta and Nb membranes have been made (fig. 5, 6), and specific experience of operation with them was got [7-11]. The essential personal contribution to these works has brought one of foreign participants of the project - Prof. J.Hatano (Japan) [4, 5, 10], the known scientist actively working in the field of physical chemistry and hydrogen technologies.

Gas-dynamic calculations of a gas mixture flow through the membrane system will be carried out by the head of research department of LLC Geolink Technologies, adviser Applied Materials, Inc (USA), prof. Ju.E.Gorbachev, the known scientist in the field of theoretical and applied gas dynamics [12].

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[1]) Investigations was carried out in the frame work of EURATOM project at Ecole Polytechnique, France, Japanese national programs at Tokyo and Nagoya Universities, at Hydrogen Isotope Research Center (Toyama University), at National Institute for Fusion Science (Gifu) and at Japan Atomic Energy Research Institute, as well as in the framework of two projects of International Scientific Technical Center jointly with laboratories of United State (LANL and Argon), Europe (Ecole Polytechnique and FZK Karlsruhe), and Japan (Hydrogen Isotope Research Center and National Institute for Fusion Science).

The second foreign participant of the project, Dr. R.Bredeson from Norway is one of leading world experts in the field of membrane technologies for hydrogen power. Under his supervision the unique technology manufacturing of composite membrane from palladium alloy [13] is developed at one of the largest research centers of Europe, SINTEF.

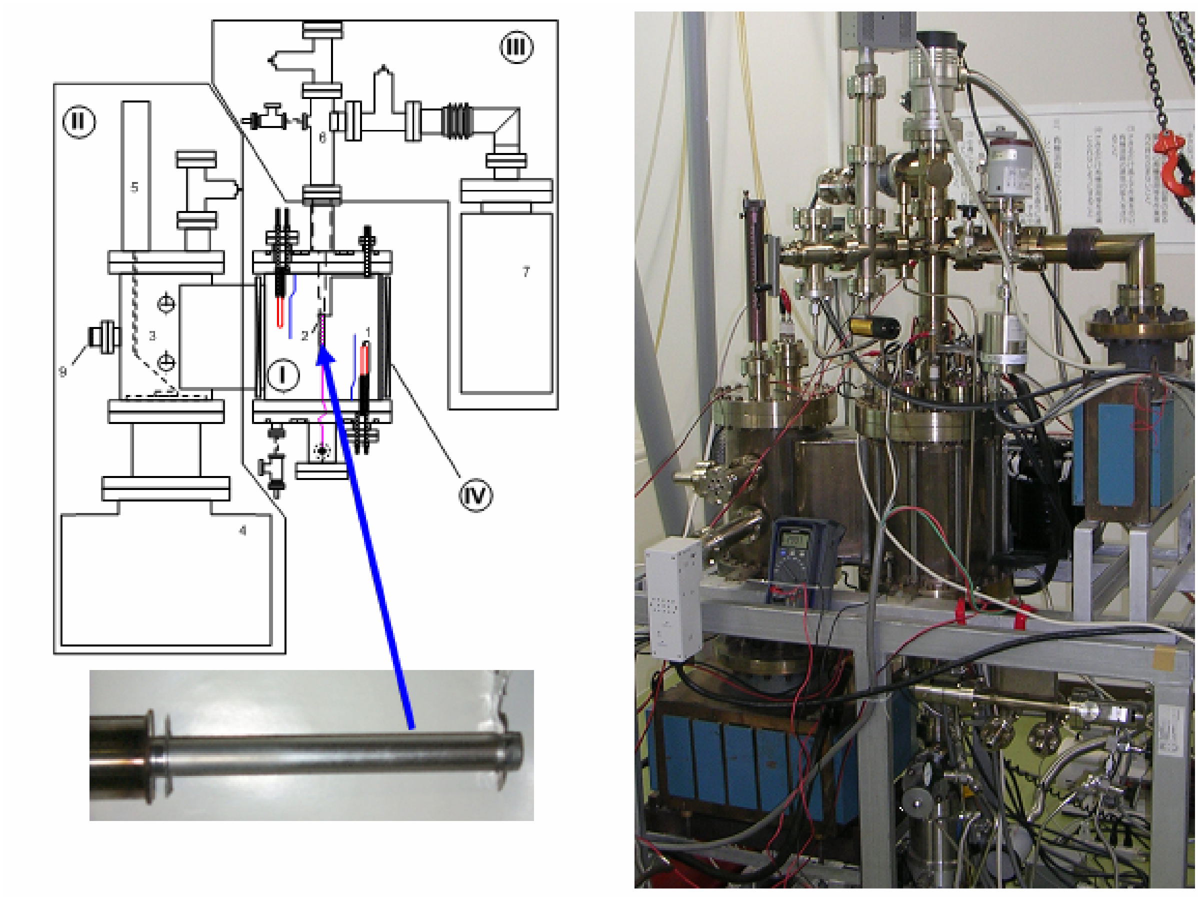

Fig. 6. Plasma-membrane setup for experiments on superpermeability of hydrogen plasma constructed by project team for Hydrogen Isotope Research Center (Japan), where they as invited scientists carry out researches jointly with Prof. Yu. Hatano, one of project foreign participant. Niobium membrane is shown in left bottom corner.

8. ***Intellectual property***

At present time intellectual property is protected by:

- **Patent for Utility model № 10541**1. Apparatus for mass-spectrometric analyses of hydrogen purity and for quantitative composition of gas impurity**.** Authors Livshits A.I., Notkin M.E., Alimov V.N., Busnyuk A. O, published 20.11.2011, Bul. №32.
- **Application for Utility model of 12.12.2011.** Product of the diven form from metal alloys. Authors: Livshits A.I., Notkin M.E., Alimov V.N., Busnyuk A. O.
- **Application for Utility model № 2011141920 of 11.10.2011**. Apparatus of joining of details of metals and/or metal alloys with various hydrogen solubility's. Authors: Avakov V.B., Landgraf I. K., Kulakov G. V., Kasatkin M. A. , Livshits A.I., Notkin M.E., Alimov V.N., Busnyuk A. O.

Patenting of inventions pointed out above is planned abroad, as well as patenting of products and technologies developed in the course of project activity such as: concrete alloys, coverings, barrier layers, ways of connection of membranes with constructional materials, etc.

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