The composite membranes based on group 5 metals for hydrogen production from organic fuels for fuel cells

1. Product description, comparison with competing solutions

1.1. _Why do we need effective membranes for hydrogen extraction at a reasonable cost._

The chemical energy of fossil fuels (natural gas, diesel fuel, methanol, bio-fuels) can be directly converted into electricity with using fuel cells. Since the electricity is generated in this case bypassing the heat engine, there is no the efficiency limitations by Carnot theorem. As a result, the chemical energy of the primary fuel can be converted into electricity with an efficiency far exceeding that which can be reached using conventional electric generators. Electrochemical generators based on the fuel cells have no moving parts, they are noiseless and ecological. Due to that they have an extensive potential market, from power supplies for portable computers and cell telephones to marine engines and power plants. Therefore, huge amounts of money are invested in this field by governments of developed countries as well as by the world's largest companies [1].

The most developed fuel cells are based on proton conductive polymer electrolytes (so called proton exchange membrane fuel cell – PEMFC) [2]. Hydrogen is the fuel that the PEMFC directly consumes. In order to avoid poisoning the platinum catalyst the hydrogen purity must be no less than 99.99%. Consequently, electricity is produced from

Fig.1. Scheme of the direct conversion of chemical energy of fossil fuels into electricity.

fossil fuels according to the scheme shown in Figure 1. Fossil fuel is converted into a gas mixture in a chemical reactor (reformer). This is usually done by steam reforming: the organic fuel is mixed with water vapor (Fig.1) and gas mixture containing H_2, CO_2, CO, H_2O, CnHm (and, as a rule, a certain amount of H_2S) is produced in the reformer. Then hydrogen of purity 99.99% should be extracted from this mixture for the electricity generation by the fuel cell (PEMFC). In large facilities hydrogen of required purity is obtained by pressure swing absorption method. However, even for the power units of megawatt scale (for example, in the case of marine engines), this method turns out too complicated technologically and the required equipment is too cumbersome.

Much easier and more efficient is to separate hydrogen using selective membranes. Typically, Pd alloys membranes are used for extraction of hydrogen of required purity. However _the price of such a membrane system is extremely high._ For example, a membrane system required for generation of electric power of 60 kW (typical car engine) costs $ 170 000 (Power and Energy, USA). This, of course, unacceptable for most applications, and significantly inhibits the development of this area of power engineering, including just now in Russia (for instance, it refers to the execution of contracts for shipbuilding, gas industry, defense industry).
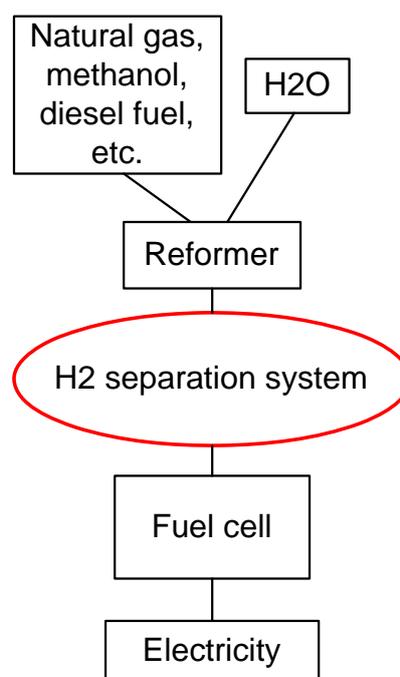
Contrary to the common opinion about the unique speed of hydrogen transfer through palladium, it turned out that the transport of hydrogen through the lattice of group V metals is orders of magnitude faster [3, 4]. This is because of the fact that hydrogen mobility and solubility in the bcc lattice of group V metals is much higher than that in Pd. However, the surface of these chemically active metals is covered with non-metallic films (mostly oxides), which block both the dissociative absorption of H2 molecules in the metal lattice and the associative desorption (in the form of H2) of H atoms from the lattice after their passing through the membrane [5]. As a result, the membranes from V, Nb and Ta are almost impermeable to hydrogen [5, 6].

In order to use the record speed of hydrogen transcrystalline transfer, it is necessary to cover the input and output surfaces of the membrane of these metals (or their alloys) with a thin layer of Pd, which (1) provides the catalysis of dissociative-associative processes at the absorption-desorption of H2 molecules, (2) protects the membrane from corrosion by the chemically aggressive gas mixtures at operating temperatures (300-600 ^{o}C), but (3) at the same time does not noticeably impede the hydrogen transport, which can provide five group metals and their alloys (the last condition is satisfied, if the palladium coating has a thickness of 1 micron or smaller).

Laboratory samples of flat membranes from V and Nb coated on both sides with Magnetron deposited palladium have been produced by the Applicant for experimental verification of above idea (Fig.2). Results shown in Fig.2 demonstrate that these membranes let through hydrogen more than an order of magnitude faster than a palladium membrane of the same thickness while the selectivity remains infinite [7 – 10]. In the case of composite membranes Pd-V-Pd and Pd-Nb-Pd consumption of palladium two orders of magnitude smaller than in the case of pure palladium membrane.
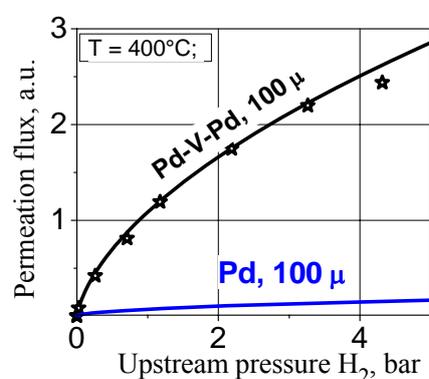

Fig.2 The laboratory sample of Pd-V-Pd composite membrane and H2 the permeation flux through it in comparison with the permeation flux through the palladium membrane of the same thickness [9].

1.3. *Product/technology to be developed.*

The following PRODUCTS and TECHNOLOGIES are planned to be developed.

(1) Composite materials based on group 5 metals (e.g. Pd-V-Pd) and their alloys with other metals (e.g. alloy V-n% Ni: Pd-(Vn% Ni)-Pd) whose permeability to hydrogen will be substantially greater (at least several times) than that of palladium alloys.

(2) Selective membranes made of the composite materials indicated above. Their specific productivity will be significantly higher (at least several times), and the precious metal content will be two orders of magnitude lower than in the case of membranes of Pd alloys with the same thickness. Accordingly, the membrane, required for separation of a given amount of pure hydrogen (or, equivalently, for generation of a given amount of electric power), would be considerably cheaper at its industrial production. At the same time composite membranes will have 100% selectivity to hydrogen (as well as the existing membranes of palladium alloys) and will be able to operate at a pressure difference of 15-20 bar (for which palladium alloy

membranes are usually designed). The membrane will be a finished product (presumably, of tubular shape). It will have a stainless steel transition allowing its routine joining/assembling.

(3) A line of the membrane modules. Each module in this series will be an assembly of membranes, referred to in item (2). Membrane module will be a finished product, which can be built into a power installation in a standard manner (or into any system where pure hydrogen should be separated from gas mixtures), as well as be simply multiplied to provide the required productivity/power. The specific row of module productivities will be selected in accordance with market needs. For example, the membrane modules for generating the electric power of 10 W, 50 W, 1 kW and 10 kW could meet the needs of the market of PEMFC-based electrochemical generators from power supplies for portable computers to marine engines and power plants.

The TECHNOLOGY is planned to be developed for production of (A) composite material referred to in item (1), (B) selective membranes made of this material (item (2)), and (B) membrane assembly (item (3)).

1.4. _What tasks should be resolved to create these products and technologies._

1.4.A. Exploration and development of palladium coating technology of group V metals and their alloys.

The technology must
(1) provide a minimum consumption of precious metals,
(2) enable to cover hard-to-reach surfaces, such as the inner walls of the tubes (membrane of tubular shape appears to be most suitable for a practical design),
(3) be as simple/cheap as possible.
We see electroless deposition as such technology of palladium coating of group V metals [11]. Currently, the Applicant has mastered technology of

Fig. 3. SEM images of palladium coating of vanadium-based composite membrane obtained by magnetron sputtering (A) and by electroless deposition (B).

electroless deposition of Pd on V and Nb, and flat composite membranes Pd-V-Pd and Pd-Nb-Pd are manufactured with this method (Fig. 3). It was shown that the membranes coated with electroless deposition technique are not inferior to the membranes prepared with the magnetron sputtering technique with respect to hydrogen permeation, as well as to the protective properties and tendency to interdiffusion [8, 19]. The technology of Pd electroless deposition on group V metals and their alloys will be continued to develop in the framework of the project. In particular, coating technology of tubes made of vanadium and its alloys (including their inner surfaces) will be developed. This technology is planned to develop to a scale, which allows manufacturing the membranes and their assemblies of required productivity.
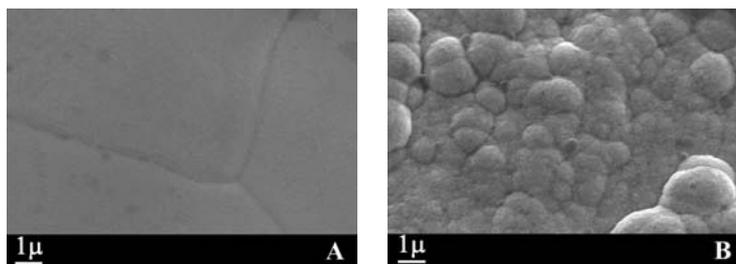
1.4.B. Development of group V metals alloys as membrane material

Possibility of production of the membranes from alloys of group V metals with other metals allows optimizing the membrane material properties, which is especially important with regard to hydrogen solubility. The hydrogen solubility is desirable to optimize such a way that the optimal concentration of hydrogen in the membrane material would be reached at operating temperature and pressure (for example, for many applications it is desirable to significantly reduce hydrogen solubility with respect to its solubility in pure V, Nb and Ta). It is also desirable that replacement of a pure metal alloy should lead to a reduction of the critical temperature of

hydride phase formation (it mitigates the problem of brittleness at accidental temperature drop, as well as reduces requirements to starting/stopping procedure).

The problem is that the alloys are usually significantly less ductile than the pure metals and it is difficult (or even impossible) to make a sufficiently thin membrane (e.g., ~ 100 μm) from them of a plain or, especially, of a tubular shape. To solve this problem, the applicant is developing a special innovative technology that allows making thin-walled components of vanadium based alloys. With using this technology the applicant has already manufactured the first tubular samples made of V-Ni alloys with the different content of Ni. The technology is planned to be developed in the framework of the project. The technology is under the patenting now.

1.4.C. Composite membrane connection with structural materials

The problem is that group V metals dissolve significant amounts of hydrogen at typical operating temperatures (300–500 °C) [6]. That causes their expansion (hydrogen dilation) and as a result the stress in the joints of group V metals (or their alloys) with structural materials (e.g. austenitic stainless steel). That can lead to a seal failure of such connections (e.g. welded or brazed), especially under conditions of hydrogen pressure cycling.

This problem is planned to be solved through the use of innovative technology developed by Applicant, namely through the employment of materials made of alloys of varying composition, which will ensure a smooth transition between the materials with high and low hydrogen solubility. The application for the invention "Method of connection of components made of metals and/or of alloys with different hydrogen solubility" is sent for review on June 25, 2011.

1.4.D. Lifetime, thermal stability

Applicant found that the main cause limiting composite membrane lifetime is the interdiffusion between the palladium coating and the base membrane material (e.g., V). The consequence of the interdiffusion mixing is the formation of low permeable alloy at the Pd-V interface and, as a result, the permeation drop [8]. Because of interdiffusion the operating temperature of composite membranes based on pure V and Nb is undesirable to rise above 400 °C [8]. On the other hand, temperature cannot be kept substantially lower since hydrogen concentration in metal exceeds the limit admissible from the standpoint of mechanical properties of the membrane because of the high exothermal solubility of hydrogen [6]. So, if one does not take special measures, composite membranes based on pure group 5 metals can operate in a very narrow range of temperatures (around 400 °C in the case of V). Note that the commercial membranes made of Pd-Ag alloys also operate at temperatures close to 400 °C.

It is desirable however to extend operating temperature range for some applications. For example, the membrane system is no longer a separate unit with independent variable temperature in a very important case of fossil fuel conversion in a membrane reactor: it is incorporated into the reactor (reformer), and its temperature is determined by the optimum temperature of the chemical processes in the membrane reactor. For example, the optimum temperature is about 300 °C in the case of steam reforming of methanol and 550-600 °C in the case of natural gas (methane) conversion [12].

We are planning to significantly extend the range of operating temperatures in order to expand opportunities for application of developed composite membranes, as well as to lengthen their lifetime.

The possibility of reducing the operating temperature (e.g. up to 250-300 ºC) will be obtained through the use of membranes based on group 5 metal alloys (see 1.4.B). The solubility of hydrogen in alloys of V, Nb, Ta with other metals are lower than in pure V, Nb, Ta, and due to this the membranes from the alloys can operate at substantially lower temperatures. Note that

a specific feature of group V metals and their alloys is either very weak (alloys) or even inverse (pure metals) temperature dependence of hydrogen permeation. Therefore, temperature decrease does not lead to a decrease in performance (in contrast to the membranes of Pd and Pd alloys). In contrast to that, the rate of interdiffusion sharply (exponentially) decreases with temperature increase and, consequently, lower operating temperature results in a drastic suppression of the main factor of degradation and thereby prolong the service life of composite membranes.

The possibility to increase the working temperature (target: 550 °–600 °C) is planned to achieve by suppressing the interdiffusion with additional barrier layer between Pd coating and main membrane material (e.g. V). This is nontrivial task because this barrier while suppressing interdiffusion should not hinder hydrogen transport. We plan to patent the composition of the barrier layer and technology of its preparation. Note that the suppression of interdiffusion with the barrier layer not only expands the range of operating temperatures but also dramatically prolongs the membrane service life.

1.5. *Why the Applicant team can solve the facing problems (item 1.4) and create the specified product (item 1.3)*

The answer of this question is given partly in section 1.4: the Applicant team has its own unique solutions of the listed problems based on the specific experience of its previous work in this field confirmed by particular experimental results which were partly published in special international journals, partly were patented or are in the course of patenting or under the preparation for patenting. Added to this is brief information about the unique experience of the project team, which consists of professional scientists in the field of physics and chemistry, as well as undergraduate and graduate students.

Project participants are:

A.I. Livshits, PhD, Professor of Department of Physics, SPbSUT, Director of Research and Education Center "New Energy Technologies for Informatics and Telecommunications" (REC NETIT), project manager; M.E. Notkin, Ph.D., senior researcher at REC NETIT, V.N. Alimov, PhD, associate professor SPbSUT, A.O. Busnyuk, PhD, researcher at REC NETIT, J.E. Gorbachev, Professor, Head of Research Geolink Technologies Ltd.; Y. Hatano, PhD, Professor, Hydrogen Isotope Research Center (Japan), R. Bredeson, PhD, Research Director, SINTEF (Norway); undergraduate and graduate students SPbSUT.

Project participants from SPbSUT (A.I. Livshits, M.E. Notkin, A.O. Busnyuk and V.N. Alimov) are physicists specializing in the field of surface physics/chemistry and hydrogen-membrane technologies. The phenomenon of "superpermeability of metals to suprathermal hydrogen particles" were discovered by these researchers [4, 14-18]. The essence of the phenomenon is that the metal membranes of usual thickness (for example, of the scale of tenths of millimeter) are able to let through the suprathermal hydrogen particles (with kinetic, internal or chemical energy of scale of 1 eV or higher) with almost the same rate as a *hole in a thin partition of the same area* at some particular state of their surface. This phenomenon has been systematically studied by the project participants in a number of foreign laboratories[1] with a view to application in fusion for the separation of D/T mixture from He [14, 15, 18, 19]. It was found by the project participants that group 5 metals are most suitable as a material for superpermeable membranes [4, 14-19]. Correspondingly, hydrogen transport through vanadium and niobium membranes at their interaction with hydrogen particles of different energies, including thermal H2 molecules was studied in detail in the course of this work [4, 6, 14, 15, 19].

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[1] The studies were conducted in the framework of several projects of EURATOM in Ecole Polytechnique, France, of the Japanese national programs in Tokyo University and Nagoya University, in Hydrogen Isotope Research Center (Toyama University), National Institute for Fusion Science (Gifu), Japan Atomic Energy Research Institute, and also of two projects of the International Science and Technology Center in cooperation with a number of American (LANL and Argon), European (Ecole Polytechnique and FZK Karlsruhe), and Japanese laboratories (Hydrogen Isotope Research Center and National Institute for Fusion Science).

Samples of membranes made of V/Nb and unique equipment for their invesigations (Fig. 4, 5) were created by the project participants directly or under their supervision [6, 20]. Note that one of the foreign participants of the project, Prof. Y. Hatano (Japan), a well-known scientists actively working in the field of physical chemistry and hydrogen technologies, has made a significant personal contribution to this work [5, 8, 9].
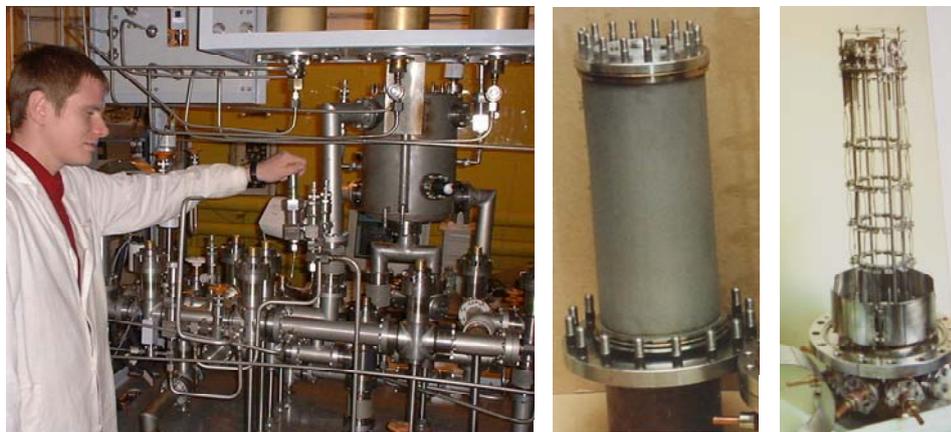

Fig. 4. Experimental stand for study of tritium superpermeation created under the guidance and with the participation of the Applicant in the Federal Nuclear Center (Sarov) in the framework of two international projects (ISTC) [19]. Right: a cylindrical membrane of Nb and an atomizer of molecular tritium.

An important achievement of the project participants regarding the purpose of this work is that they have managed to deepen understanding of boundary process kinetics in the systems H2-V/Nb/Ta [6, 14-18]. Findings obtained by project participants on the effects of non-metallic impurities (O, C, S) on the interaction of groups 5 metals as well as of palladium with hydrogen appears to be important for this work (these data were published only in part, for example, in [6, 14, 15, 21, 22]). Basing on these results we, in particular, assume to make a barrier layer between palladium coating and main membrane material that prevents interdiffusion between Pd and V, Nb, Ta but does not hinder hydrogen transport.

A research director of Geolink Technologies ltd., a consultant of Applied Materials, Inc (USA), Prof. Y.E. Gorbachev, renowned scientist in the field of theoretical and applied gas dynamics, the author of 150 publications, including monographs (for example, the last publication [23]) will perform gas dynamic calculations of gas flows through the membrane system with extraction of one of the mixture components. It has already been mentioned about the specific competence of Prof. Y. Hatano and about his close involvement into the joint researches with SPbSUT group on topic of the Project [5, 8, 9]. The second foreign participant in the project, Dr. R. Bredeson from Norway, is one of the world's leading experts in the field of membrane technologies for hydrogen energy. A unique technology for production and extensive methods for investigations of composite membranes has been developed under his leadership in SINTEF, one of the largest research centers in Europe [24].

2. Current project state

At the moment, R&D phase of the project is mostly finished, the basic idea was confirmed experimentally and core technologies were tested. Specifically the following was done.

Laboratory samples of composite membranes Pd-V-Pd and Pd-Nb-Pd of plane shape were manufactured by magnetron sputtering. They have demonstrated the performance more

than an order of magnitude higher than performance of Pd of membranes at 100% selectivity (Fig. 2).
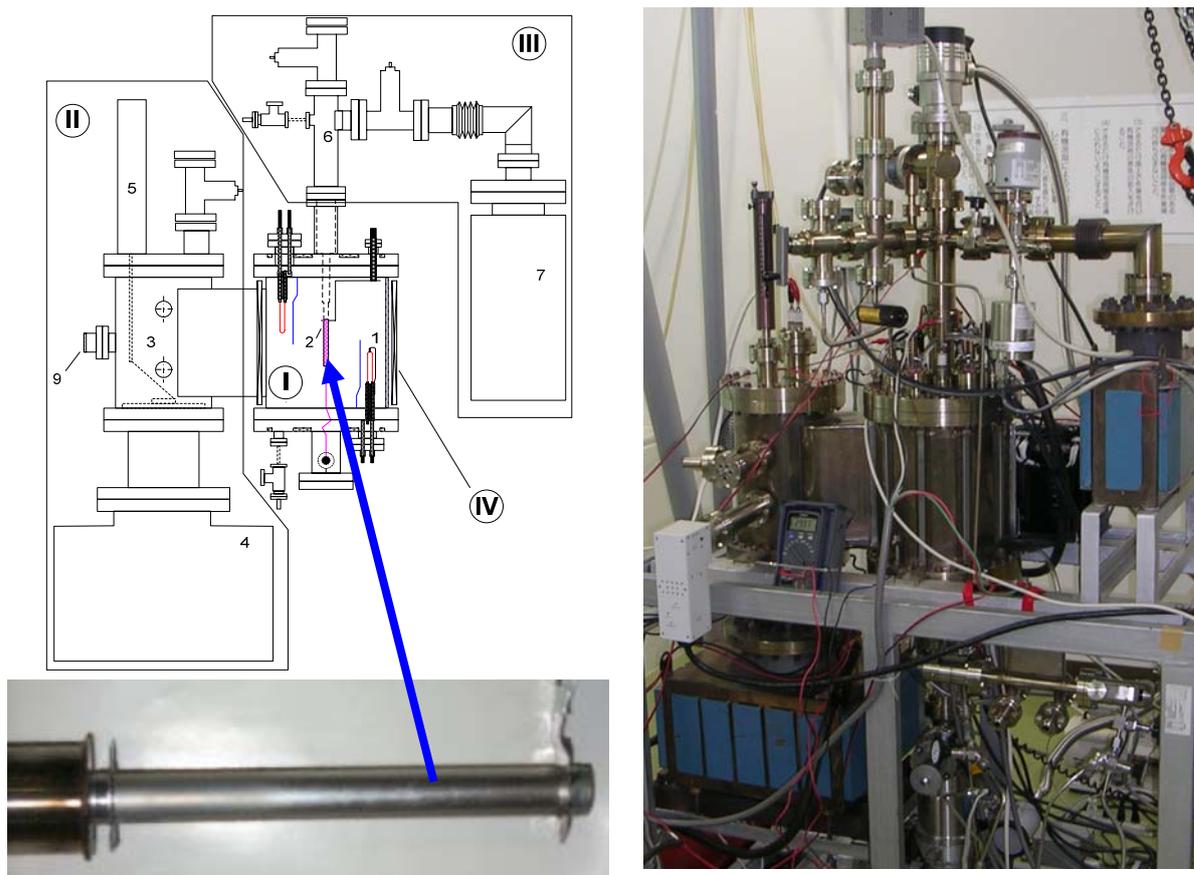

Fig.5. Membrane of Nb (bottom left) for study of plasma-driven superpermeation. The membrane and a plasma-membrane experimental setup presented to the right were made by the project participants together with Prof. Hatano [5, 8, 9] for Hydrogen Isotope Research Center (Japan) where researches from SPbSUT work as an invited scientists in collaboration with Prof. Hatano.

A technology of electroless palladium deposition on V was developed, which is more economical than the magnetron sputtering and allows the covering inner surfaces (e.g. inner surfaces of tubular membranes) (Fig. 3) [10, 11]. It is shown experimentally that, despite the specific surface morphology (Fig. 3), the membranes with a electroless coating do not yield the membranes coated with magnetron sputtering with respect to hydrogen permeation as well as to resistance to interdiffusion and protective properties when operating in typical gas mixtures (syngas) [10, 11].

A possibility to make the thin-walled components (e.g. of tubular shape) *of vanadium alloys was demonstrated*. The corresponding technology is being patented.

3. Characteristics of the market, the commercialization scheme

As it was mentioned above (Section 1.1) the generators of electricity based on the direct conversion of chemical energy of fossil fuels into electricity using PEMFC, have a huge potential market. The economically acceptable method of fuel cell grade hydrogen separation from reformates is one of the key problems, and market volume depends largely on its solution. For example, the market price of the membrane system of palladium alloy, which provides the flow of pure hydrogen required for generation of 60 kW of electricity is 170 thousand US dollars

(the company "Power and Energy", USA, http://www.powerandenergy.com/newsletter_02-2011.html). Probably it is acceptable for special purposes (military equipment, energy supply of data processing centers, etc.), but it is unacceptable for application in power systems for transport, community facilities, etc. Accordingly, the cost reduction of the membrane system will lead to a significant expansion of the real market of electric generators based on the direct conversion of chemical energy of fossil fuels into electricity using the most advanced and promising fuel cell PEMFC.

Solution of this problem proposed in this project can be divided into the following standard steps.

The first stage: research and development. This stage is mainly completed by the Applicant (see Section 2).

The second stage: research and engineering development. **This phase of the project is being implemented in the present**, additional funding is required for its continuation and completion. Through the implementation of this stage of work the following results will be achieved: (1) new composite materials for selective membranes based on 5 groups of metals and their alloys (samples), (2) samples of membranes of optimal shape (e.g. tubular) and of optimal alloy composition, (3) sample of the module of these membranes, (4) appropriate technologies, (5) patents and know-how. For implementation of this step, including the involvement of the required funds, as well as for other R&D on hydrogen energy technologies we plan to arrange a company in the framework of SKOLKOVO.

In the third stage (from 2014) it is planned *that intellectual property* obtained will serve as a basis for private and governmental (for example, for defense-industrial sector) investments to create prototypes of membrane systems and their small series for specific market segments: relatively large electrochemical generators, e.g. for marine purposes; medium, e.g. aimed to supply suburban housings; and portable, for example, for portable computers and mobile telephones. At this stage the marketing researches and promotion of the product to the market (including the manufacture of products for individual orders) are planned. Active involvement of the project team in this stage is supposed, along with the involvement of engineers and managers.

Fourth stage (2015): production. For this purpose, either the company organized under Skolkovo will be sold, (for example, to a major manufacturer of power supplies), or a special production company will be found.

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