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Development of a membrane – based fuel processor for fuel cell (FC) power plants

Ivanov I.V., Brizitski O.F., Terentyev V.Ya.
RFNC-VNIIEF, Sarov, Russia

V.V. Barelko
Institute of Problems of Chemical Physics
Chernogolovka, Russia

Developing hydrogen economy requires creation of small and low-price devices for hydrogen generation, first of all, from hydrocarbon raw products. Nowadays, the hydrogen generation with the usage of natural gas steam conversion is the most effective technique that is why we have chosen it as a basic one.

Since in the process of natural gas steam reforming we obtain the mixture consisting of hydrogen (H2), carbon oxide (CO2) ,carbon monoxide (CO) and water it is necessary to implement different technologies to purify hydrogen from CO2 and CO impurities.

Generation of pure hydrogen is the most topical task to be solved for alkaline fuel cell (AFC) - based power plants where CO and CO_2 content in hydrogen must be 10 ppm or less. For the power plants based on proton exchange membrane fuel cells (PEMFC), the CO_2 content has no limitations and CO content may be 20-30 ppm.

Among the existing techniques of fuel processing for AFC- based power plants it is possible to use PSA (pressure swing adsorption) technique or that one of hydrogen separation while it passing through membranes made of palladium alloy.

For PEMFC-based power plants, besides the above-mentioned techniques one can use also that one of hydrogen purification implementing additional reactors for reactor for water-gas shift conversion , CO selective oxidation ,and (or) methanation

Our calculations and estimations show that the well-proven technique for hydrogen purification in chemical industry by removing CO_2 and CO from the products of natural gas steam conversion using the PSA technique demonstrates less efficiency as compared with the other ones, hence, its implementation in a particular FC-based power plant must be thoroughly substantiated and reasoned.

A widely-used scheme for hydrogen purification in FC-based power plants with the implementation of reactors for water-gas shift conversion, CO selective oxidation, and (or) methanation can not be also considered as that universal one. First, it is not suitable for AFC- based power plants, second, when applied in PEMFC- based power plants one may face a problem of the PEMFC anode poisoning with additional amount of CO produced in FC if there is large amount of CO_2 in the anode gas.

It should be noted that both schemes for purification of the converted gas are multistage ones, have large dimensions and low dynamic characteristics, they also require a complex system for reactors control.

The membrane fuel reactor may have one steam converter and to be based on advanced concept of simultaneous hydrogen generation and separation, hence, it can be fabricated as a compact device being more efficient than the other ones intended for the hydrogen generation. Moreover, control of the membrane fuel processor is identical to control of a steam reformer that is definitely its advantage as compared to the other types of fuel processors.

In spite of its evident advantages, the membrane fuel processor is not widely applied nowadays. Among a variety of reasons impeding commercialization of this technology the most essential and important one is the lack of inexpensive and reliable hydrogen-permeable membrane as well as the technology to incorporate it into a membrane module.

R&D work that we carried out within last years showed that solution of this task requires development of production technique for a flat ultra thin membrane (at least 10 μm) made of palladium alloy.

The membrane thickness is of great importance because its the reduced thickness contributes to better hydrogen permeability, increased efficiency and allows decreasing of the membrane and fuel processor costs.

Our approach to the Pd-alloy composition is based mainly on domestic developments. The multicomponent alloy based on B1 palladium (palladium-silver alloy) was developed in Russia. It demonstrates stable behavior in the medium of conversion products and is plastic that is very important for setting up of the technology for ultra-thin membranes.

The development of the other alloys is also underway. These are low cost alloys as compared to silver-platinum ones. The research work on these alloys is continued.

Table 1 shows the characteristics of diffusion elements made of B1 alloy depending on the membrane thickness proving that we have took a proper approach to solution of the task on the membrane thickness reduction.

Table 1
Characteristics of diffusion elements made of B1 alloy

Membrane modules characteristics	Membrane thickness, μm			
H_2 permeation rate ($nm^3/m^{2*}h$) at T=600°C, ΔP=5bar	100	50	30	10
Membrane surface at production rate of $1nm^3/h$, m^2	10	20	33	70
Membrane weight for production rate of 1 nm^3/h, kg	0.1	0.05	0.03	0.014
Pd alloy material cost, $	0.1	0.025	0.009	0.002
Diffusion element cost, $				

In order to fabricate the ultra-thin palladium membranes we worked out several techniques:

a) a composite membrane with porous ceramic substrate made by magnetron deposition of palladium alloy film of 2÷3 μm thickness. Until now, this technology does not allow us to achieve stable and long-term operation of such membranes;

b) a composite membrane made of niobic (Nb) foil and 2÷3 μm thick palladium film. At this stage of development we did not manage to achieve stable behavior;

c) a composite membrane consisting of several alloys of metal substrate and palladium film of 7 ÷10 μm thickness made with the usage of a special high-precision roll-out technique. This technology allowed us to achieve stable behavior of the membrane and was chosen as a basic one for further research work.

At present we continue the work on optimization of the form and composition of the metal substrate for the composite membrane including development of the technology to incorporate the composite membranes into membrane modules of the fuel processor.

Table 2 shows the results of the membrane testing for hydrogen-permeability of several samples of the composite membrane consisting of the metal substrate and B1 palladium alloy of 7 μm thickness.

Table 2

Temperature ^{0}C	**Pressure, , atm**	**Hydrogen permeability, nm3 /m2-**
400^0	**1.0**	**10**
	3.0	**26.1**
	5.0	**86.6**
	8.0	**121.6**
500^0	**1.0**	**30.5**
	3.0	**60.5**
	5.0	**117.2**
	8.0	**166.9**
600^0	**1.0**	**36.6**
	3.0	**101.3**
	5.0	**151**
	8.0	**217.2**

Simultaneously, we carried out the work on development of the catalyst for steam conversion of fuel (natural gas) allowing increase of partial pressure of hydrogen in the steam conversion products.

This can be achieved due to reduction of a water steam/natural gas ratio in base mixture. Moreover, the reduced water steam/natural gas ratio entails reduction of the evaporation related power costs as well increases overall efficiency. The industrial catalysts for natural gas steam conversion usually use nickel as an active component and has a high steam/natural gas ratio (higher than 3:1). Taking this into account, we developed and fabricated a small batch of the pilot catalyst based on ruthenium oxide.

The development of a new catalyst for conversion of hydrocarbon raw products intends achievement of two goals, namely:

- Possibility of operation at a low steam/hydrocarbon ratio to increase hydrogen concentration in humid converted gas while extracting hydrogen from reaction zone;
- To exclude probability of free carbon fall-out at possible water consumption reduction for the technology.

We developed and tested the catalyst that does not contain nickel. The catalyst composition (percentage by mass): RuO_2- 1.0; LaO – 0.2; Al_2O_3 – the rest. Fractional composition of the catalyst: small balls of 1.5-2.0 mm size.

We tested the catalyst in a specially developed apparatus made of stainless steel with external resistance heating. The internal parts of the apparatus were made of copper, thus, preventing errors of experimental results since the reactions were proceeding on the construct surfaces of the apparatus. The apparatus was loaded with 5 cm^3 of catalyst.

We carried out 4 series of experiments. Table 3 shows the results of these experiments.

The duration of every experiment did not exceed 5 hours.

Table 3

Experimental conditions	**Dry converted gas composition (% vol).**			
	CH_4	H_2	CO_2	CO
1. $t = 800^0C, P = 1.1$ MPa, steam/gas = 2.0, $W_{CH4} = 500$ hr^{-1}	**4.6**	**73.1**	**5.7**	**16.6**
2. $t = 800^0C, P=0.6$ MPa, steam/gas =2.0, $W_{CH4}=500$ hr^{-1}	**1.3**	**73.8**	**3.9**	**21.0**
3. $t= 800^0C$, P=0.6 MPa, steam/gas=1.5, $W_{CH4}=2000hr^{-1}$	**3.0**	**74.7**	**3.7**	**18.6**
4. $t=800^0C$, P=0.6 MPa, steam/gas =1.0, $W_{CH4}=2000hr^{-1}$	**7.9**	**70.8**	**2.1**	**19.2**

The experiment's results showed that the converted gas composition is close to fractional one and at a steam/gas ratio = 1 there was no free carbon deposition on the catalyst. From our own experience it is impossible to avoid sooting on nickel catalyst. This proves that utilization of ruthenium catalyst in fuel processor holds much promise. However, this catalyst needs long-term testing in hard operational environment.

The target goal our work for the near future is development of a commercial membrane fuel processor with hydrogen output 4-5 m^3/hr.

Photo 1 shows the membrane module for fuel processor and Photo 2 presents the assembled fuel processor. The testing of manufactured samples of the membrane module and fuel processor is currently underway and will be completed in August, 2007.

Photo 1. Membrane module

Photo 2. Fuel Processor