

# DEVELOPMENT OF CERAMIC MOLECULAR MEMBRANES TO SEPARATE HYDROGEN FROM HIGH TEMPERATURE CO-CONTAINING FLOW FOR FUEL CELL-BASED UNIT APPLICATION

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**Abstract.** Current power machines with solid polymer electrolyte/external reformer – based fuel cells required materials able to separate H<sub>2</sub>/CO mixtures at temperatures 800-900 °C. The existing techniques to separate these gases employ only the palladium metal molecular membranes with a limited gas mixture temperature ≤ 550 °C. The present paper reports the tests of ceramic molecular membranes with meso-porous structure of the mean diameter 7 nm for high temperature H<sub>2</sub>/CO separation. Initial test samples of the disc ceramic molecular membranes were manufactured on the base of ZSM-5 zeolite. The tests were performed using the homemade 'hydrogen' test bed which provides the possibility to get temperatures above 800 °C at pressures up to 2 Mpa and to study the the water vapor effect on the membrane material. Formation of nanopores in the entire membrane bulk with sizes required to separate CO and H<sub>2</sub> was shown basing on these results, membrane devices can be designed and manufactured. Thus, through the use of natural gas instead of pure hydrogen, application of solid polymer fuel cells in industry can be significantly expanded; they can be applied both as independent power sources and as a part of hybrid engines. As a result, the efficiency of the power systems can increased up to 55-65% and higher.

## 1. INTRODUCTION

An effective way to increase the efficiency of modern power is a combined operation of a fuel cell and gas turbine engine [1]. At present, introduction of fuel cells (FC) into power systems is accompanied with developments of the so-called 'hybrid engines' including a gas turbine unit (GTU) and a fuel cell operating as DC electric generator. Using a higher air pressure downstream of the GTE compressor, one can significantly reduce mass and sizes of a fuel cell. At the same time, utilization of the exhaust gas heated up to 550-950 °C allows preheating air/fuel and producing steam. The latter is re-

quired to start the process of conversion of the baseline liquid or gaseous fuel into synthetic gas - H<sub>2</sub>/CO mixture. So, it becomes possible to improve the efficiency of the fuel cell up to 55-65%. In turn, GTE environmental and efficiency characteristics can be increased when it is operated as a part of a hybrid engine in combination with FC. This is due to decrease in the consumption of fuel necessary to heat the working media up to a required initial temperature at the turbine inlet. The FC efficiency also increases up to 28-30%, while the greenhouse gas emissions and toxic component exhaust are decreased. Summarizing available reference data, one

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can expect that the hybrid engine efficiency can be increased up to 70% and even higher.

FC with solid electrolytes, polymer exchange membranes at low temperatures or ceramic membranes at high temperatures, seems to be the most efficient for above goals; however, high temperature solid electrolyte fuel cells (SOFC) are considered to be more effective because their efficiency increases with the increase in the initial temperature of fuel and oxidant flow. In addition, CO-containing reagents not affect negatively on the electrolyte-electrode unit since there are no platinum-type catalysts here.

On the other hand, since the gas contains some additional components besides  $H_2$  and CO ( $N_2$ ,  $CO_2$ ,  $H_2O$ ,  $O_2$ , etc.), their negative effect should be accounted for. Indeed, these gases are not involved into the electric-chemical reactions on the anode; so they can be considered as inert gases. They reduce the contact surface between electrolyte and catalysts filling up some catalyst pores. As a result, the volt-ampere characteristics degrade [2]; see Fig. 1.

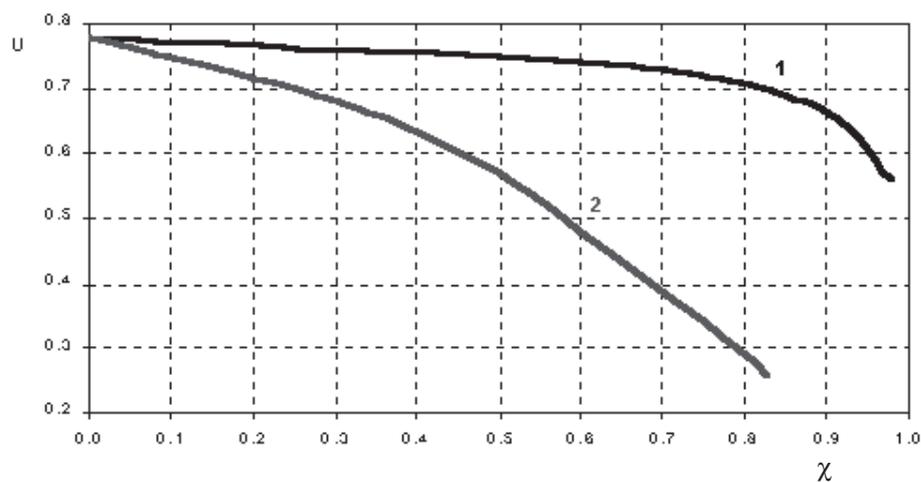
Hydrogen content in the synthetic gas is ~ 40-60 vol.% (8-12 wt.%); so, the mass-size characteristics of FC operating with this gas mixture increase. The negative effect of inert components of the synthetic gas was discussed above. In addition, carbon monoxide affects adversely the FC reliability and exploitation time due to CO pyrolysis causing soot deposits on the internal surface of the fuel cell. Therefore, the efficiency, compactness, and stability of a power plant can be improved via the gas mixture separation providing hydrogen delivery to the SOFC anode with no concurrent gases.

So, an aim of the present study was to develop a concept of molecular ceramic membranes structure and to work up its manufacturing. Such molecular ceramic membranes (MCM) with structurally inherent reformer (Fig. 2) should allow hydrogen separation from CO-containing hydrocarbon fuel reforming products at high temperatures of 800-950 °C and pressures  $\leq 2$ MPa.

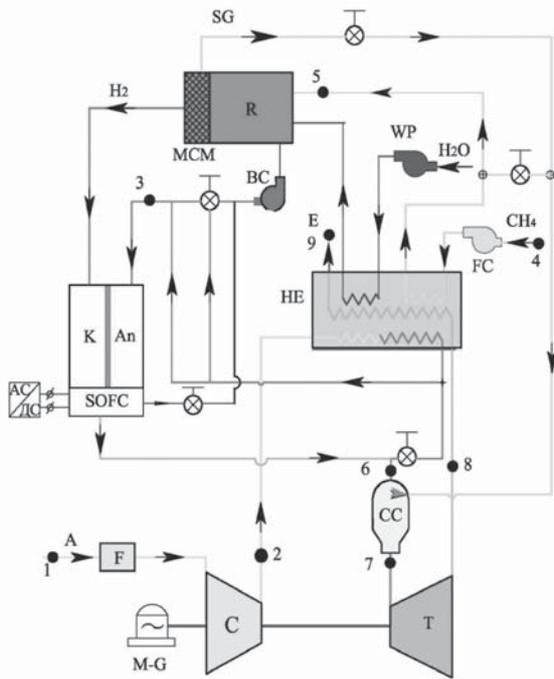
As an illustration, Fig. 2 demonstrate calculations performed for a hybrid (SOFC+ mGTE) engine with effective power of 4.5 kW. Here we assume that all the reagents from the reformer are completely separated into (1) a pure  $H_2$  flow (CO < 0.01 vol.%) that enters SOFC and (2) a flow that contains all other synthetic gas components (CO,  $CO_2$ ,  $N_2$ ,  $N_2O$ ,  $O_2$ , etc.) which is delivered to the mGTE combustor with a power of ~500 W. The total efficiency of the hybrid engine was estimated as 65%. Note that the efficiency of the current electric-chemical SOFC generators does not exceed 45-50% [3] in modern FC-power plants.

Similar  $H_2/CO$  separation can be provided by MCM in PEMFC equipped with electrodes with platinum metal group catalytic coating. However, their use is limited for natural gas as fuel because a catalyst poisoning occurs at CO percentage as low as >0.01 vol.%. The use of techniques based on metal molecular membranes (e.g. Pd-based) requires the gas mixture cooling down to 500-550 °C [4-8] from 650-900 °C typical at the reformer exit. Thus, the total efficiency of PEMFC of plant decreases to 35-40 % [4-8].

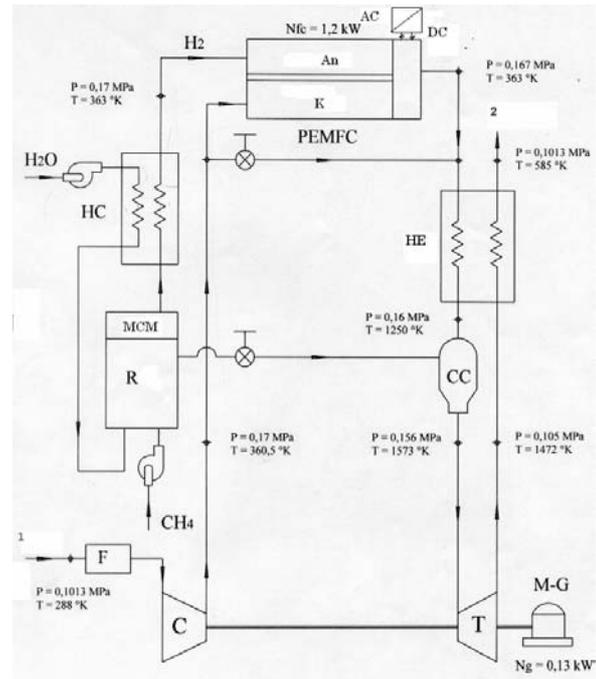
Fig. 3 shows the thermodynamic scheme of hybrid engine (PEMFC+  $\mu$ GTU) with the net power of 1.2 kW and main parameters in the characteristic



**Fig. 1.** Voltage (V) on FC versus percentage  $\chi$  of neutral gas applied at the current density  $0.4 \text{ A/cm}^2$  (data replotted from [2]); 1 – admixture to oxygen, 2 – admixture to hydrogen.



**Fig. 2.** Thermodynamic scheme of hybrid (SOFC +  $\mu$ GTE) engine. Designations: A-air, F-filter, C-compressor, T-turbine, M-G - motor-generator, CC - combustor, HE - heat exchanger, MCM- molecular ceramic membrane, R - reformer, BC - booster compressor, WP - water pump, FC- fuel compressor, SG - synthetic gas, E - exhaust gas, AC- alternating current, DC- direct current, K - cathode, An - anode.



**Fig. 3.** Thermodynamic scheme of hybrid engine (PEMFC +  $\mu$ GTU). Designations: 1- air; 2 – outlet; AH – hydrogen cooler; R – reformer; C – compressor; PEMFC – fuel cell; M – G – motor – generator; F – filter; MCM – molecular ceramic membrane; HE – air heater; CC – combustor; T – turbine An – anode; K – cathode; AC – alternating current; DC – direct current.

points of the cycle. As can be seen from the figure, mass-size and cost values of the power plant could be reduced by utilization of the reagents heat, while the efficiency of the PEMFC hybrid engine increases up to 55 %.

## 2. MOLECULAR CERAMIC MEMBRANES

Within the last decade, a number of leading companies in US, Japan, and Germany have been involved into R&D of high temperature (800-1200 °C) molecular composite and ceramic membranes capable to provide an efficient and stable operation of FC-based (particularly, PEMFC) conventional and hybrid engines [7,8]. A promising feature of zeolite application for such membranes is a possibility to increase their exploitation temperature up to 800-900 °C. The analysis of data reported in [9,10] allow to conclude that the trend of the current R&D is to

develop surface type MCMs. At such approach, nanopores that separate gas with a certain maximum size of the molecule are formed only within rather thin ( $\leq 100$  micron) surface layer of the macroporous metal or ceramic carrier. This dramatically constraints feasibilities of designing proper MCMs proper geometry and, also, developing membrane devices, reformers, fuel cells with inside reforming, *etc.*

The aim of the present study was to develop zeolite-based MCM that would build up nanopores using structural spaces of the membrane forming zeolite. To separate hydrogen from the synthetic gas flow, such volume molecular ceramic zeolite-based membranes should meet the following requirements specifications:

- Pore size  $\leq 3.1 - 3.2$  Å;
- Mesopore size  $\leq 10$  nm;
- Macropore size  $\leq 8.0$  mm;
- Open porosity  $\leq 50\%$ ;

- Operation temperature – 800-950 °C;
- Mechanical strength at compression - 20–30 Mpa;
- Life-time  $\geq 8000$  hours;
- Water steam resistance – 100%;
- CO content in flow downstream the membrane device –  $\leq 0.01$  vol.%;
- Nanopore formation zone within carrier structure - all across its volume.

Sample MCMs were 26 mm diameter and 5 mm thick discs manufactured from ZMS-5 zeolite. ZSM-5 is high silicon zeolite; this mainly determines its special properties such as thermal stability at the temperatures 1000 °C and higher, acidity up to pH = 3, and a significant mechanical strength. At synthesis, the final zeolite structure does not fill up all the space, it contains some space as prisms and channels. Formation of the inlet windows and syngony of zeolite depend on many variable factors and, primarily, the nature and sizes of the mixed cations. This enables to govern the syngony of the zeolite obtained and to change the sizes and configurations of the inlet window from the circular to ellipsoid. Zeolite ZMS-5 crystals (Fig. 4) have a monoclinic structure with orthorhombic syngony of sizes of around 50000 nm with parameters of the elementary cell  $a=2.01$  nm,  $b=1.94$  nm, and  $c=1.34$  nm. The porous system of ZMS-5 zeolite includes a system of intersecting channels - forward and sine-shaped. The elementary cell of ZMS-5 contains two intersecting channels (forward and sine-shaped) formed by 10-member rings of oxygen atoms. The

sine-shaped channel has sizes of elliptic windows 0.54 x 0.56 nm, forward one – 0.51 x 0.55 nm. The pore volume in ZMS-5 zeolite is 0.17 cm<sup>3</sup>/g. Microscopic analysis and X-ray patterns confirmed that obtained structure was ZMS-5 crystals.

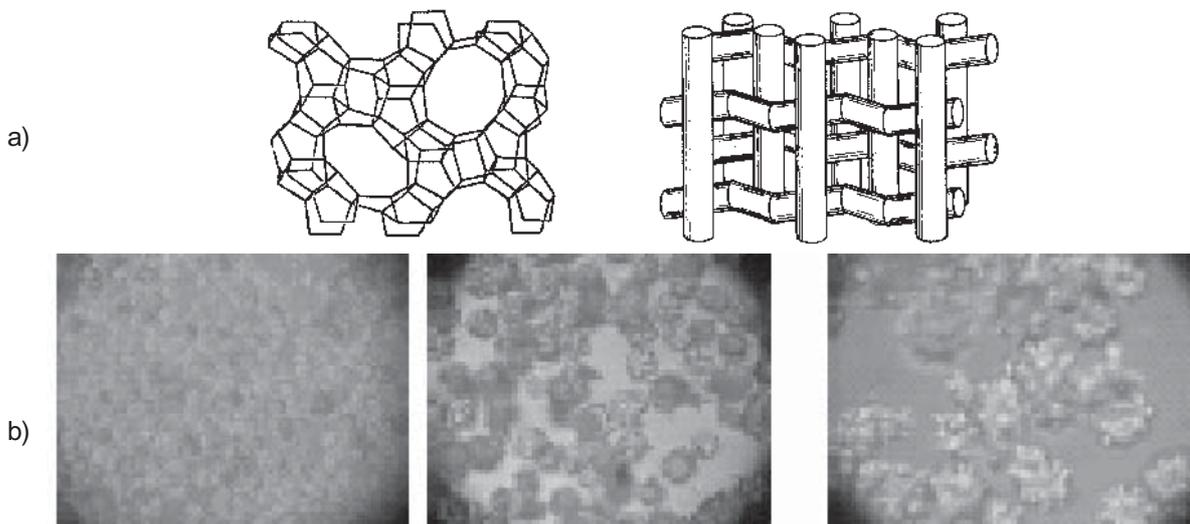
Molding of a required volume structure included the following operations :

- hydrothermal synthesis of zeolite in an autoclave at high temperatures and pressures;
- preparation of glass: founding in crucible, water strengthening, grinding, fraction selection;
- preparation of binder – glass+kaolin+ZMS-5;
- mixing;
- molding;
- sintering at 750 °C in the tube gradient-free furnace.

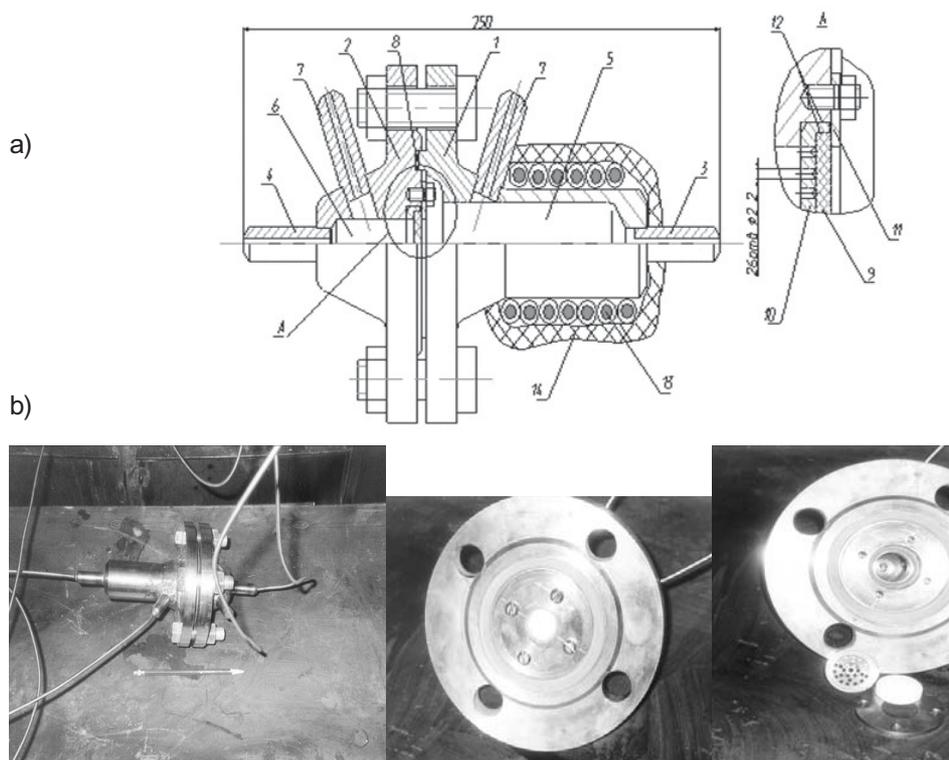
The carriers manufactured of ZMS-5 for experimental membranes had the total porosity within 40-45% at the macropore sizes of ~ 5-7 microns with a very narrow distribution range. A fraction of these macropores formed by the binder introduced during the membrane formation process was less than 4-5% of the total porosity.

### 3. EXPERIMENTAL CELL

An experimental cell (Fig. 5) was designed and manufactured to test the ceramic supports and molecular membranes. The cell includes two solid metal casings – inlet 1 and outlet 2 with connecting flanges; pipelines 3 and 4 for supplying and dis-



**Fig. 4.** Microstructure of zeolite crystals ZMS-5. a –stereodiagram of porous zeolite system ZMS-5; b – scheme of mutual location of intersecting channels of zeolite ZMS-5; c – micrograph of zeolite ZMS-5 (200 to 800 magnification).



**Fig. 5.** Experimental cell. a, b - experimental cell; c - outlet casing of experimental cell with gas distribution membrane mounted therein; d - dismantled outlet casing of experimental cell with thrust holder, gas distribution membrane, pressing ring. Designations: 1 – inlet casing; 2 – outlet casing; 3 – gas supply pipe connection; 4 – gas discharge pipe connection; 5 – inlet cavity; 6 – outlet cavity; 7 – pipe connection for instruments impulse tubes; 8 – packing of annealed copper; 9 – MCM; 10 – metal yoke; 11 – pressing ring; 12 – high temperature sealant; 13 – electric heating spiral; 14 – insulation.

charging gases; inlet – 5 and outlet – 6; pipeline 7 to connect impulse tubes of the measuring instruments. The casing and pipelines were made from stainless steel 12X18H10T (Russian classification). To ensure a reliable air-tightness of the internal cell, a flange connection was made as pin-groove with packing (8 in Fig. 5) made from annealed copper. The cell was intended to operate reliably when it is exposed to the excess internal pressure of 2 MPa and the gas temperature up to 1000 °C.

A metal yoke 10 with perforated bottom was mounted inside the flange connection of the casing; it was hold there by a pressing ring 11. MCM tablet (9 in Fig. 5) was placed inside the yoke on its bottom. To forestall likely leaks, annular gaps between the yoke and cylindrical wall of the boring in the outlet casing flange and between the yoke and the tablet were smeared with a high temperature sealant (12 in Fig. 5).

With the yoke with tablet secured by ring 11, the area through which the gas supply to the membrane is decreases. This parameter was characterized by so-called effective diameter used to calculate hydraulic membrane resistance. A stressed state of MCM (see computations in Fig. 6) is fairly acceptable; the maximum compression stress in the tablet was about around 10 MPa at the pressure drop on the tablet of 2.5 MPa even with account of the yoke effect.

The space 5 of the inlet casing 1 is longer and has greater volume. This allows its use for heating the gas mixture and its supply to the whole surface of filtrating membrane. The casing and separated gas were heated by a resistive heater (12 in Fig. 5) which was a coil wrapped around the unit. Soft insulation 14 was used to cover the inlet casing 1 and coil 12.

#### 4. INSTALLATION TO TEST MCM

Fig. 7 demonstrates the scheme of an installation used to test  $H_2/CO$  mixture separation by the direct flow measurements. The gas separation molecular membrane was placed in the experimental cell (1) mounted between the inlet (2) and outlet (3).

Both inlet (2) and outlet (3) were connected by a system of pipelines and valves (8), (9), (10), (11), and (12) with  $H_2$ , CO, and air cylinders marked in Fig. 7 as (5), (6), and (7), respectively. The outlet (3) was connected with a flowmeter (16) via membrane (4) and a valve (13) to measure the gas flow supplied to the volume. Pipelines for pressure measurements in the inlet and outlet regions were also connected. A blow-down of the experimental cell was carried out through the same pipelines using valves (14) and (15).

Pressure measurements were conducted by the sample pressure gauges установленными перед кранами (14) and (15) with an accuracy of  $\pm 0.1\%$ . The gas temperature in the inlet and outlet regions was measured by chromel-alumel thermocouples (18) with electrode diameter of 1.0 mm; the uncertainty of measurement was  $0.1\text{ }^\circ\text{C}$ . Since the effect of cold soldering was under an automatic control, the error in temperature measurements was less than  $\pm 0.1\text{ }^\circ\text{C}$ .

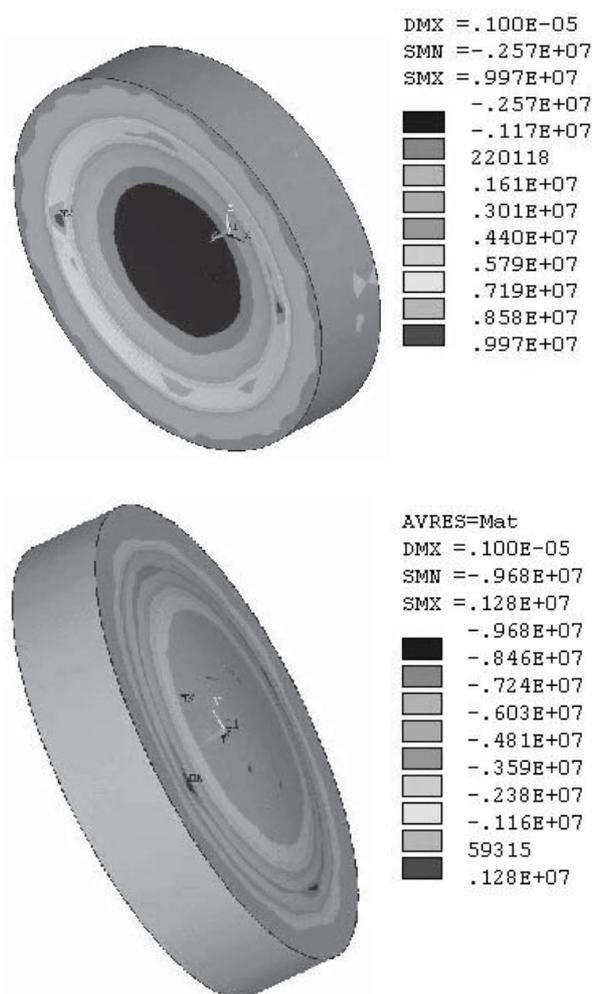
The direct identification of gas volume passing through the molecular membrane from the inlet to outlet cell was employed to measure the flow. A flowmeter (16) including a vessel (20), output siphon (22) and a measuring glass (21) was used here. Vessel (20) was filled with the service water during the adjustment tests or with the co-called 'twice-distilled' product, i.e. liquid that does not solute  $H_2$  or CO. Liquid supply and discharge into the measuring glass (21) from the vessel (20) is conducted through plug (24); a hole with valve (25) provide air exit when the vessel is filled up.

When the valve (13) opens, gas that supplies into the vessel (20) under pressure squeezes liquid into the measuring glass (21) via the siphon discharge (22). At the same time, as the measuring glass (21) begins to be filled up, the timer (23) is switched on and the pressures are measured.

The error of the flow measurements is a function of the measuring glass scale division (5 milliliter) and error at time measuring by timer ( $< 1\text{ sec}$ ); the total uncertainty is less than 10%.

#### 5. RESULTS

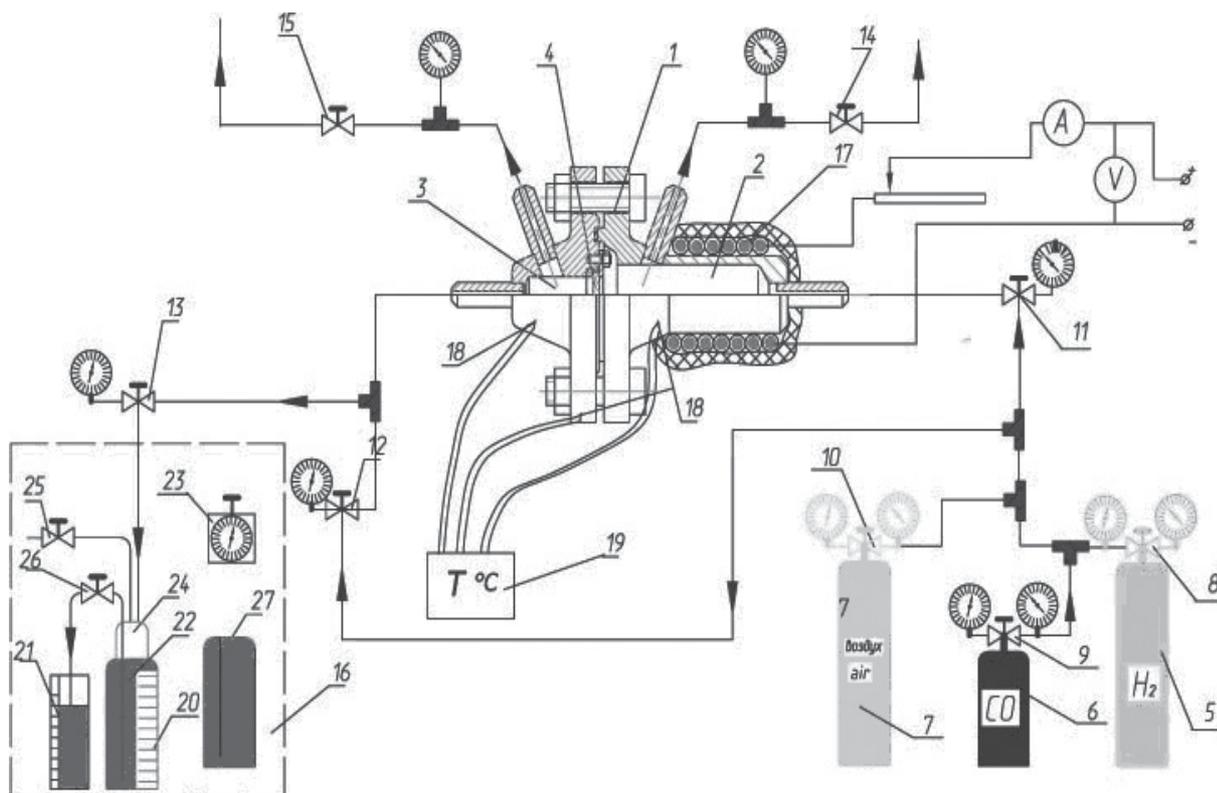
Fig.8 presents the pressure ratio  $P_1/P_2$  upstream and downstream of the membrane (1n) versus the



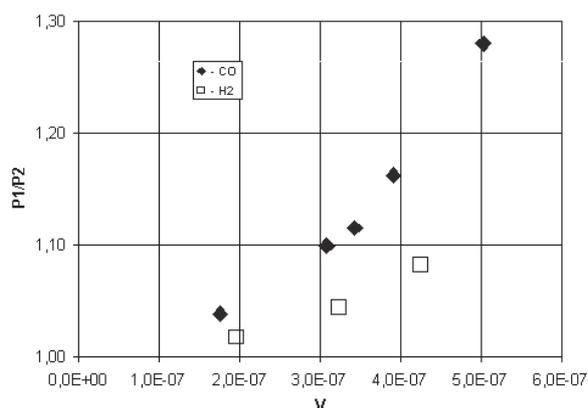
**Fig. 6.** Stressed state of membrane (main stresses in Pa). Membrane without support on metal yoke at pressure drop on membrane  $P=2.5\text{ MPa}$ .

volume flow  $V\text{ (m}^3\text{/s)}$  of carbon monoxide (CO) and hydrogen ( $H_2$ ). As seen from the figure, the hydrogen flows are 1.5 – 1.7 time higher than CO flows at equal pressure ratios on the zeolite membrane. So, we conclude that the developed technology provides the formation of three-fold porous system over all the volume of zeolite ZSM-5 mixture.

Analysis of the experiments data allowed elaboration of an optimum procedure of zeolite molecular membranes manufacturing to obtain necessary technological parameters and a selection of optimum ratios between the mass of nanoporous filter and macroporous carrier; the latter was found to be about  $\sim 15\%$ . Note that the data in Fig.8 deals with the above discussed membrane design.



**Fig. 7.** Scheme of experimental installation. Designations: 1 – experimental cell; 2 – inlet cavity; 3 – outlet cavity; 4 – molecular membrane; 5,6,7 – bottles with  $H_2$ , CO, air; 8 – 15 – flow control cocks; 16 – flow meter; 17 – electric heater; 18 – thermocouples; 19 – multimeter; 20 – vessel with liquid; 21 – measure capacity; 22 – siphon; 23 – timer; 24 – air-tight plug with output; 25 – air cock; 26 – siphon valve; 27 – capacity with flow liquid.



**Fig. 8.** Pressure ratio  $P_1/P_2$  on zeolite membrane (1n) versus CO and hydrogen flow ( $m^3/s$ ).

## 6. SUMMARY

1. Molecular ceramic membranes consisting of the high temperature zeolite ZSM-5 and the nanoporous molecular filter of ZSM-5, sodium-boron-silicon glass and kaolin mixture introduced all across its volume are suggested to separate  $H_2$  and CO flows at the temperatures ranging from 800 to 1000 °C and pressures over 1 MPa.
2. The MCM membrane device on the basis of zeolite ZSM-5 can guarantee meeting all target specifications including the CO content in the  $H_2$  less than 0.01 vol.%.
3. The cost of the developed MCM at serial production is much lower that of the molecular membranes based on palladium or its alloys.

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