

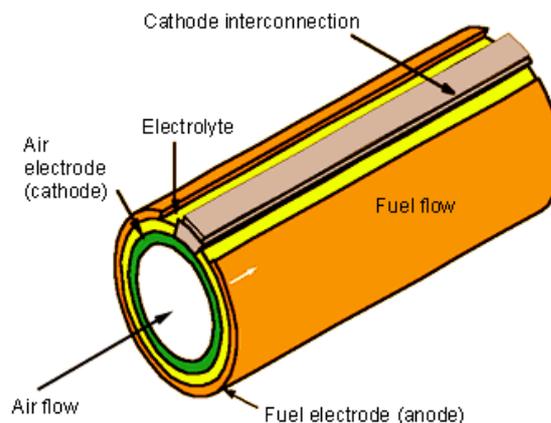


## 2. Fuel cells

A fuel cell is an energy conversion device that converts the chemical energy a fuel gas directly to electrical energy without the need for direct combustion as an intermediate step. A fuel cell operates as long as both fuel (it can be natural gas) and oxidant (air ) are supplied to the electrodes (fig.2). Fuel cells are generally classified by temperature of operation. The first type is fuel cell which temperature is about 50-210 °C (Alkaline Fuel Cell, Direct Methanol Fuel Cell, etc.) and it is used in small devices. The second type is high temperature fuel cell (600-1000 °C), which can be used in a large power station, for example with a gas turbine. Among these types are Solid Oxide Fuel Cell (SOFC) and Molten Carbonate Fuel Cell (MCFC).

## 3. Solid Oxide Fuel Cells

Among the SOFC technologies, tubular SOFC stacks with internal reforming seem to be one of the most popular devices. They promise to be extremely useful in large, high-power applications such as full-scale industrial stations and large-scale electricity-generating stations. The SOFC are developed as planar fuel cells as well, but they are still in much early development stage [5]. The tubular SOFC have been mainly developed by Siemens –Westinghouse company for over 40 years (fig.2).



**Fig.2 Siemens tubular SOFC technology.**

A SOFC consists of two electrodes sandwiched around a hard ceramic electrolyte such as the remarkable ceramic material called zirconia (YSZ-yttria stabilized zirconia). Hydrogen (fuel) is fed into the anode (NiO/YSZ) and oxygen (oxidant) enters the cell through the cathode (LaSrFeO<sub>3</sub>). The result of reaction of oxygen and hydrogen are a steam, a electrical current and thermal energy. The high operating temperature allows for internal reforming, so a fed fuel can be a natural gas consisting of methane and other hydrocarbons. Hence, at first hydrocarbons have to be convert to hydrogen in reforming and shifting reactions by means of steam which is produce in SOFC. It requires to use an additional elements in fuel cells i.e. mixer, pre-reformer (fig.3).

#### 4. Solid oxide fuel cell model

Our model of SOFC belongs to zero dimensional models (0D), because it contains an algebraical integral formulation of typical balances: mass, momentum, and energy and equilibrium models of reactions [1,2,3].

The SOFC with an internal reforming is divided into main five elements i.e. mixer, pre-reformer, anode side, cathode side and a post-combustion chamber (fig.3).

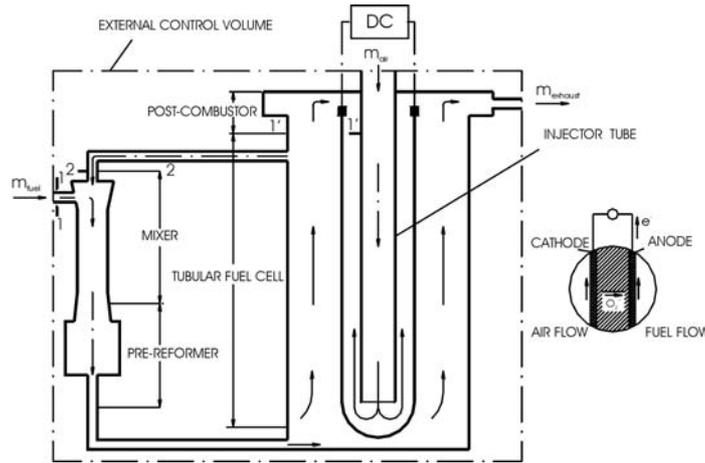
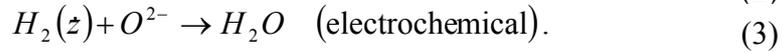
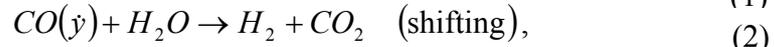
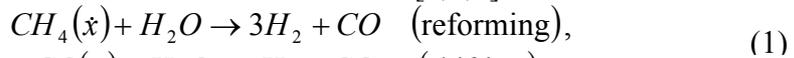


Fig.3 A lay-out of the tubular SOFC.

Three types of reactions are considered inside the fuel cell [1,2,3]:



Where:

- $x$  is the number of  $CH_4$  moles which react in reaction (1),
- $y$  is the number of  $CO$  moles which react in reaction (2),
- $z$  is the number of  $H_2$  moles which react in reaction (3).

It is assumed that in the pre-reformer (which is a typical catalytic reactor where hydrogen and carbon dioxide are produced from methane and steam) take place reforming (1) and shifting (2) reactions. Only the part of methane is able to react in the pre-reformer, so it is assumed as follows [1]:

$$\dot{x} = pre_r \cdot \dot{n}_{CH_4}^i$$

where  $pre_r = 10 - 15\%$  is a typical value of percentage of methane, which is able to react in the pre-reformer. The CO-shifting reaction is considered to reach thermodynamic equilibrium: <sup>(4)</sup>

$$K_{p,shift}(T) = \frac{\dot{n}_{H_2} \cdot \dot{n}_{CO_2}}{\dot{n}_{H_2O} \cdot \dot{n}_{CO}}. \quad (5)$$

An equilibrium constant is function of outlet pre-reformer temperature  $T$

$$\log K_{p,shift} = A \cdot T^4 + B \cdot T^3 + C \cdot T^2 + D \cdot T + E. \quad (6)$$

On the anodic side, all reaction (1), (2), (3) are considered. The shifting reaction on the anodic side is in an thermodynamic equilibrium similarly to pre-reformer's shifting reaction.

The electrochemical reaction is progressed on the anodic side, where an electrical current is generated. It is assumed that the fuel utilization factor  $U_f$  is responsible for electrical current flow as follows [1]:

$$U_f = \frac{\dot{z}}{\dot{n}_{H_2}^i + \dot{n}_{CO}^i + 4 \cdot \dot{n}_{CH_4}^i}. \quad (7)$$

The standard value of  $U_f$  is about 85 %, because the electrical power reaches the maximum value. Since one mole of  $H_2$  reacts ( $z$ ) in one second, the corresponding generated current is 96439 A. Thus:

$$I_c = 2 \cdot z \cdot F. \quad (8)$$

Usually, similarly to combustion process, the above reaction (3) needs to fed much more oxygen:

$$\dot{n}_{O_2}^{i,\min} = \frac{\dot{z}}{2 \cdot U_a}. \quad (9)$$

where  $U_a$  - the air utilization factor.

The choice of  $U_a$  (15-25%) depends on several exploitation problems such as a deactivation of cathode and strong thermal stresses within electrodes.

The evaluation of electrodes voltage  $V_c$  is the most difficult part of modeling process. In general, calculation of the cell voltage is performed as current density, the operating temperature, operating pressure and reactant and products composition function. Then, the voltage  $V_c$  is calculated as a difference between reversible ideal Nernst potential  $V_{oc}$  and irreversible potential  $V_{irr}$  [1]:

$$V_c = V_{oc} - V_{irr}.$$

where the Nernst potential is given [1,2]:

$$V_{oc} = \frac{-\Delta G}{2 \cdot F} + \frac{R_G \cdot T}{2 \cdot F} \ln \frac{p_{H_2} \cdot p_{O_2}^{0.5}}{p_{H_2O}}. \quad (11)$$

The Nernst potential is reduced, when the electrical cell circuit is closed due to the following irreversibilities [1,2]:

$$V_{irr} = (R_{OHM} + R_{ATTIV}) \cdot I_c. \quad (12)$$

where:  $R_{OHM}$  - ohmic resistance of the cell elements,

$R_{ATTIV}$  - polarization resistance of the electrodes,

The electrical current, thermal energy and steam are produced in the fuel cell. Part of steam is re-circulated from anodic side to mixer, where is mixed with fuel and then it is fed via a jet pump to pre-refomer. We have to assume a re-circulation ratio  $\alpha_{rec}$  such that reactions (2) and (3) will be very efficient. Hence, the steam to carbon ratio is defined as

the mole fraction of steam in the recirculated anode exhaust gas to all combustible species, implicate carbon, in supplied fuel (fig.3). It must be equal to 1.8-2.0 [1,2,3].

$$S / C = \frac{\dot{n}_{H_2O}^2}{\dot{n}_{CH_4}^1 + \dot{n}_{CO}^1}. \quad (13)$$

The mathematical model of the SOFC presented above is implemented in the Lahey Fortran 90 and Borland Delphi (similar to the COM-GAS code). In order to calculate SOFC module we have to know input values such as [1]:

- air mass flow rate and temperature,
- pressure of the cell,
- the recirculation ratio  $\alpha_{rec}$ ,
- the air utilization factor  $U_a$ , the fuel utilization factor  $U_f$ ,
- percentage of methane  $pre_r$ , which reacts in the pre-reformer.

The subroutine calculates the composition and the temperature of the exhaust gas for each part of the SOFC module, using these input parameters. Next, the program calculates the electrical current, the voltage and the electrical efficiency (LHV) of the SOFC module.

An electrical efficiency and the power output, increase when operation pressure of SOFC module increases, what is shown for single tubular cell (Siemens-Westinghouse) on fig.4 [1]. This feature and high operation temperature may be used in hybrid cycles consisting of the gas turbine (GT) and the fuel cell (SOFC).

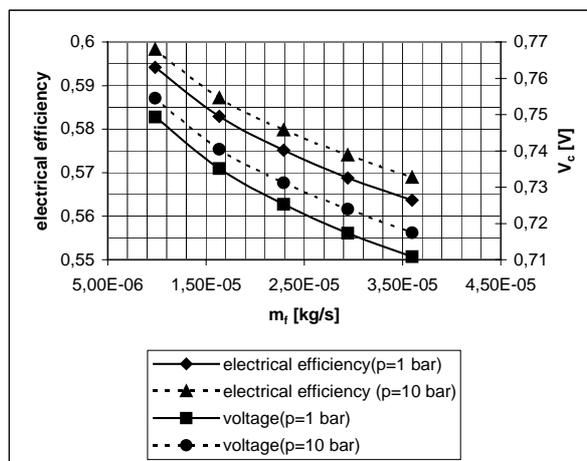


Fig.4 The single fuel cell parameters for different pressures.

## 5. Hybrid Cycles (SOFC+GT)

Among the hybrid cycles (SOFC+GT) there are considered four main types:

- a gas turbine with the atmospheric SOFC (fig.5),
- a gas turbine without the combustion chamber and with the SOFC (fig.6),
- a gas turbine with the pressurized SOFC before the combustion chamber (fig.7),
- a gas turbine with the pressurized SOFC before the combustion chamber and the atmospheric SOFC (fig.8).

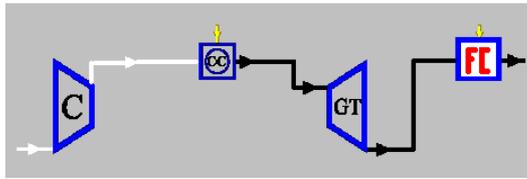


Fig.5 The gas turbine with the atmospheric SOFC.

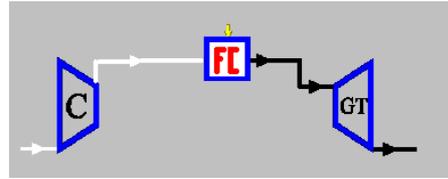


Fig.6 The gas turbine with the pressurized SOFC.

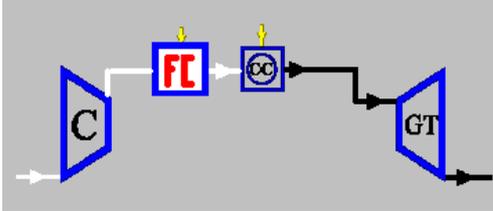


Fig.7 The gas turbine with the pressurized SOFC before the combustion chamber.

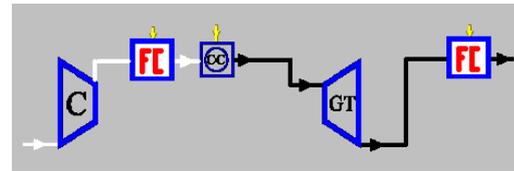


Fig.7 The gas turbine with the pressurized SOFC before the combustion chamber and the atmospheric SOFC

The gas turbine with the atmospheric SOFC (fig.5), which recovery part of hot gas energy is a least effective device, because SOFC gas exhaust temperature is bigger than from a gas turbine. Hence, it is necessary to use a heat recovery steam generator. The hybrid cycles with the pressurized SOFC (fig.6, fig.7) are expected to be the most effective solution. However, these hybrid cycles have a limitation connected with SOFC operation temperature, so the combustion chamber is used to increase temperature hot gas before a gas turbine.

Some of results calculations hybrid cycles with a gas turbine GT8C are presented in Table.1. These results are obtained by means of subroutine implemented into in-house code called COM-GAS. The SOFC stack consists of a tubular cells which are produced by Siemens-Westinghouse (outlet diameter 2.2 cm, length 1.5m ).

Tabl.1 The results of hybrid cycles.

Type	Power [MW]	Electrical Efficiency [%]	Number of cells [-]	Gas exhaust temperature [°C]
Gas Turbine GT8C	56,3	34	-	500
Gas Turbine GT8C with the atmospheric SOFC (fig.5)	126.0	46	406375	810
Gas Turbine GT8C with the pressurized SOFC (fig.6)	123.7	79	597080	288
Gas Turbine GT8C with pressurized SOFC before the combustion chamber (fig.7),	142	63	592570	370
Gas Turbine GT8C with the pressurized SOFC before the combustion chamber and the atmospheric SOFC (fig.8).	151.5	63	592570+ 56277	672

The most effective are hybrid cycles with pressurized SOFC what is shown in Table.1. The hybrid cycles with the atmospheric SOFC may be use with additional devices which decrease gas exhaust temperature. One of them is an Inverted Brayton Cycle.

### 6. Inverted Brayton Cycle (IBC)

Disposing of a hot exhaust gas at the ambient pressure from turbine or the fuel cell, a net positive specific work can be obtained first by expanding the gas, then by cooling it and, finally, by re-compressing it up to the ambient pressure. All these thermodynamic transformations may be performed by a turbine, a heat exchanger and a compressor. This cycle is commonly named Inverted Brayton Cycle IBC (fig.9, fig.10) [4].

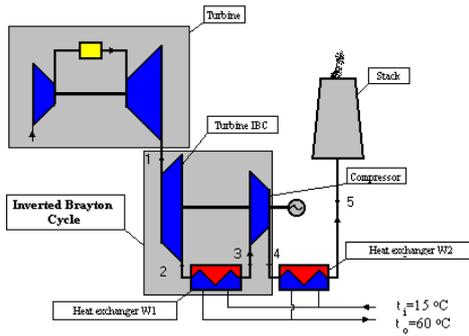


Fig.9 The Inverted Brayton Cycle.

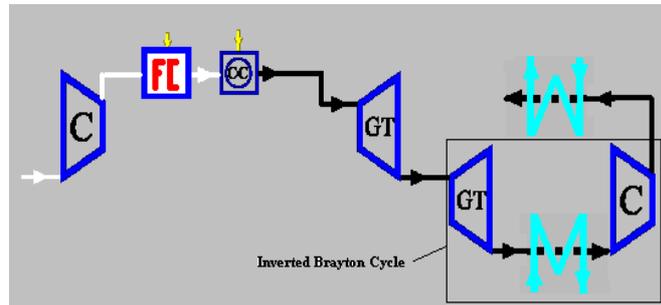


Fig.10 Hybrid Cycles with the Inverted Brayton Cycle.

The IBC engine may reduce the hot exhaust gas temperature producing additional electric power without any variation of the cold side temperature at the thermal utility inlet. Proper assumed turbine pressure ratio may increase an electrical efficiency and the electrical power, what is presented on fig.11.

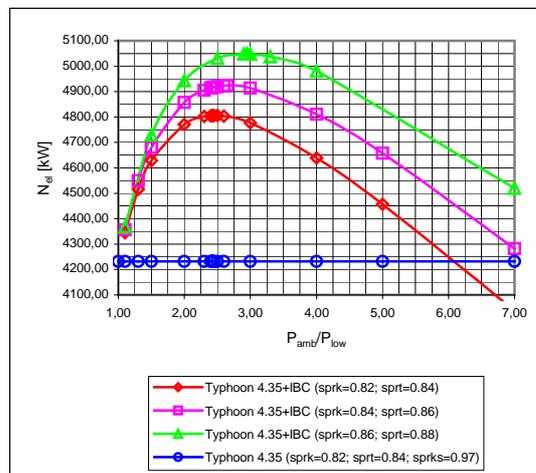


Fig.11 The electrical power of the gas turbine with Inverted Brayton Cycle.

The gas turbine used in modeling is Typhoon 4.35, which an electrical power is about 4.2 MW and an electrical efficiency is about 27 %. For the gas turbine Typhoon 4.35 with IBC engine an electrical efficiency increases up to 32% and, consequently, an electrical power growth of about 17 % to 4.9 MW ( the fuel input power is constant in both cases). Produce of an thermal energy is equal 8 MW [4].

## 7. Conclusions

In this paper, the mathematical model of SOFC, some results of analysis of Inverted Brayton Cycle and hybrid cycles have been presented. The SOFC electrical efficiency increases with the growth of operation pressure. The analysis of hybrid cycles has shown that the biggest an electrical efficiencies reach hybrid cycles with the pressurized SOFC. The hybrid cycles with the atmospheric SOFC have to use with a heat recovery steam generator or the Inverted Brayton Cycle. The gas turbine associated with the Inverted Brayton Cycle is the most effective for pressure ratio equal two. Application of IBC with the SOFC-GT systems may eliminate in the future a heat recovery steam generators from the power systems.

## 8. Literature

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