JOURNAL OF ENGINEERING annals OF FACULTY OF ENGINEERING HUNEDOARA
Tome V (year 2007), Fascicole 2, (ISSN 1584 – 2665)

LONG-TERM TESTS OF FUEL CELLS POWERED BY BIOGAS

[1.]Ján GADUŠ, [2.]Miroslav BOŠANSKÝ, [2.]Miroslav VEREŠ

[1.] SLOVAK UNIVERSITY OF AGRICULTURE IN NITRA,
FACULTY OF AGRICULTURAL ENGINEERING, SLOVAKIA
[2.] SLOVAK UNIVERSITY OF TECHNOLOGY IN BRATISLAVA,
FACULTY OF MECHANICAL ENGINEERING, SLOVAKIA

ABSTRACT:
One of the preferred research areas supported by the European Commission is renewable energy sources. This paper presents results of long-term tests of Molten Carbonate Fuel Cells (MCFC) powered by biogas aimed on their life-time and efficiency. These tests were carried out in frame of a EU project Holistic integration of MCFC technology towards a most effective systems compound using biogas as a renewable source of energy, EFFECTIVE-Project N°: NNE5-1999-00224.

KEY WORDS:
fuel cell, biogas utilization, biogas powered fuel cells, MCFC – Molten Carbonate Fuel Cell, long-term testing

1. INTRODUCTION

A fuel cell is a device that generates electricity by the means of a chemical reaction. The principle of the fuel cell was discovered by German scientist Christian Friedrich Schönbein in 1838 and the first fuel cell was developed by Welsh scientist Sir William Robert Grove in 1843. The fuel cell he made used similar materials to today's phosphoric-acid fuel cell. Later in 1959, British engineer Francis Thomas Bacon and his colleagues demonstrated a practical five-kilowatt unit capable of powering a welding machine. In the 1960s, Pratt and Whitney licensed Bacon's U.S. patents for use in the U.S. space program to supply electricity and drinking water. UTC's power subsidiary was the first company to manufacture and commercialize a large, stationary fuel cell system for use as a co-generation power plant in hospitals, universities and large office buildings. UTC Power continues to be the sole supplier of fuel cells to NASA for use in space vehicles, having supplied the Apollo missions and currently the Space Shuttle program, and is developing fuel cells for automobiles, buses, and cell phone towers; the company has demonstrated the first fuel cell capable of starting under freezing conditions with its proton exchange membrane automotive fuel cell.

Every fuel cell has two electrodes, one positive and one negative, called, respectively, the cathode and anode. The reactions that produce electricity take place at the electrodes. Every fuel cell also has an electrolyte, which carries electrically charged particles from one electrode to the other, and a catalyst, which speeds up the reactions at the electrodes. Hydrogen is the basic fuel, but fuel cells also require oxygen. In practice, many fuel cells are usually assembled into a stack. A cell or a stack, the principles are the same. Today, the main electrolyte types are alkali, molten carbonate, phosphoric acid, proton exchange membrane and solid oxide. The first three are liquid electrolytes; the last two are solids.

Alkali fuel cells (AFC) operate on compressed hydrogen and oxygen (Figure1). They generally use a solution of potassium hydroxide (chemically, KOH) in water as their electrolyte. Efficiency is about 70 percent, and operating temperature is from 150 to 200 degrees C. Cell output ranges from 300 watts (W) to 5 kilowatts (kW). Alkali cells were used in Apollo spacecraft to provide both electricity and drinking water. They require pure hydrogen fuel, however, and their platinum electrode catalysts are expensive. And like any container filled with liquid, they can leak.

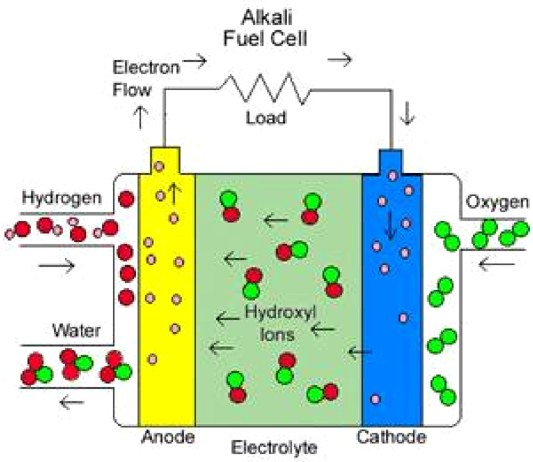


Figure 1. AFC Operational Diagram

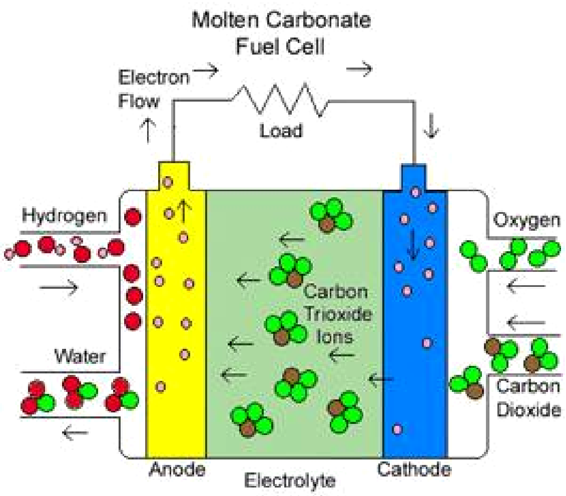


Figure 2. MCFC Operational Diagram

Molten Carbonate fuel cells (MCFC) use high-temperature compounds of salt (like sodium or magnesium) carbonates (chemically, CO_3) as the electrolyte (Figure 2). Efficiency ranges from 60 to 80 percent, and operating temperature is about 650 degrees C. Units with output up to 2 megawatts (MW) have been constructed, and designs exist for units up to 100 MW. The high temperature limits damage from carbon monoxide "poisoning" of the cell and waste heat can be recycled to make additional electricity. Their nickel electrode-catalysts are inexpensive compared to the platinum used in other cells. But the high temperature also limits the materials and safe uses of MCFCs—they would probably be too hot for home use. Also, carbonate ions from the electrolyte are used up in the reactions, making it necessary to inject carbon dioxide to compensation.

Proton Exchange Membrane (PEM) fuel cells work with a polymer electrolyte in the form of a thin, permeable sheet (Figure 3). Efficiency is about 40 to 50 percent, and operating temperature is about 80 degrees C. Cell outputs generally range from 50 to 250 kW. The solid, flexible electrolyte will not leak or crack, and these cells operate at an enough low temperature what makes them suitable for homes and cars. But their fuels must be purified, and a platinum catalyst is used on both sides of the membrane, raising costs.

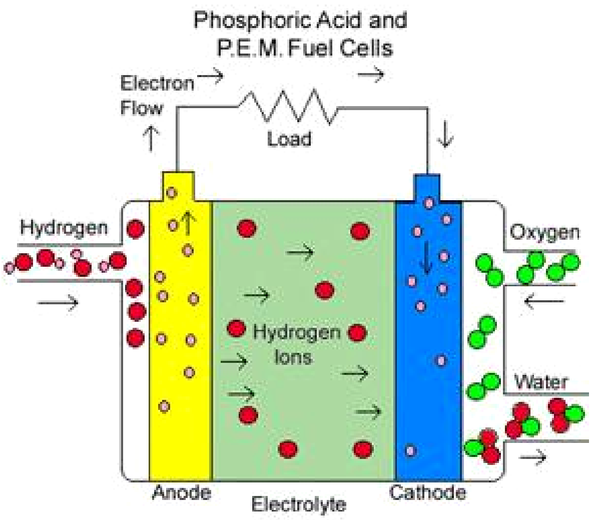


Figure 3. PEM Operational Diagram

Solid Oxide fuel cells (SOFC) use a hard, ceramic compound of metal (like calcium or zirconium) oxides (chemically, O_2) as electrolyte (Figure 4). Efficiency is about 60 percent, and operating temperatures are about 1,000 degrees C. Cells output is up to 100 kW. At such high temperatures a reformer is not required to extract hydrogen from the fuel, and waste heat can be recycled to make additional electricity. However, the high temperature limits applications of SOFC units and they tend to be rather large. While solid electrolytes cannot leak, they can crack.

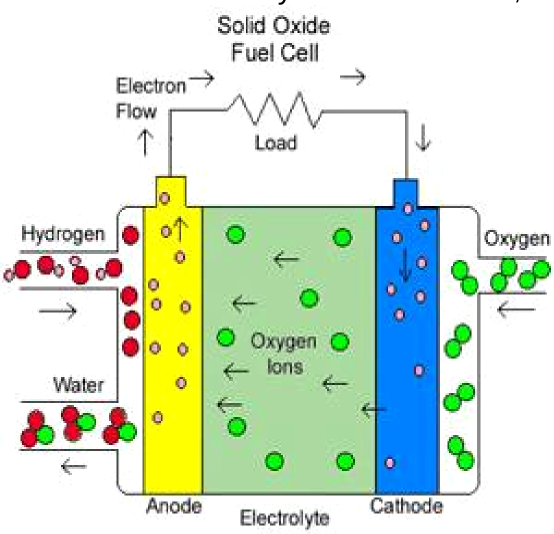


Figure 4. SOFC Operational Diagram

2. METHODOLOGY

A molten carbonate fuel cell operates at approximately 650°C. The high operating temperature is needed to achieve sufficient conductivity of its carbonate electrolyte yet allow the use of low cost metal cell components. An effect associated with this high temperature is that noble catalysts are not required for the cell electrochemical oxidation and reduction processes. Molten carbonate fuel cells are being developed for natural gas and goal-based power plants for industrial, electrical utility and military application. Currently Europe has three developers pursuing the technology of the MCFC: Brandstofel Netherland B.V (BCN), MTU Friedrichshafen, Ansaldo (Italy). MTU Friedrichshafen is an European leader of the MCFC technology with a new MCFC product "Hot Module". One Hot Module has an output approximately 250 - 300 kW with efficiency at about 65 %.

Simple operating principle

Individual cells are built as flat sandwiches. Two electrodes (anode and cathode) enclose a foil which is filled with the electrolyte lithium and potassium carbonate. When the hydrogen flows over one electrode and there are flows over the other one in an environment of 600°C, a process is started which generates electricity. This process employs low flow velocities at atmospheric pressure. The electron exchange takes place via the molten electrolyte with carbonate ions (CO_3^{2-}). They discharge on the anode side, give off an oxygen atom that combines with the hydrogen flowing by forming water (H_2O). The carbon dioxide (CO_2) takes one electron and an oxygen atom from the air which flows by and returns to the process as carbonate ion (CO_3^{2-}). The CO_2 content remains balanced. The hydrogen splits off from the natural gas (or biogas) at a catalyst in the anode chamber. High-temperature MCFCs can extract hydrogen from a variety of fuels using either an internal or external reformer. They are also less prone to carbon monoxide "poisoning" than lower temperature fuel cells, what makes coal-based fuels more attractive for this type of fuel cell. MCFCs work well with catalysts made of nickel which is much less expensive than platinum. MCFCs exhibit up to 60 percent efficiency, and this can rise to 80 percent if the waste heat is utilised for cogeneration.

Electrochemical reactions occurring in MCFC are:

$$H_2 + CO_3^{=} \rightarrow H_2O + CO_2 + 2e^- \tag{1}$$

at the anode (A), and

$$\tfrac{1}{2} O_2 + CO_2 + 2e^- \rightarrow CO_3^{=} \tag{2}$$

at the cathode (C).

The overall cell reaction is:

$$H_2 + \tfrac{1}{2} O_2 + CO_2(C) \rightarrow H_2O + CO_2(A) \tag{3}$$

Besides the reaction involving H_2 and O_2 to produce H_2O, the equation shows a transfer of CO_2 from the cathode gas stream to the anode gas stream with 1 mole CO_2 transferred along with two Faradays of charge or 2 gram moles of electrons. The reversible potential for an MCFC, taking into account the transfer of CO_2, is given by the equation:

$$E = E^0 + \frac{RT}{2F} \ln \frac{P_{H_2} P_{O_2}^{1/2}}{P_{H_2O}} + \frac{RT}{2F} \ln \frac{P_{CO_{2,c}}}{P_{CO_{2,a}}} \tag{4}$$

where the subscripts a and c refer to the anode and cathode gas compartments, respectively. When the partial pressures of CO_2 are identical at the anode and cathode, and the electrolyte is invariant, the cell potential depends only on the partial pressures of H_2, O_2 and H_2O. Typically, the CO_2 partial pressures are different in the two electrode compartments and the cell potential is affected accordingly as shown equation. It is usual practice in an MCFC system that the CO_2 generated at the anode is routed to the cathode where is consumed. This will require some scheme that will either:

1) transfer CO_2 from the anode exit gas to the cathode inlet gas (CO_2 – transfer devices)
2) produce CO_2 by combustion of the anode exhaust gas, which is mixed directly with the cathode inlet gas
3) supply CO_2 from an alternate source

Construction of the molten carbonate fuel cell

Current status of cell component technology for a molten carbonate fuel cell:

Anode: Ni - Cr/Ni - Al
3 - 6 m pore size
45 - 70% initial porosity
0,2 – 1,2 mm thickness
0,1 - 1 m^2/g

Cathode: lithiated NiO
7-15 m pore size
70 – 80% initial porosity
60 – 65% after lithiation and oxidation
0,5 – 1 mm thickness
0,5 m^2/g

Electrolyte: mixture $Li_2CO_3 + K_2CO_3$
0,5 – 1 mm thickness

These electrolyte structures were relatively thick (1 – 2 mm) and difficult to produce in large size because large tooling and presses were required. The electrolyte structures produced by hot pressing are often characterised by:

1) void spaces (< 5 % porosity)
2) poor uniformity of microstructure
3) generally poor mechanical strength

The electrolyte composition affects the performance and endurance of MCFC in several ways. Higher ionic conductivities, and hence lower ohmic polarisation, are achieved with Li-rich electrolytes because of the relatively high ionic conductivity of Li_2CO_3 compared to that of Na_2CO_3 and K_2CO_3. However, gas solubility and diffusivity are lower, and corrosion is more rapid in Li_2CO_3. The major problems with Ni-based anodes and NiO cathodes are structural stability and NiO dissolution, respectively.

Performance of the MCFC

Factors affecting the selection of operating conditions are stack size, heat transfer rate, voltage level, load requirement and cost. The performance curve is defined by cell pressure, temperature, gas composition an utilisation. Typical MCFC will generally operate in the range of 100 to 200 mA/cm^2 at 750 to 900 mV/cell. Typical cathode performance curves obtained at 650°C with an oxidant composition (12,6 % O_2, 18,4 % CO_2, 69 % N_2) that is anticipated for use in MCFC. The basic operating parameters which have affect on MCFC performance are:

- effect of pressure

$$\Delta V_p (mV) = 20 \ln \frac{P_2}{P_1} \tag{5}$$

($P_1=P_{1,a}=P_{1,c}$ and $P_2=P_{2,a}=P_{2,c}$)

- effect of temperature

$$\Delta V_T (mV) = 1{,}40(T_2 - T_1) \tag{6}$$
$$600^oC \le T \le 650^oC$$

- effect of reactant gas composition and utilisation
- effect of impurities
- effect of current density

$$\Delta V_J (mV) = -1.76 \Delta J \tag{7}$$
$$150 \le J \le 200 mA / cm^2$$

- effect of cell lifetime

$$\Delta V_{lifetime} = -5mV / 1000hours \tag{8}$$

3. BIOGAS POWERED MCFC

An effort to build an inexpensive, efficient, reliable fuel cell lead to the idea to use biogas to power the Molten Carbonate Fuel Cells. Efficiency and life-time of such fuel cells stacks (Figure 5.) were tested within a EU project Holistic integration of MCFC technology towards a most effective systems compound using biogas as a renewable source of energy, EFFECTIVE-Project N°: NNE5-1999-00224.

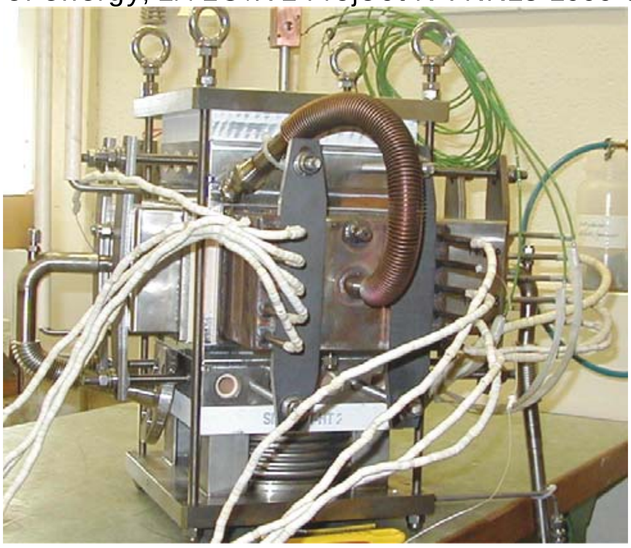


Figure 5. The Tested MCFC Stack

The tests were carried out by the Slovak University of Agriculture in Nitra (Slovakia) at the university biogas plant located in Kolinany. The supplier of the MCFC for their testing in application with biogas was the project partner MTU Friedrichshafen (Germany).
The parameters of the tested fuel cells were:

- type MCFC with an internal reforming of the biogas
- installed performance of the fuel cell 300W – nominal
- fuel hydrogen, natural gas, biogas (mixture CH_4/CO_2)

- operating temperature 600 – 650°C
- output voltage 7, 5 V (max. 11V – min. 6,5V)
- output current 35 A (max. 41A – min. 0A)
- active surface of the cell 250 cm^2

The main objectives were long-term endurance tests of an MCFC stack operating on biogas at various operating modes (Figure 6). Until then there were tested and used only MCFC stacks operating on the natural gas for which the achieved parameters have been usually the following:

- current density (loading) 100 – 200 $mA.cm^{-2}$
- achieved voltage 750 – 900 mV

Figure 6. MCFC Testbed

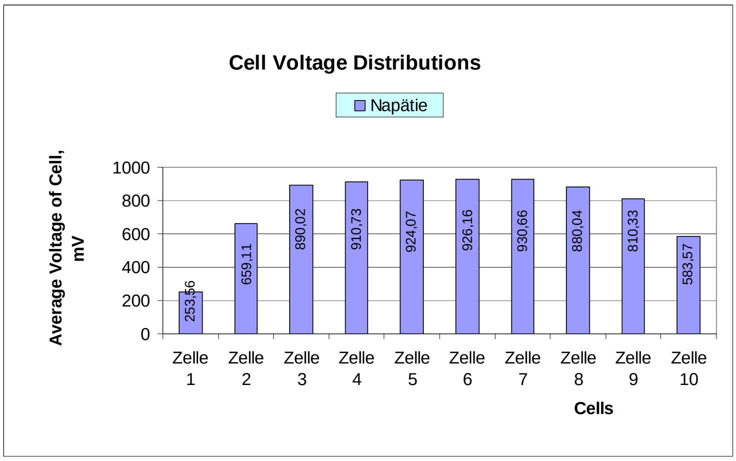
In our experiments influence of different parameters on the stack operation was monitored. In the concrete it was influence of the gas operating pressure (overflow), operating temperature, gas contaminants, current density and operating time. As an energy source for the MCFC stack we used a biogas which was a product of an anaerobic fermentation process. The processed biomass was cattle manure with these characteristic values: 60 – 65 % CH_4, 1 – 5 ppm H_2S, max 3 % O_2, 35 – 40 % CO_2.

4. CONCLUSION

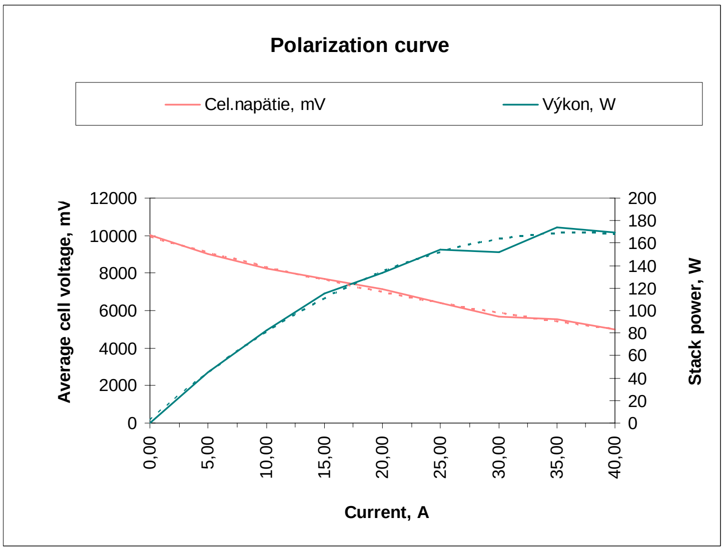
The total reached operating time of the tested MCFC stack was 1648 hours. Within that duration a full power operation was run 1648 hours.

Maximal output voltage of the stack U_{max} = 10351 mV was reached at the operation time 432,92 hours and maximal performance P = 182,7 W at 1245,58 hours of the operation time (Graph 1).

At an optimal current loading 100 – 140 $mA.cm^{-2}$ the fuel cells showed a right function: the reached voltages on the separate cells at the maximal loading 140 $mA.cm^{-2}$ were within an interval 750 – 800 mV while the usual voltage value of the fuel cells operating on the natural gas at similar load ranges from 750 to 900 mV (Graph 2).



Graph 1. Average Voltage On The Stack During The Operation



Graph 2. Polarization Curves Of MCFC Stack

The tests were focused on the composition of the biogas entering into the process, output voltage on the fuel cell in dependence on the load (current density), fuel cell output performance and on the temperature of the separate cells in the stack. The results showed that the use of the MCFC fuel cells operating on a biogas is possible, because the achieved performance parameters are comparable with the other up to now tested or running fuel cells operating mostly on the natural gas.

REFERENCES

[1.] Holoubek, D.: Palivové články – decentralizovaný zdroj blízkej budúcnosti, Magazín Energia, 2001
[2.] Kessler, M.; Ziegler, S.; Hoffmannn, J.: Brenstoffzellen – Ein Energiekonzept fur Zukunft, 2001
[3.] Knupper, O.: Dokumentation – ProjektBrennstoffzehlenprufstand MTU Friedrichshafen, 2002
[4.] M.C. Power Corporation: Molten Carbonate Fuel Cell Product Development Test – Final Report (September 1992- March 1997) for U.S . Department of Energy, Morgantown, West Virginia
[5.] Wiliams, M. C.: Fuel Cell, U.S. Department of Energy, Office of Fosil Energy, Morgantown, West Virginia 1999