SIMULATING FUEL CELLS WITH ECOSIMPRO

Eusebio Huélamo Martínez , Ramón Pérez Vara, Alfonso Méndez-Vigo, Jesús Álvarez González
Empresarios Agrupados, A.I.E.
Magallanes 3 - 28015 MADRID
Tel: 913 09 80 00. Fax: 915 91 26 55. E-mail: ehm@empre.es

Abstract

This work contains the following:

1. A description of a model for Alkaline Fuel Cells developed with the aid of EcosimPro for the European Space Agency, and the results of the experiment.

In order to build this model, specific components had to be programmed for the actual fuel cells and for the membrane separators (spacers). The physical phenomena contemplated in each one will be addressed.

2. A description of the model of the San Agustín de Guadalix Experimental Fuel Cell Plant constructed under the "Spanish Fuel Cell Programme".

To simulate this plant it was necessary to formulate the dynamic behaviour of Molten Multicarbonate Fuel Cells. All the main equipment and controls were included so that we could study all foreseeable operating modes as well as those which were reasonably possible but whose response had to be known a priori so as to be certain that they would not cause irreparable damage to the cell.

Key Words: Simulation, EcosimPro, fuel stack, anode, cathode, fuel cell.

1. INTRODUCTION

This paper is divided into two parts:

a) A description of the application of EcosimPro to the simulation of alkaline fuel cells
b) A description of the Simulation Model of the San Agustín de Guadalix Experimental Fuel Cell Plant which is in the construction stage under the Spanish Fuel Cell Programme

2. SIMULATION WITH ECOSIMPRO OF AN ALKALINE FUEL CELL

2.1. SYSTEM DESCRIPTION

Under contract by the European Space Agency, Empresarios Agrupados developed a model to study the dynamic behaviour of alkaline fuel cells.

The system selected for the model is based on supporting electrolyte alkaline cells designed for the Hermes space shuttle. The model built with EcosimPro is illustrated in Figure 2.

The system comprises the following:

- Main component:
  - Fuel stack
- Hydrogen loop:
  - Membrane separator
  - Centrifugal compressor
  - Jet compressor
  - Pipes
- Cooling loop:
  - Pump
  - Heat exchanger
  - Electric heater
  - Valves
  - Pipes
  - Joints or branches
- Control loops:
  - Heat sensors
  - PID controllers
  - Control systems

In each of the cells that comprise the stack, the hydrogen and oxygen react to generate electric current, producing water and generating heat. The hydrogen circulates through the jet compressor, assisted at low speeds by the compressor. The water produced in the fuel cells is transported in the form of steam by the hydrogen, and is partially extracted in the membrane separator.

The pump maintains the flow in the cooling loop which in turn extracts the heat produced in the fuel stack. The water passes through a heat exchanger which forms part of the Heat Control System of the Hermes space shuttle.

There is a controller which keeps the water temperature at its optimum operating point by branching off part of the water flow outside the heat exchanger. There is also a second control loop which regulates the temperature of the hydrogen at the outlet of the membrane separator, so as to ensure that the electrolyte concentration in the cells is within acceptable limits.

When the startup sequence begins, the system temperatures are usually below normal operating points. During this stage, all the cooling water is branched off and does not pass through the heat exchanger. Furthermore, it is preheated with the help of the electric heater which is in turn fed by the energy generated in the fuel stack itself. It need not be said that operation in these circumstances is most inefficient, producing a great deal of heat which makes the temperatures rise very quickly. Having completely bypassed the heat exchanger means that water cannot be extracted from the hydrogen flow and could lead to an electrolyte concentration, rendering the system inoperative. If the concentration becomes too low, the electrolyte could pass into the hydrogen loop and cause fuel stack failure.

This means that the startup stage is relatively critical and its study is therefore of great interest.

2.2. FUEL STACK MODEL

Inside each alkaline fuel cell the hydrogen gas passes through the porous electrode to the hydrogen which is in contact with the electrolyte and is absorbed inside the catalyser embedded in the anode where it reacts with the hydroxyl ions from the electrolyte to free electrons at the same time as it forms water. The loop is closed by the migration of ions from the cathode, through the electrolyte to the anode.

The simplified chemical reactions produced are as follows:

$$2H_2 + O_2 = 2H_2O$$

and in the electrodes:

$$H_2 + 2OH^- = 2H_2O + 2e^-$$

in the anode, and

$$O_2 + H_2O + 2e^- = 2OH^-$$

and in the cathode

Therefore, two water molecules are produced in the anode of which only one is consumed in the cathode. The other evaporates as it is transported by the hydrogen flow and extracted in the membrane separator.

A fuel cell of this type comprises the following:

1. Hydrogen channel
2. Anode
3. Matrix
4. Cathode
5. Oxygen channel
6. Wall
7. Cooling channel
8. Wall

The physical-chemical phenomena contemplated in the model are divided into three main calculation areas:

- Electrical solution
- Hydraulic solution
- Thermal solution

During the evaluation of the electrical solution, the stack operating point is calculated, and so is the mass, hydrogen, oxygen and water consumption or production. The cell operating point is determined by the voltage and density of current, based on behaviour curves which give the operating point as a function of thermodynamic variables, taking into account other electrochemical effects.

Knowing the operating point, the hydrogen and oxygen consumption and the amount of water produced can be calculated by directly applying Faraday's law.

Evaluation of the hydraulic solution facilitates the calculation of electrolyte concentrations and pressure losses in the different loops.

Evaluation of the thermal solution facilitates the calculation of heat flows due to evaporation, convection and conduction, as well as the heat produced by chemical reactions.

Figure 3 illustrates the cell model that was built.

This model, with six nodes, is sufficient to calculate the physical-chemical phenomena that occur in the cell and, therefore, to carry out the complete simulation.

Nodes 11, 15 and 17 represent the fluid channel inlets. Node 21 represents the hydrogen bed with hydrogen and water vapour. Node 23 represents the electrodes, the matrix and the oxygen; it is in this node where the chemical reaction takes place and where the heat produced is calculated. Finally, node 27 represents the cooling channel and the walls.

2.3. ECOSIMPRO MODEL FOR THE FUEL STACKS

Figure 3 contains a sketch of the model which was built to study the alkaline fuel cells. This sketch is a graphic representation of the topology of the EcosimPro model.

There is a clear relationship between this sketch and the actual system diagram, although the following differences should be noted:

The pipes of the hydrogen and cooling loops are not represented in the model because the pressure losses produced by them can be grouped as pressure losses of the actual components represented in the model. Likewise, no consideration is give to the thermal delays induced by these pipes, which are not significant from the point of view of simulation as they are very small compared to those caused by the thermal capacity of the components.

An accumulator has been introduced which, in fact, does not form part of the real system. It is however necessary so that we can obtain a mathematical solution of the cooling loop, avoiding having a redundant equation in it (of mass conservation) and helping to fix its operating pressure.

The three-way valves (real) have been represented by pairs of two-way valves whose characteristic curves (C_v in terms of opening) correspond to the former main line and lateral branch, respectively.

2.4. EXPERIMENTS STUDIED

In this work the term experiment has the actual meaning assigned to it in the nomenclature of the EcosimPro package. Using the model described, the following experiments have been studied:

- Steady state of the system under different loads
- Simulation of different types of transients, different power-time profiles
- Simulation of system behaviour during the startup stage, with the following initial conditions:
    - Initial power demand nil
    - Complete system at ambient temperature
    - Cooling pump working at rated velocity
    - Hydrogen circuit compressor working at rated velocity

Figures 4, 5 and 6 contain the model response graphs for an experiment.

3. SIMULATION OF THE SAN AGUSTÍN DE GUADALIX EXPERIMENTAL FUEL CELL PLANT

3.1. GENERAL

The San Agustín de Guadalix Experimental Fuel Cell Plant was modelled with EcosimPro as shown in Figure 7 and represents the complete Plant model.

The control systems are modelled in their entirety enabling studies to be carried out for their design/setting, and correct Plant operation can be obtained.

The final aim is to avail of an overall model of the Experimental Plant in San Agustín de Guadalix so that, always from the engineering point of view, the following can be carried out:

- Studies of behaviour, comparisons between the real values measured in a determined experiment and the calculation results. As well as serving to validate the model, they will also serve to modify it so that it better adapts to reality in an iterative process

- "What happens if …" analyses, so that the resulting effects can be predicted before performing a certain operation, adjusting control parameters, etc. The greater the approximations obtained as a result of the previous point, the more reliable this will be

The system comprises three main loops. Three additional models have been built representing each of them, but they have been simplified as much as possible to be able to study the individual behaviour of each of the parts, assuming that the behaviour of the rest is known and imposed as boundary conditions.

3.2. ANODE LOOP

The anode loop is modelled as shown in Figure 8 and includes:

- H_2 tank
- Steam boiler
- CO_2 tank
- N_2 tank
- First and second stage heaters
- Interconnecting pipes
- Control valves
- Anode recirculation blower
- The following controls:
    - CO_2 and steam flow control (eventually N_2 control)

  - Temperature control at the outlet of the first stage heater
  - Temperature control at the outlet of the second stage heater
  - Temperature control at the inlet to the stack
  - Recirculation blower bypass control

3.3. CATHODE LOOP

The cathode loop is modelled as shown in Figure 9 and includes:

- Inlet air
- Air compressor
- Steam boiler
- CO_2 tank
- N_2 tank
- First and second stage heaters
- Interconnecting pipes
- Control valves
- Cathode recirculation blower
- The following controls:

  - CO_2 and steam flow control (eventually N_2 control)
  - Temperature control at the outlet of the first stage heater
  - Temperature control at the outlet of the second stage heater
  - Temperature control at the inlet to the stack
  - Recirculation blower bypass control

3.4. EXHAUST, RECIRCULATION AND BLOWDOWN LOOP

This loop is modelled as shown in Figure 10 and includes:

- Containment
- N_2.tank
- CO_2.tank
- Addition of water
- Heating with steam
- Blowoff gas chiller
- Blowoff gas recirculation blower
- Interconnecting pipes
- Control valves
- The following controls:

  - Pressure control in the loops based on the differential pressure between them and the containment
  - Pressure control in the containment
  - Control of the blowdown loop recirculation blower bypass

3.5. FUEL STACK MODEL

To simulate this equipment, a series of assumptions were made:

- The fuel stack is formed by individual cells connected together in series, so the same electric current runs through all the cells

- Each cell comprises four basic components:
  - An oxidising gas compartment (cathodic)
  - A fuel gas compartment (anodic)
  - An electrode/electrolyte assembly embedded in an inert matrix
  - A bipolar separator which keeps the anodic and cathodic cell compartments apart

- The current is a pre-established boundary condition

- All the cells behave in the same way and their main operating parameters (gas supply, temperature, pressure, etc) are identical. Consequently, the voltage of the stack will be the product of the voltage of one cell and the total number of cells that comprise the stack

- The stack is fed by means of an external methane reforming plant, so the fuel gas comprises the corresponding mix of hydrogen, carbon monoxide, carbon dioxide and water

- The gases that constitute the fuel maintain a chemical change reaction equilibrium at all times:

$$CO + H_2O = CO_2 + H_2$$

- A simplified, initial approximation has been made which only considers an average temperature value for each cell. If deemed necessary the model could be refined, giving consideration to a two-dimensional distribution of temperatures throughout the complete surface of the cell

The main response we want is for the stack to generate electric power. To this effect it is necessary to calculate the voltage of each cell. This is determined by a maximum thermodynamic voltage quantified by the Nernst equation, minus some ohmic losses due to the resistance of the cell components, and some kinetic losses caused by the fact that the velocity of the electrochemical reactions verified in the electrode/ electrolyte interfaces has a finite value.

The voltage losses are a function of the properties of the materials from which the cell components are manufactured and of certain operating parameters which also condition the thermodynamic voltage.

The model is based on the voltage calculation of a reference cell operating in standard conditions, to which some corrective factors are applied calculated on the basis of the real operating conditions of the simulated cells.

The following are the main corrective factors which have been taken into account:

1. Use of fuel and oxidising gases

The mass balance has to be obtained in order to calculate the composition and flow of the fuel and oxidising gases at the stack outlet. This is based on the electrochemical reactions which take place in the electrodes and the chemical equilibriums which are maintained in the fuel gas.

The electrochemical reactions which take place in the cell are divided into:

- Cathodic semireaction:

$$1/2\ O_2 + CO_2\ (\text{cathode}) = CO_3^{2-}$$

- Anodic semireaction:

$$H_2 + CO_3^{2-} = CO_2\ (\text{anode}) + H_2O$$

The quantity of species consumed and produced per unit of time is a function of the current.

The elements which comprise the fuel gas maintain a chemical change reaction equilibrium, as indicated at the beginning of this section. After calculating the compositions of discharge gases due to electrochemical reactions, it is usual to have to readjust them so that they fulfil the conditions of equilibrium.

With the information obtained we can ascertain the mass flows of active elements at the outlet of the cells, and with them calculate the use and therefore quantify the corresponding electrical losses.

2. Operating pressures

The operating pressures of the oxidising and reducing gases are calculated based on the mass flow values obtained in the mass balance and on the calculation of the pressure losses between the stack inlet and outlet. These losses are conditioned by the path of the gases as they circulate through the cathodic and anodic compartments of each cell.

3. Temperatures of the gases and the stack

The gas temperatures at the stack outlet and the stack temperature must be calculated on the basis of the dynamic heat balance. This heat balance is based on:

- The calculation of the variations in enthalpy of the fuel and oxidising gases between the inlet and outlet, taking into account the enthalpy from the formation of reaction products and the enthalpy from the chemical change reaction
- The calculation of heat produced in the electrode/matrix assembly due to the passage of current through a resistive medium (Joule effect)
- The transfer of heat from the separator and the electrode/matrix assembly to the fuel and oxidising gases

A model of the fuel stack module is shown in Figure 11.

Lastly, Figures 12 to 16 illustrate the results of an experiment consisting of load increase in steps of 10%, after conditioning between open circuit and full load.

4. CONCLUSIONS

The simulation models correctly reproduce the real behaviour of all the relevant parameters of the systems.

The resulting models make it easy to study system response quickly during the critical stages of operation, and to analyse the effects of possible interactions with other systems which are affected.

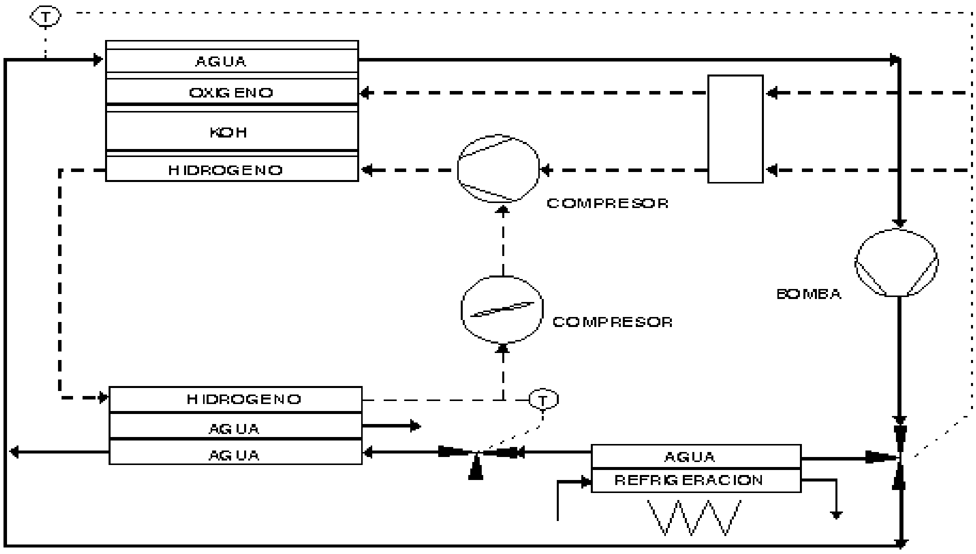

FIGURE 1: SKETCH OF THE ALKALINE FUEL STACK INSTALLATION

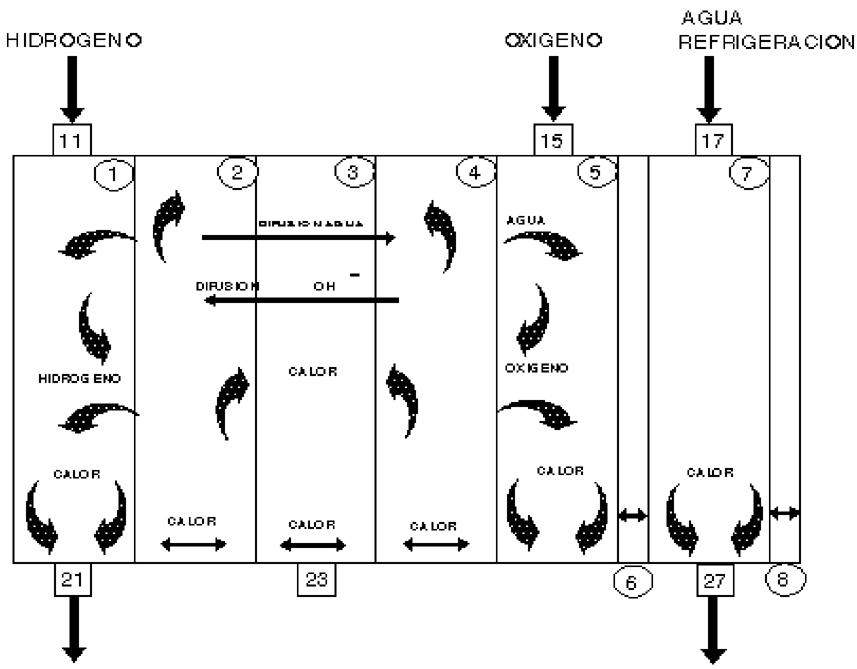

FIGURE 2: SKETCH OF THE ALKALINE CELL MODEL

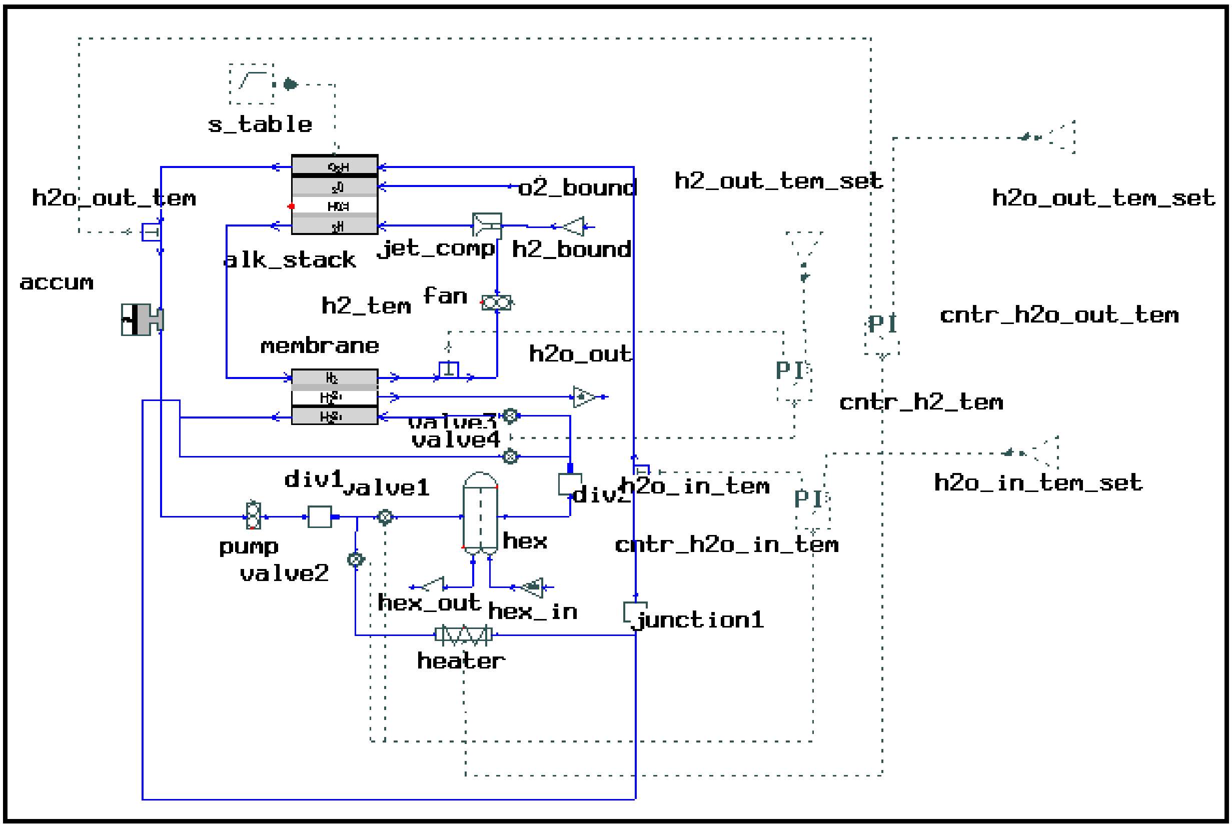

FIGURE 3: ECOSIMPRO MODEL OF THE ALKALINE FUEL STACK

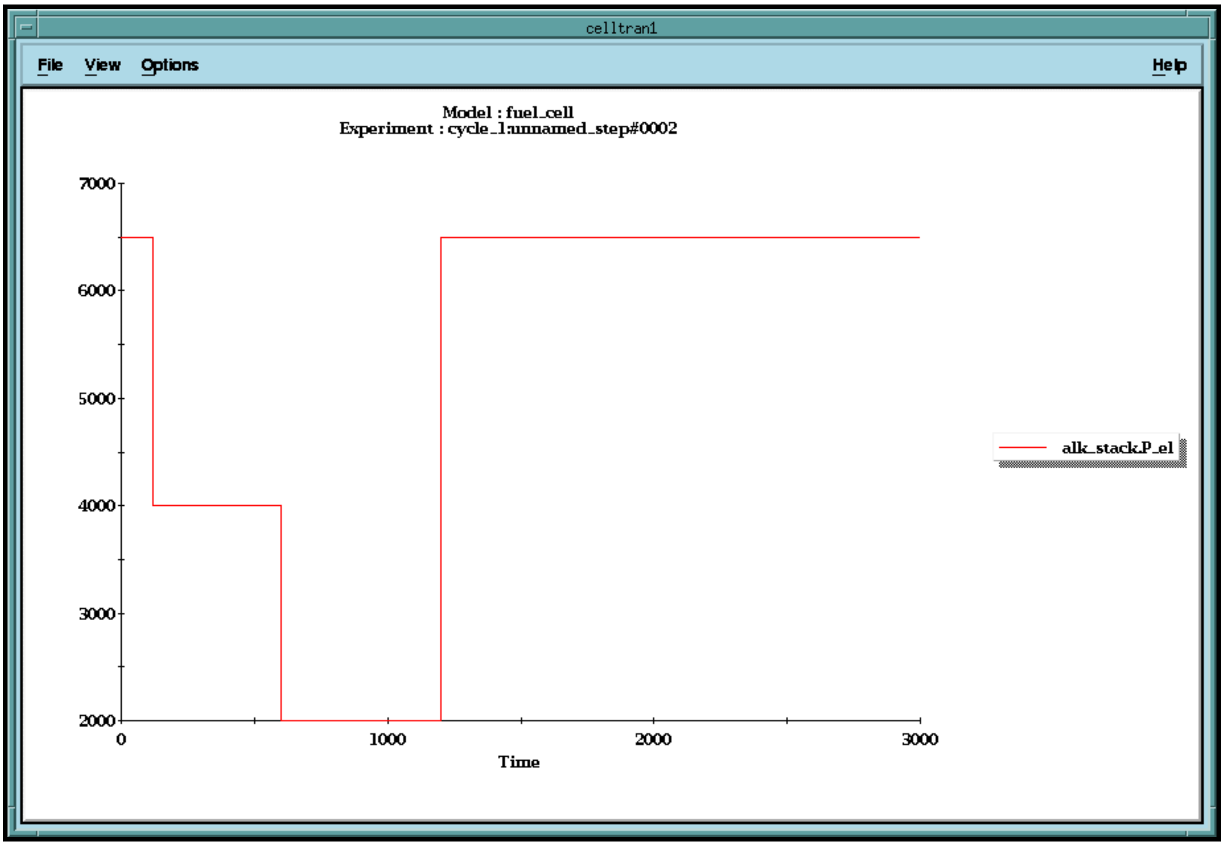

FIGURE 4: POWER DEMAND AS A FUNCTION OF TIME

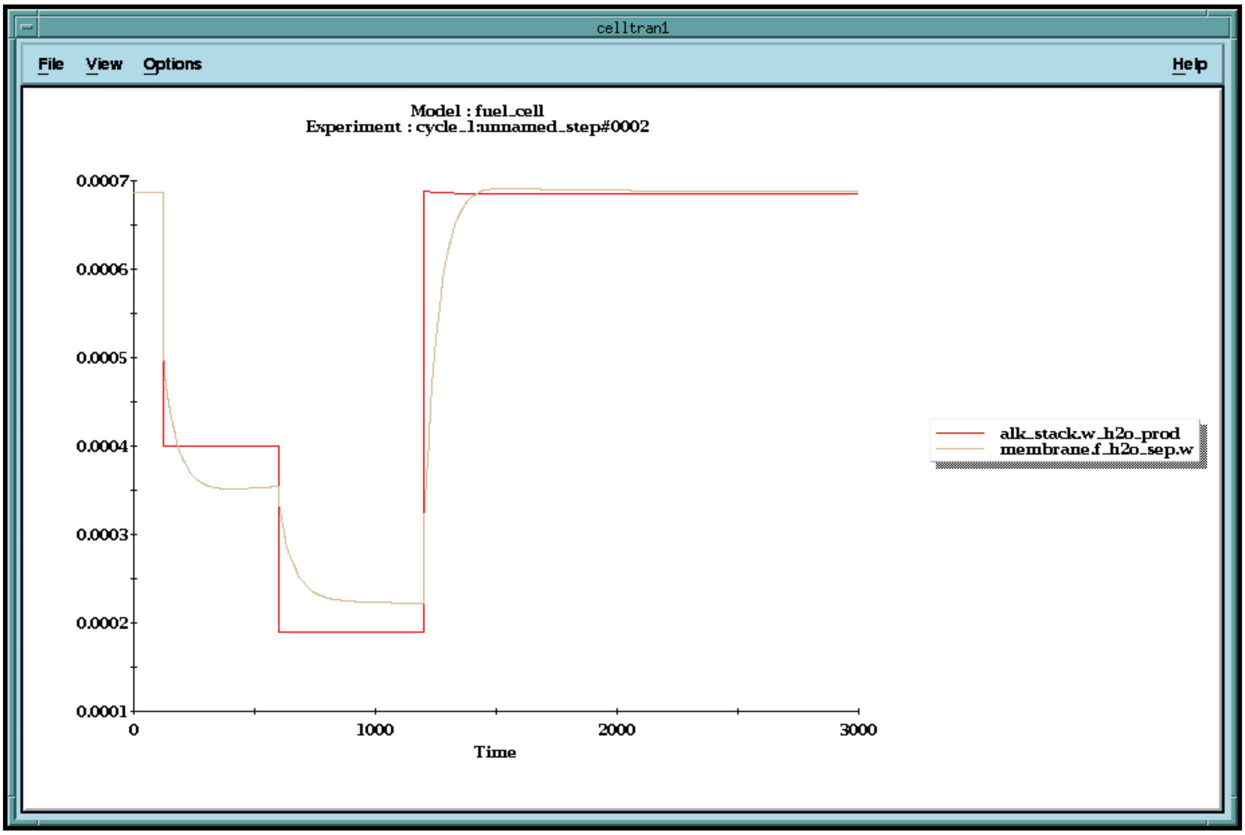

FIGURE 5: WATER PRODUCED IN THE STACK AND WATER SEPARATED IN THE MEMBRANE DURING THE TRANSIENT SHOWN IN FIGURE 4

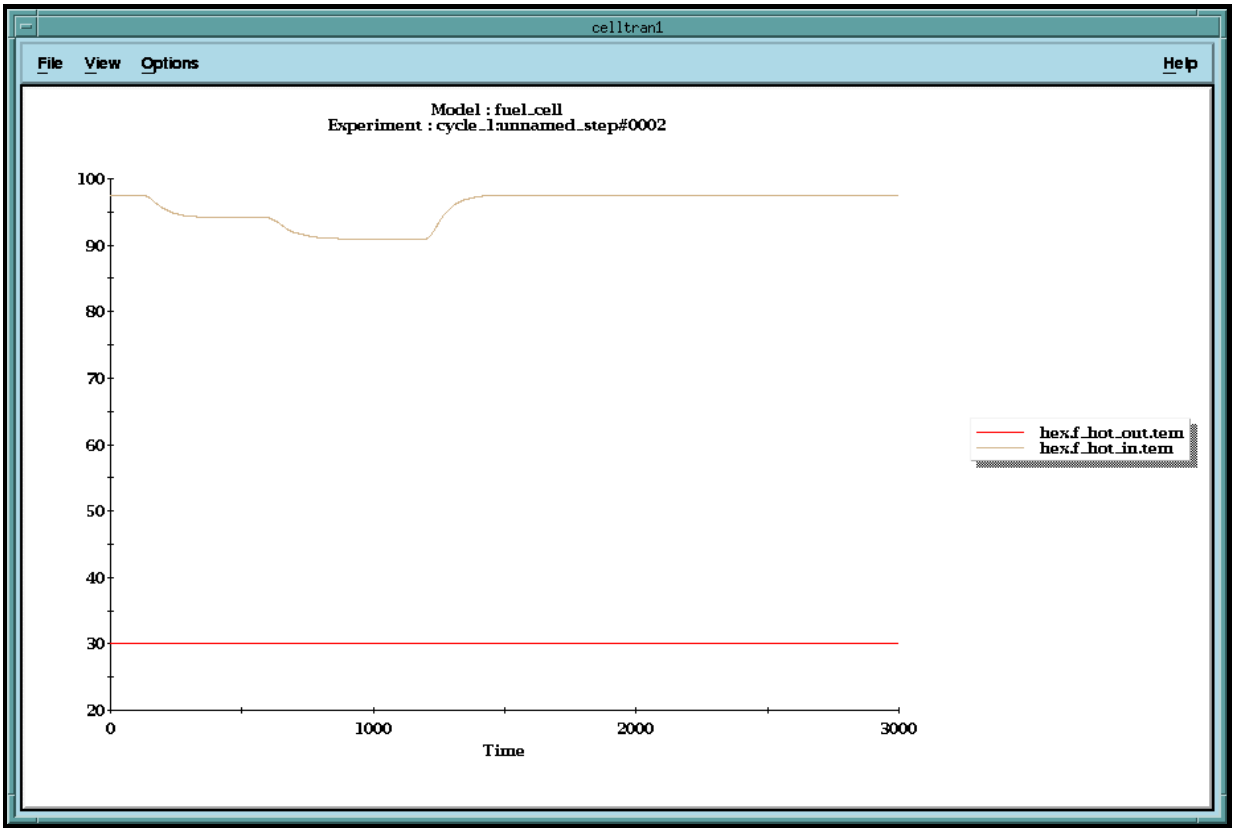

FIGURE 6: HEAT INLET AND OUTLET TEMPERATURE DURING THE TRANSIENT SHOWN IN FIGURE 4

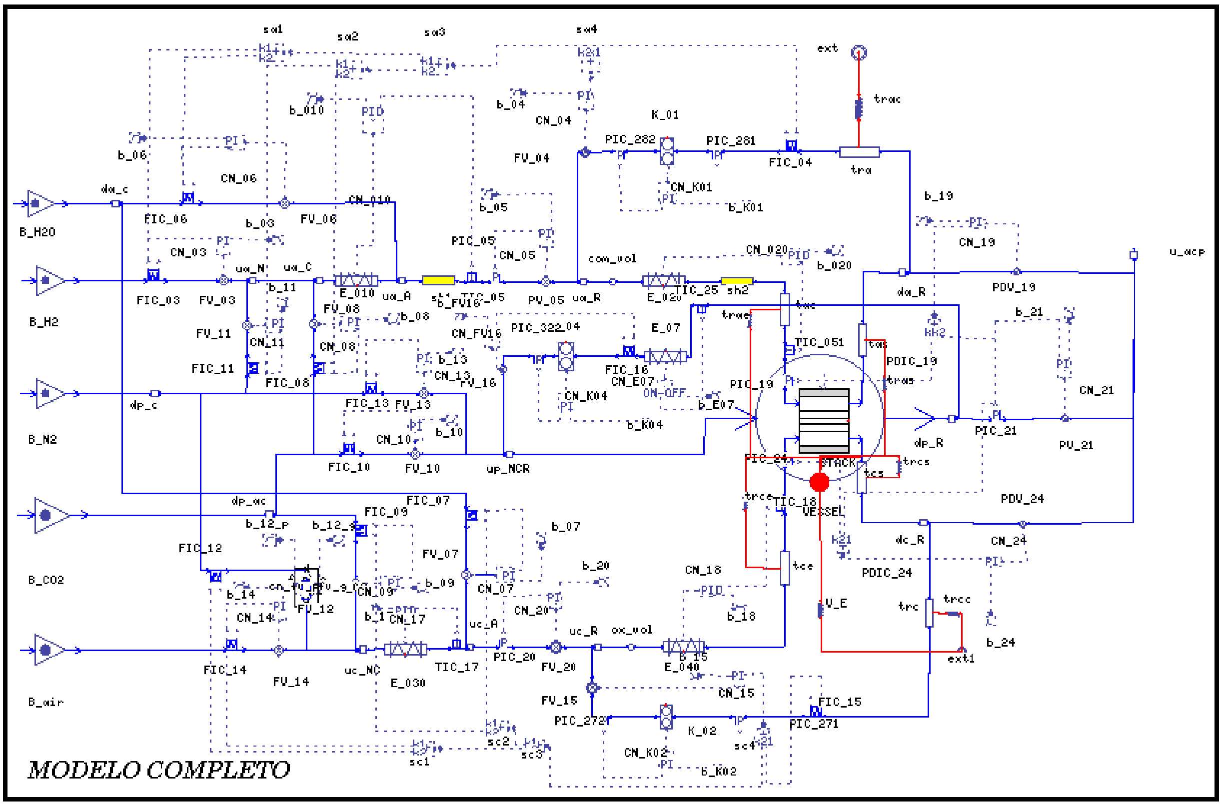

FIGURE 7: MODEL OF THE EXPERIMENTAL FUEL CELL PLANT IN SAN AGUSTÍN DE GUADALIX

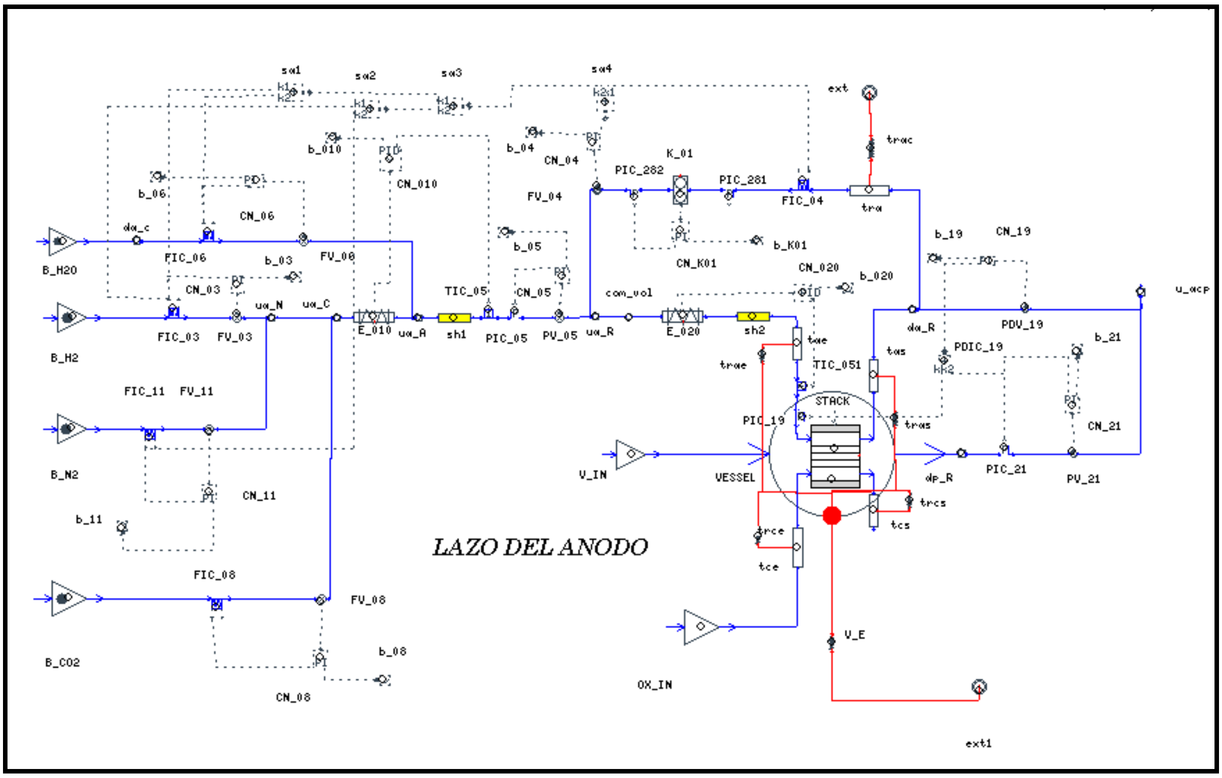

FIGURE 8: MODEL OF THE ANODE LOOP OF THE EXPERIMENTAL FUEL CELL PLANT IN SAN AGUSTÍN DE GUADALIX

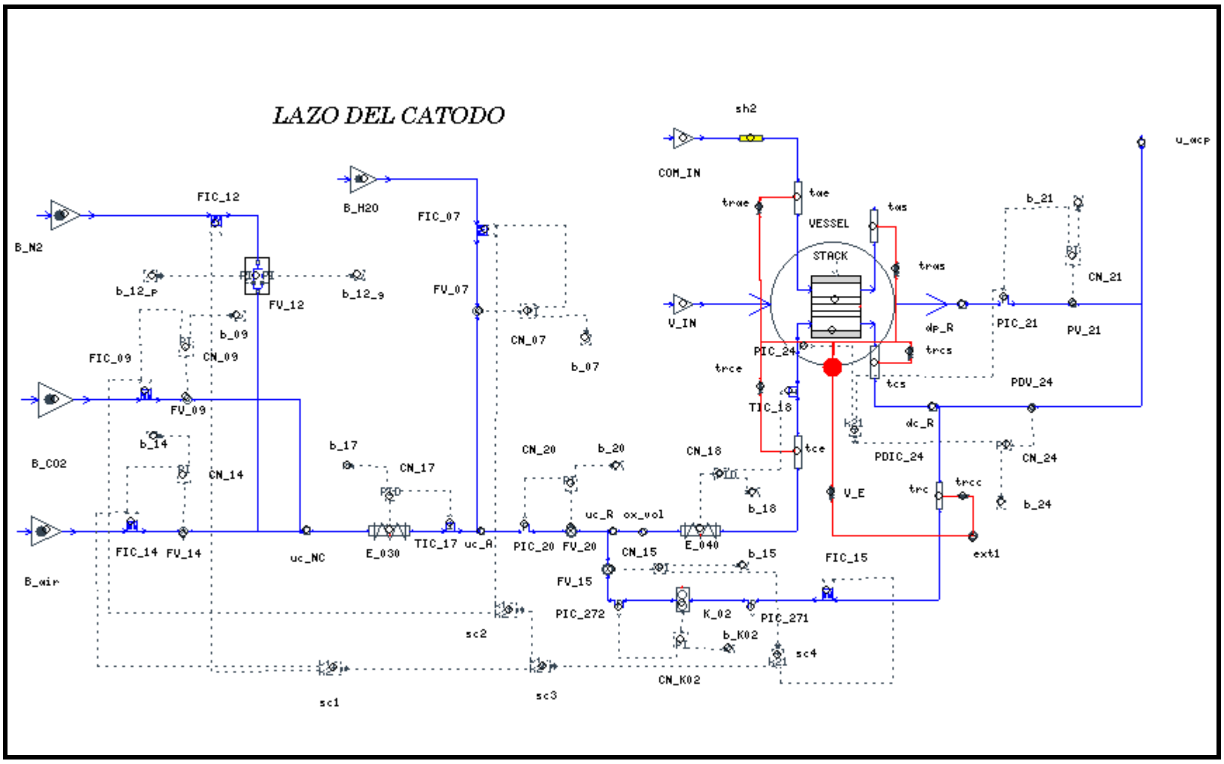

FIGURE 9: MODEL OF THE CATHODE LOOP OF THE EXPERIMENTAL FUEL CELL PLANT IN SAN AGUSTÍN DE GUADALIX

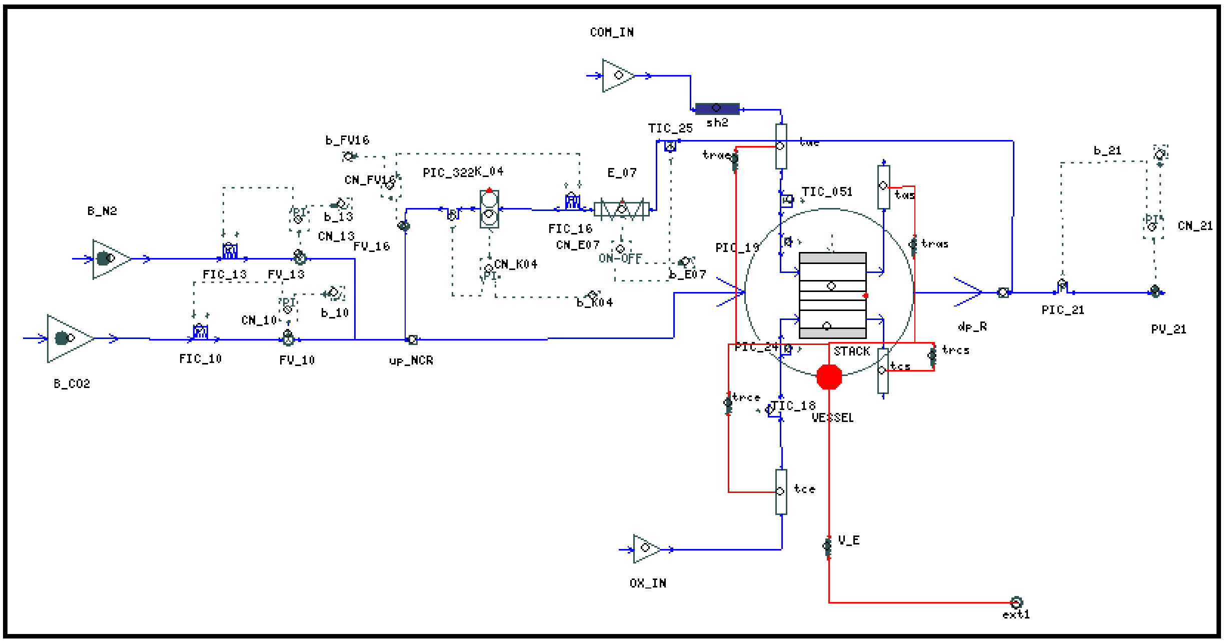

FIGURE 10: MODEL OF THE BLOWDOWN LOOP OF THE EXPERIMENTAL FUEL CELL PLANT IN SAN AGUSTÍN DE GUADALIX

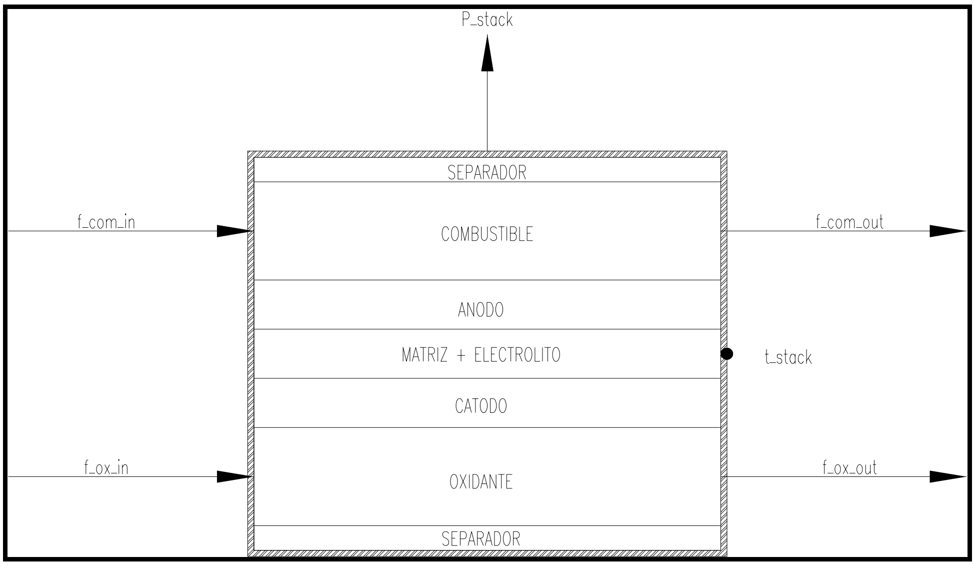

FIGURE 11: MODEL OF THE FUEL CELL

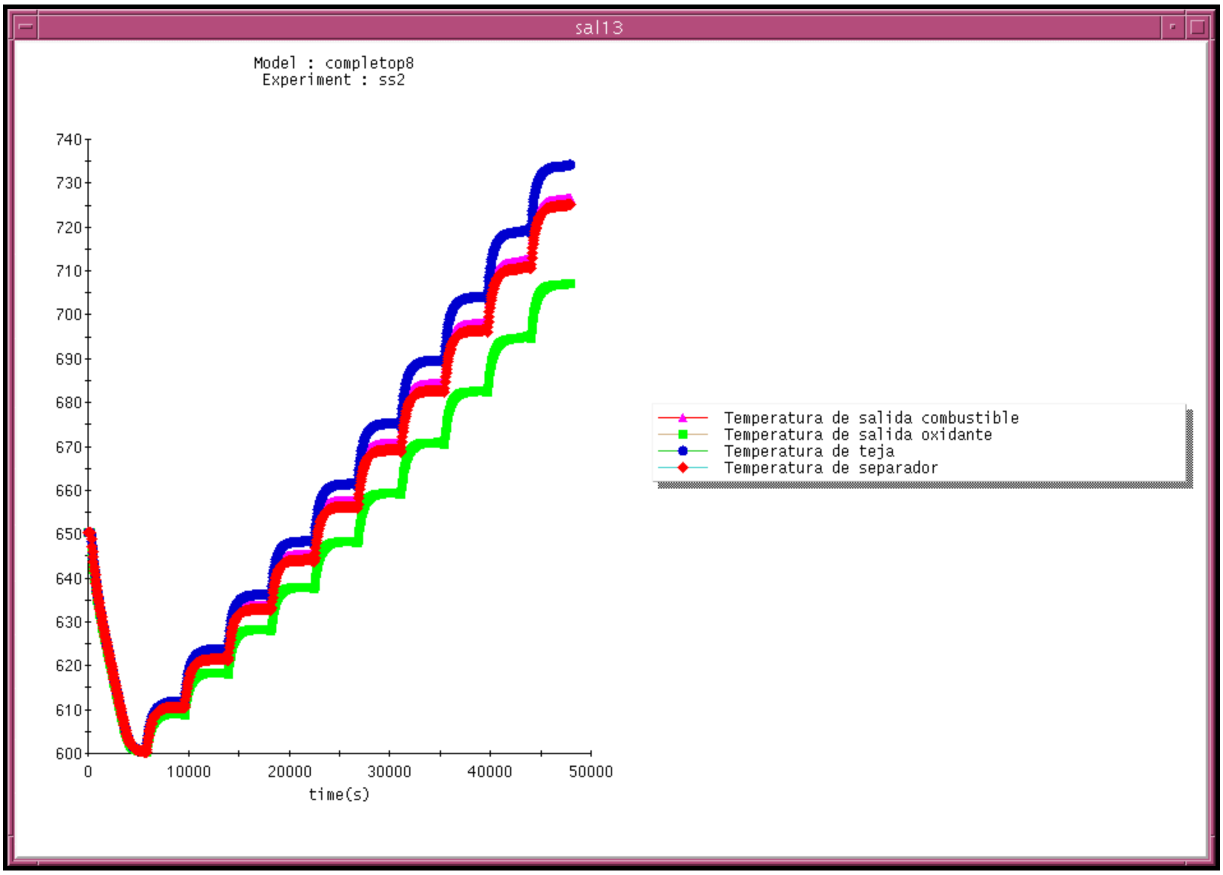

FIGURE 12: OXIDISING GAS DISCHARGE, FUEL GAS DISCHARGE, SEPARATOR AND [TEJA???] ROOF TILE TEMPERATURES DURING LOAD INCREASE TRANSIENT

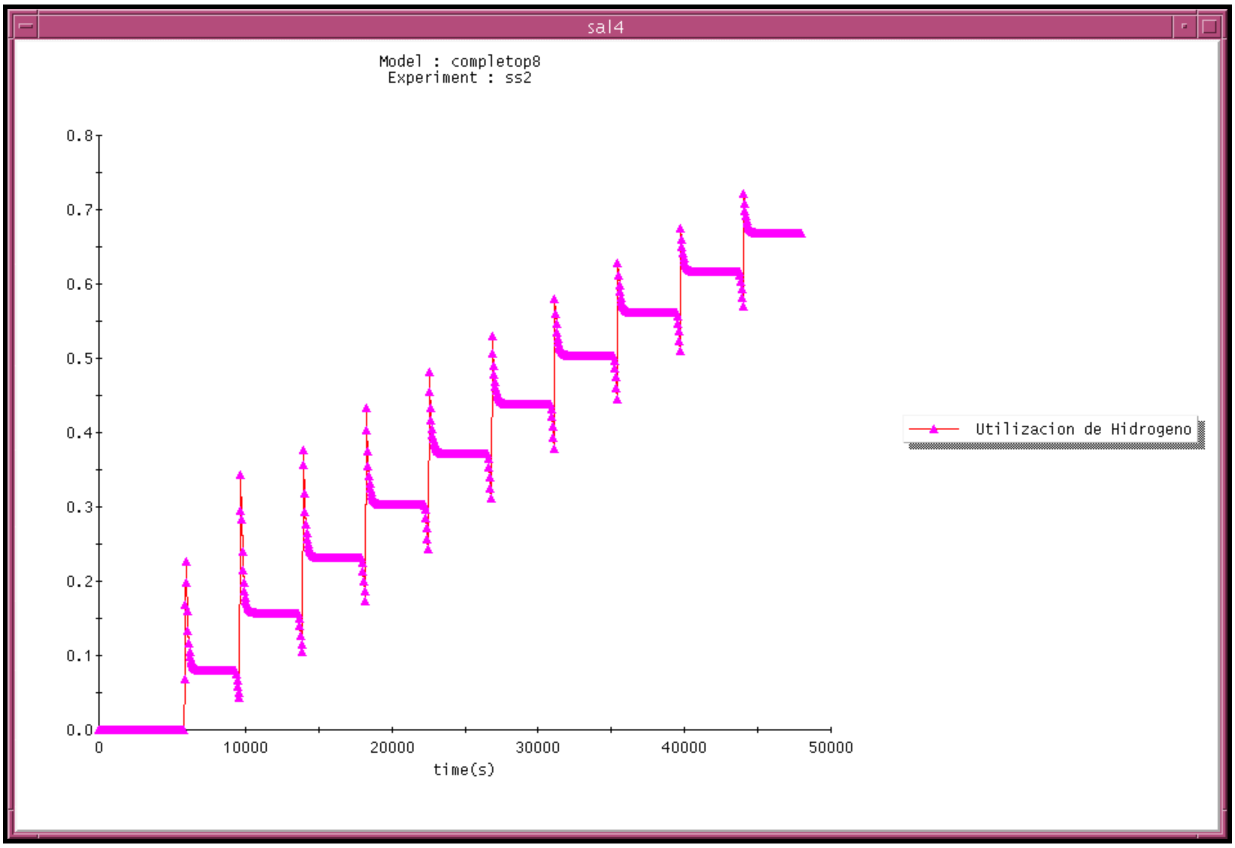

FIGURE 13: USE OF H_2 DURING LOAD INCREASE TRANSIENT

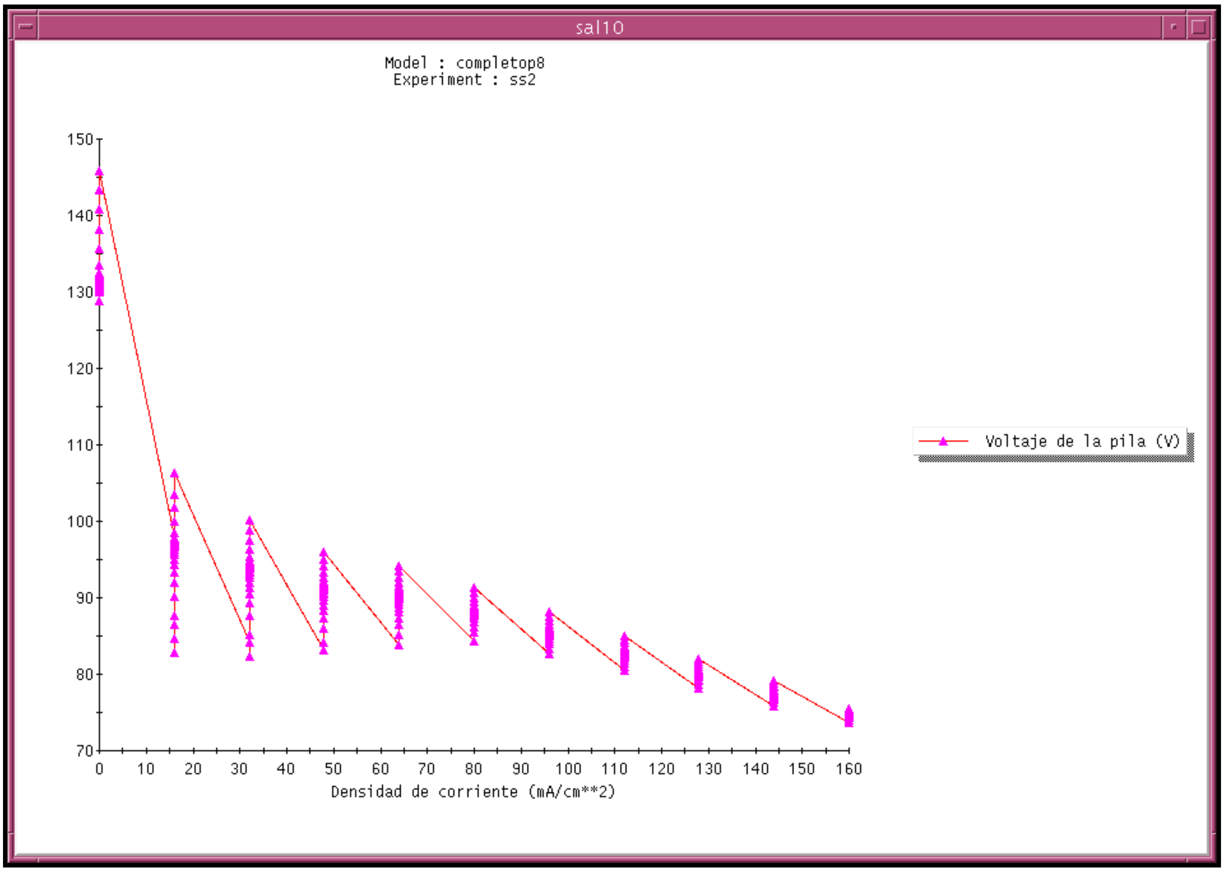

FIGURE 14: VOLTAGE AS A FUNCTION OF CURRENT DENSITY

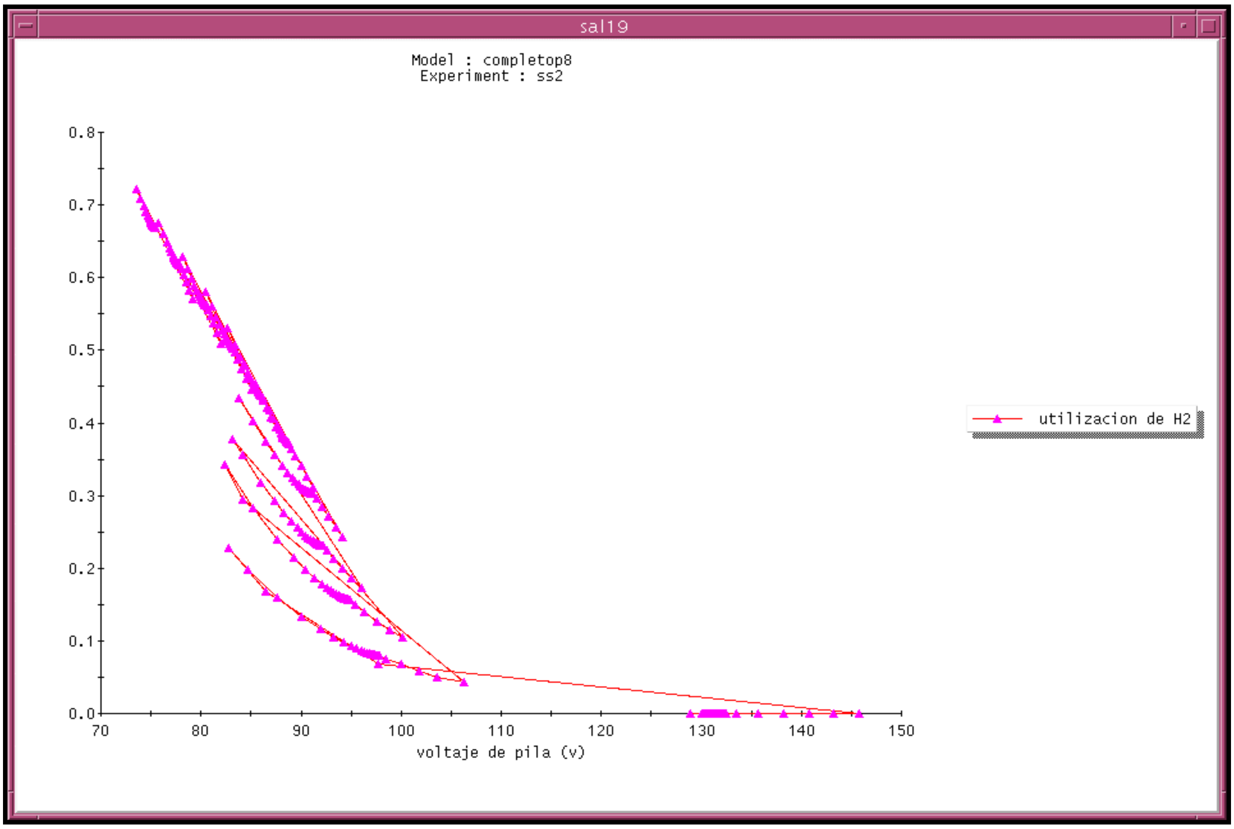

FIGURE 15: USE OF H_2 AS A FUNCTION OF THE STACK VOLTAGE

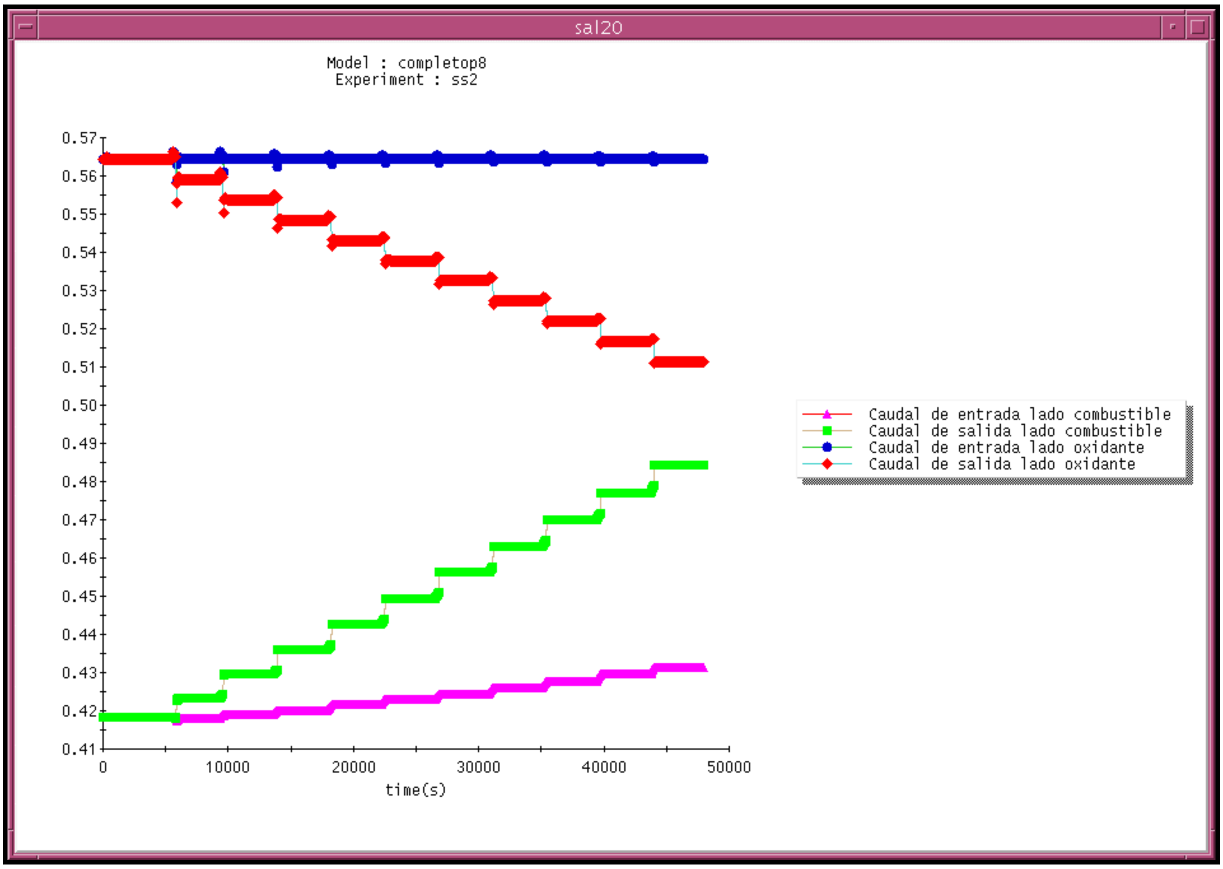

FIGURE 16: INLET AND OUTLET FLOWS DURING LOAD INCREASE TRANSIENT