Guidance page for practical work 4: model of a SOFC (setting out and correction)

1) Objectives of the practical work

The project objective is to study the operation of a high-temperature solid oxide fuel cell SOFC, and show how it can be modeled realistically with Thermoptim

In a solid oxide fuel cell (SOFC), oxide ions O^{2-} migrate from the cathode to the anode where water is produced.

The stack behaves as a quadrupole: In Figure 1, which represents a cell stack, hydrogen enters in the top left of the stack, combines at the anode with ions O^{2-} to form water, and exits in the lower left, enriched in water, while air enters in the top right and exits in the bottom right depleted in oxygen.

SOFC CELL

➢ **600-1000°C**

➢ **water at the anode**

At the anode: $H_2 + O^{2-} \rightarrow H_2O + 2e^-$

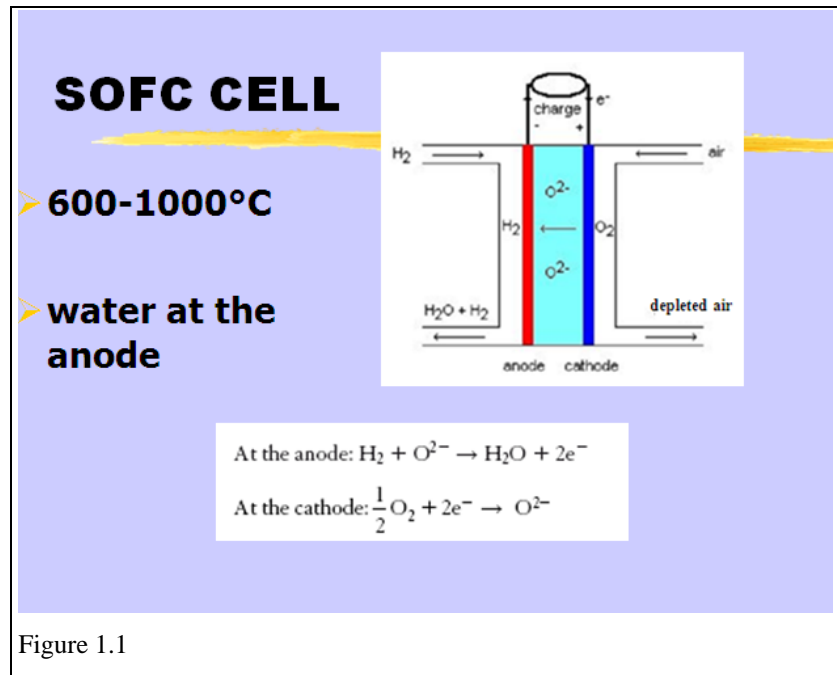At the cathode: $\frac{1}{2} O_2 + 2e^- \rightarrow O^{2-}$

Figure 1.1

A SOFC works at very high temperatures (between 600 and 1000 °C), so that water at the outlet is in gaseous form.

The practical work allows students to build fuel cell models of increasing complexity:
- Very simple model with two parameters of cell supplied with pure hydrogen
- Consideration of the equation of polarization of the stack, then introduction of a cooling of the stack
- Coupling of the cell to a gas turbine to form a high-efficiency cogeneration plant
- Replacement of hydrogen by a fuel such as methane.

This guidance page is similar to sessions S61En to S63En[1].

2) References

Chapter 27 of the book GICQUEL R., Energy Systems : A New Approach to Engineering Thermodynamics, CRC Press, October 2011

---

[1] Session S61En http://www.thermoptim.org/sections/enseignement/cours-en-ligne/seances-diapason/session-s61en

Session S62En http://www.thermoptim.org/sections/enseignement/cours-en-ligne/seances-diapason/session-s62en

Session S63En http://www.thermoptim.org/sections/enseignement/cours-en-ligne/seances-diapason/session-s63en

3) Main practical work

3.1 Setting out

The objective is that students become familiar with the operation of SOFC by building models of gradually increasing complexity. They begin by studying a simple two parameter model of fuel cell supplied with pure hydrogen, then take into account the equation of polarization of the cell, before introducing a cooling of the stack. The coupling of the cell to gas turbine allows them to form a high efficiency cogeneration installation. Finally, they generalize the model of the cell by replacing the hydrogen by a fuel such as methane.
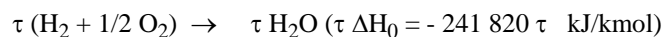
This practical work is well suited for interactive work with students, alternating the following activities:
- writing equations of phenomena during an exchange of views with the class
- Use of the external classes provided to test the model sensitivity to different parameters, and to see how the component can fit as part of a system
- Possibility, if time permits, study or even change of the implementation of the external classes (this implementation is discussed in the documentation for each class).

3.2 Two parameters model of cell supplied with pure hydrogen

The first model we develop is very simple: rate of hydrogen τ and energy efficiency ε are assumed known.
At the anode, only a fraction of τ is transformed in the cell, the rest emerging from it. Typically, $\tau = 0.5$. The overall reaction giving the outlet species is written:
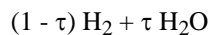For the part used:

$$\tau (H_2 + 1/2\ O_2) \rightarrow \quad \tau\ H_2O\ (\tau\ \Delta H_0 = -\ 241\ 820\ \tau \quad kJ/kmol)$$

For the unused part:

$$(1 - \tau)\ H_2$$
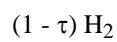
We get therefore at the anode outlet:

$$(1 - \tau)\ H_2 + \tau\ H_2O$$

$\tau\ \Delta H_0$ represents the theoretical energy put into play by the conversion of the part used. A fraction ε of this energy is converted directly into electricity, and $(1 - \varepsilon)$ is transformed into heat.
Moreover oxygen is withdrawn from the oxidizer air at the cathode. λ representing the flow of incoming air, we get:

Intake air: $\lambda\ (O_2 + 3{,}76\ N_2)$

depleted air exiting: $(\lambda - \tau/2)\ O_2 + 3{,}76\ \lambda\ N_2$
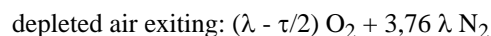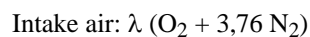
The model retained is the following:

1) species composition is given by solving equations (5.1.1) to (5.1.5): one determines hydrogen and air inlet molar flows, which provides the value of λ, from which we deduce molar flows at the outlet, τ and ε values being known;

2) heat released by fraction $\tau\ (1 - \varepsilon)$ of the fuel is used to provide energy to heat gases.

$\dot{m}_{mol}$ being the molar flow of hydrogen, enthalpy released is equal to $\dot{m}_{mol}\ \tau\ \Delta H_0$. It is split between electricity $\dot{m}_{mol}\ \varepsilon\ \tau\ \Delta H_0$, and energy to heat gases $\dot{m}_{mol}\ \tau\ (1 - \varepsilon)\ \Delta H_0$.

A fuel cell has the distinction of being traversed by two separate streams, which exchange ions or protons through a medium impervious to other chemical species. It behaves like a quadrupole receiving two input fluids, and of out which come two others.

This poses a slight difficulty to build up a Thermoptim model, since the only components available are either processes or nodes. The solution is to form the quadrupole by combining an inlet mixer and an outlet divider, the two being connected by a process-point playing a passive role.
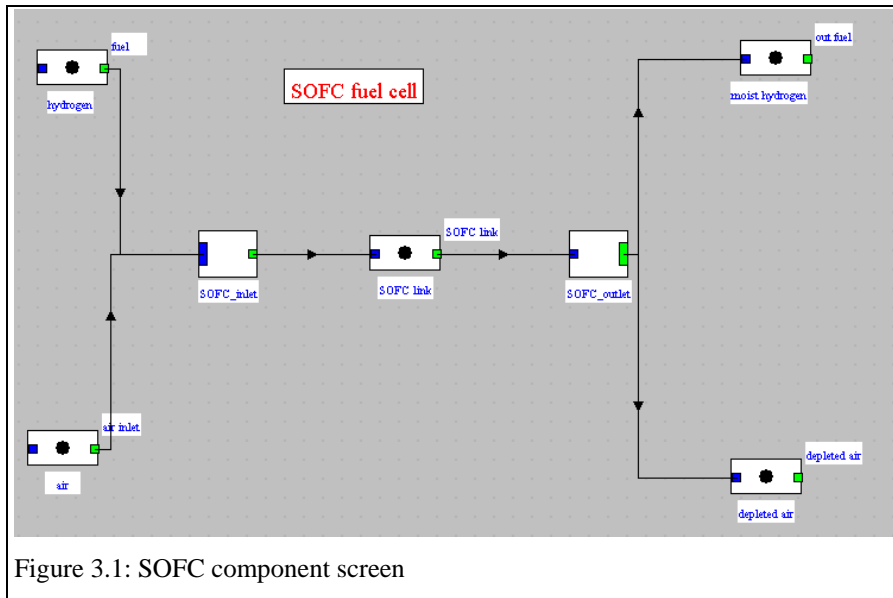
Figure 3.1: SOFC component screen

For the model to be consistent, it synchronizes the calculations of both nodes. Specifically the outlet divider takes control of the mixer, whose role is limited to update the coupling variables associated with flow entry. The model structure is that presented Figure 3.1

Figure 3.2: SOFC component screen

The only difficulty encountered when constructing the model is the selection of external classes. It is easily lifted by referring to the note Using external classes or by operating as shown in the first steps of the session S07En_ext Diapason[2]. The class names are "SOFC H2 Inlet" and "H2 SOFC outlet".

The SOFC component screen is given in Figure 3.2. Input data labels are displayed in blue, and it was assumed that gases enter the cell at 500 °C.

It is a cylindrical stack technology such as that developed by Westinghouse, corresponding to a 100 kWe system, where τ = 0.48 and ε = 0.44.

With the following settings (4 g/s of hydrogen and 120 g/s of air entering the cell at 1 bar and 500 °C), gas compositions obtained are given in Figures below.

component name	molar fraction	mass fraction
N2	0.781	0.7555302
Ar	0.009	0.01241636
O2	0.21	0.2320534

Figure 3.3: Air entering the cell, flow rate 120 g/s

component name	molar fraction	mass fraction
H2	0.52	0.1081169
H2O	0.48	0.8918831

Figure 3.4: Humidified hydrogen at the outlet, flow rate 19.24 g/s, LHV : 11,230 kJ/kg

component name	molar fraction	mass fraction
N2	0.8824047	0.8654283
Ar	0.01016856	0.01422242
O2	0.1074267	0.1203493

Figure 3.5: Air depleted in O_2 flow-rate 104.76 g/s

Figure 3.6: Synoptic view of the SOFC
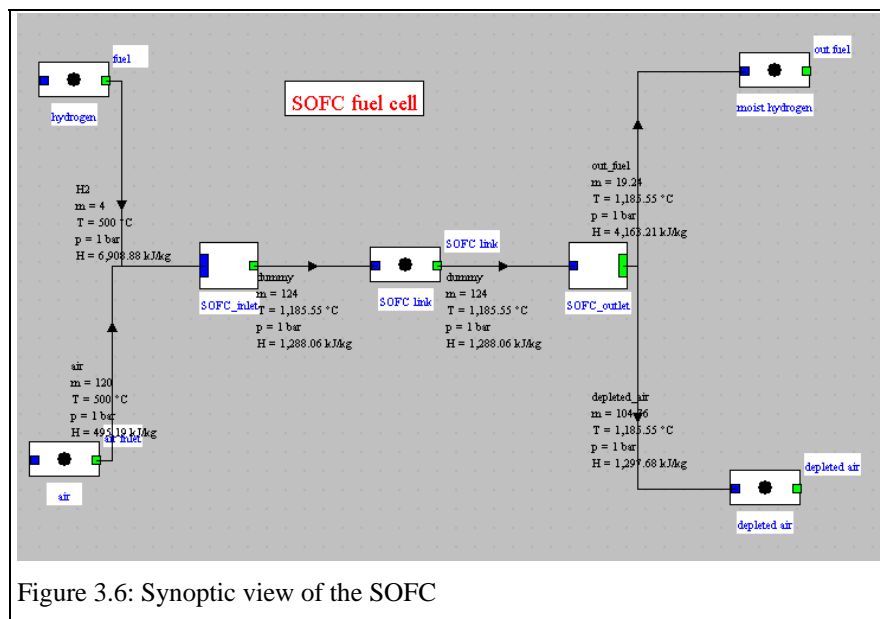
[2] Session S07En_ext: http://www.thermoptim.org/sections/enseignement/cours-en-ligne/seances-diapason/s07en_ext-introduction

3.3 Improvement of the cell model

In this second model we assume that rate of hydrogen use τ and energy efficiency ε are determined from an electric model (classes SOFCH2ElecInlet.java and SOFCH2ElecOutlet.java).

3.3.1 Modèle électrique retenu

To calculate the cell voltage V_{cell} knowing the intensity and the active surface (Figure 3.7), various models have been proposed. We retain that which was developed at the Center for Energy and Processes of École des Mines de Paris. Its equation is:

Figure 3.7: Polarization curve of the cell

$$V_{cell}(J) = E + \frac{b}{\ln(J/J_d) - 2} + \left(\frac{b}{4J_d} - \Delta\right)J$$

where $J = I/A$ is the current intensity (intensity divided by the active area A), in A/cm^2.

E, J_d, b and Δ are four parameters *a priori* dependent on the cell temperature and the hydrogen pressure. They can be considered constant as a first approximation, but the influence of temperature and partial pressure of H_2 on each parameter can also be taken into account if necessary.
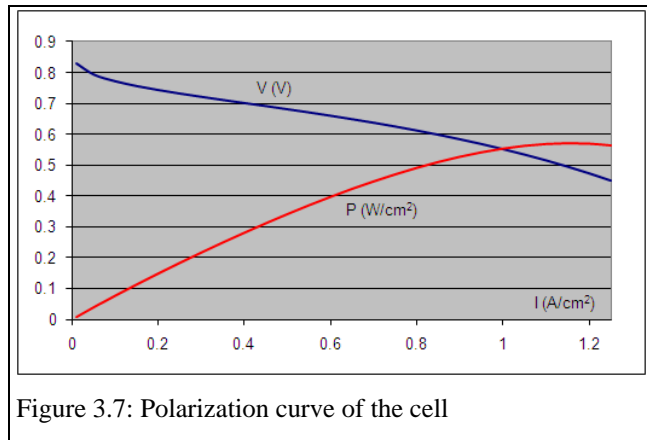

Figure 3.8: SOFC component screen

Knowing V_{cell}, it is possible to simply calculate the cell capacity: $P_{elec} = V_{cell} \, I \, N_{cell}$

The rate of hydrogen use is assumed to be proportional to the current density J, which corresponds in first approximation to what happens in practice: the fraction of hydrogen consumed is zero in a physically open circuit, and increases when the output current increases. We choose the following law: $\tau = 1.2$ J.

New model parameters are: number of cells N_{cell}, current intensity sought I, and active surface of a cell A. The model calculates τ and ε as well as output voltage V.

The SOFC component screen is given in figure 3.8, input data labels being displayed in blue (it was assumed that the gases enter the cell at 500 °C).

It is a cylindrical stack technology such as that developed by Westinghouse, each cell having a diameter of 19 mm and a length of 1.5 m, an area of 900 cm^2, leading to an intensity of 360 mA with a current density of 400 mA/cm^2.

Calculation results for a set of 400 cells, corresponding to a 100 kWe system are given below: $\tau = 0.48$, $\varepsilon = 0.44$, V = 281 V. In terms of electrical power and heat, this model leads to the same values as the simple model developed previously.

3.3.2 Proposed work

From this model, it is possible firstly to refine the parametric study of the behavior of the cell by playing on the new input data, and also to study the corresponding external class and improve it, including the introduction of various tests to check the consistency of the data used, because they can not be chosen completely independently. For example, the current density must be between 0 and 700 or 800 mA/cm^2, otherwise the calculations become meaningless

3.4 Model with a thermocoupler

The third model is an extension of the previous one, which assumes that the fuel cell is cooled by water at 40 bar, its temperature rising from 200 °C (liquid) to 450 °C (steam). External classes are SOFCH2ThermoInlet and SOFCH2ThermoOutlet

Stack cooling is modeled by a thermocoupler connected to the outlet divider.

The thermocoupler mechanism is complementary to the heat exchangers allowing components other than "exchange" processes to connect to one or more "exchange" processes to represent thermal couplings.

This mechanism has a number of benefits, because it can be used to represent many thermal couplings that do not constitute a heat exchange in the traditional sense, like for example cooling the walls of the combustion chamber of a reciprocating engine, cooled compression, and above all supply or removal of heat from multi-functional external components such as a fuel cell.

Please refer to the reference manual for a detailed presentation of thermocouplers.

We assume in this model that a third of the heat in the stack is recovered by steam cooling, the rest being used to heat gases that enter the fuel cell. The thermocoupler setting is explained below.

Figures 3.9 to 3.11 show model changes. With the new assumptions, the thermocoupler allows us to heat 17.4 g/s of water at 40 bar from 200 °C to 450 °C.

The screen of the stack component is almost the same as the previous one. It is distinguished by the white field entitled "SOFC Cooler" located under the table of the node branches. Double-click in this field to open the thermocoupler (figure 3.10).

Figure 3.9: SOFC component screen

Figure 3.10: Thermocoupler screen

Figure 3.11 shows the new synoptic view

Figure 3.11: Synoptic view of the SOFC with thermocoupler
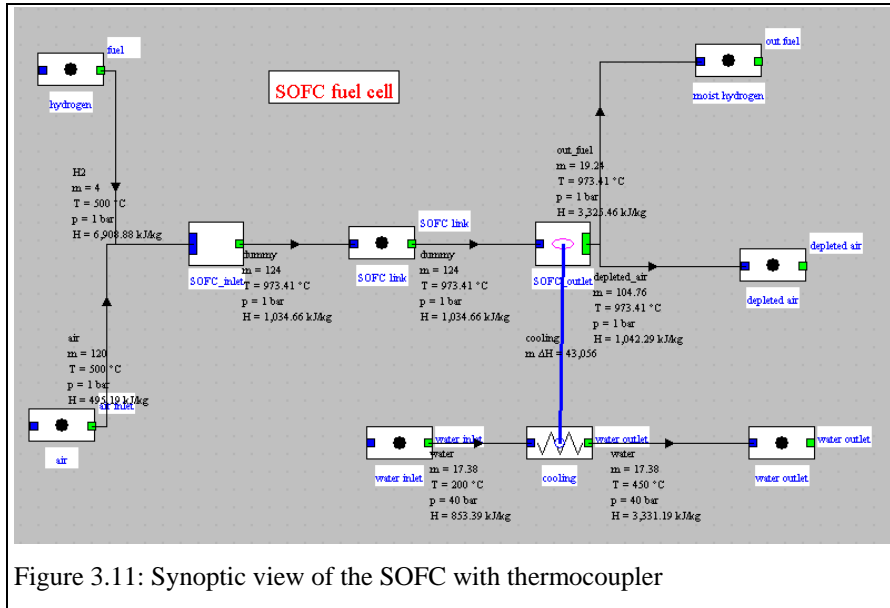
3.5 Coupling of a SOFC fuel cell with a gas turbine

If students have not already modeled a simple gas turbine cycle, they must begin by working on the session S24En[3].

Figure 3.12: Thermoptim diagram of the facility
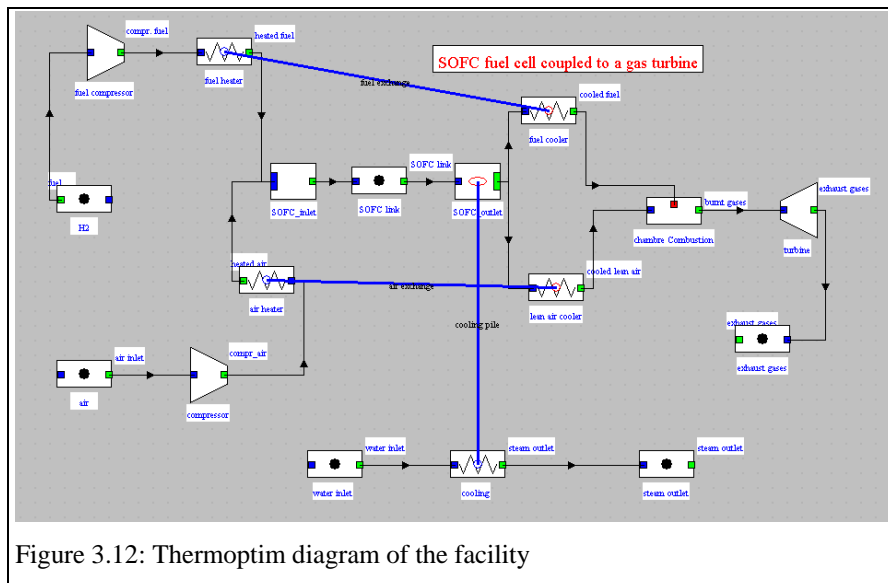
The facility diagram is given figure 3.12.

Air and hydrogen are initially at 15 °C and 1 bar. Their respective flow rates are 300 g/s and 4 g/s (we have greatly increased the airflow to on the one hand have enough oxygen in the depleted air to burn all the residual hydrogen at the stack output, and secondly to limit the turbine inlet temperature at a reasonable value.

Air and hydrogen are compressed at 20 bar by compressors of isentropic efficiency 0.85, then preheated before entering the cell by exchange with gas leaving the anode and cathode. 43 kW heat is provided by the cell to produce steam at 40 bar and 500 °C.

___

[3] Session S24En http://www.thermoptim.org/sections/enseignement/cours-en-ligne/seances-diapason/session-s24en-simple-gas

Depleted air and humidified hydrogen are then burnt in the combustion chamber and flue gases expanded in the turbine of isentropic efficiency 0.9.

Figure 3.13 shows the synoptic view of the facility for such a simulation.

While the cell efficiency is only equal to 44%, the electrical efficiency of this facility is already equal to 45.4%, and in addition 43 kW of steam and approximately 180 thermal kW are available in the exhaust gas exiting the turbine at about 600 °C.

The available cogeneration power is equal to 230 kWe, plus 223 kW thermal energy at a cost of 506 kW. The overall efficiency is therefore equal to 89.5%.
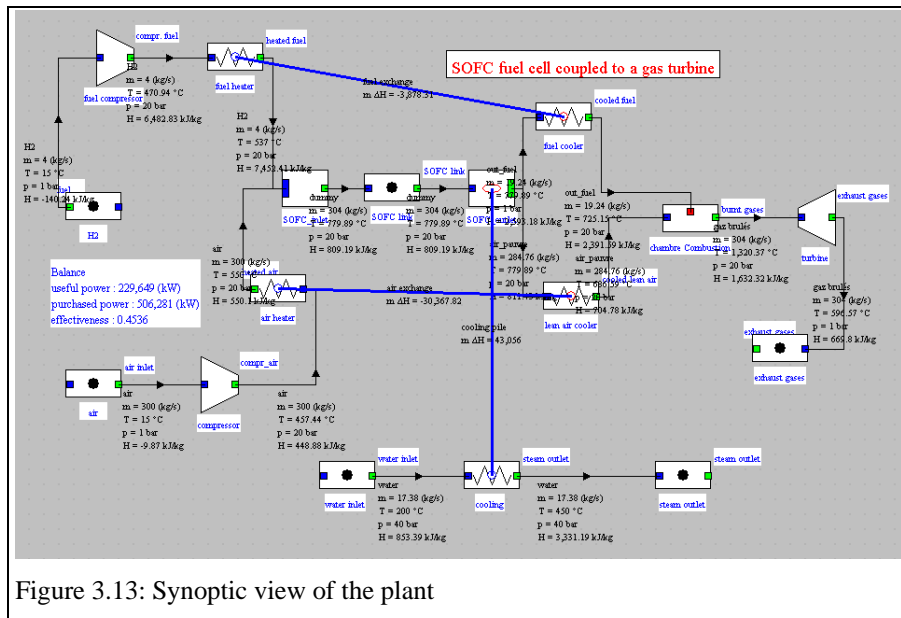

Figure 3.13: Synoptic view of the plant

3.6 Change in the model to replace H_2 by CH_4

The models we have developed so far only allowed for pure hydrogen as fuel. In reality, it is very rare that one has hydrogen, which must be produced from another fuel. This is called reforming.
The basic equation for reforming a fuel such as methane, is:

$CH_4 + H_2O \rightarrow CO + 3 H_2$ (ΔH = 206 140 kJ/kmol)

$CH4 + H2O \rightarrow CO + 3 H2$ (ΔH = 206 140 kJ/kmol)
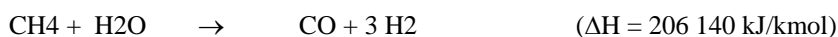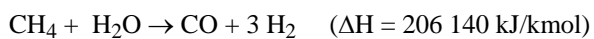
Reforming converts fuel into hydrogen, but requires water and heat supply, and produces carbon monoxide, which is a poison for some fuel cells such as PEMFC, where it is then necessary to also convert CO.

Note that one advantage of SOFC technology is that it tolerates the presence of CO well, while in other cases a shift reaction is necessary to convert it into CO_2. The energy efficiency of the whole is improved.
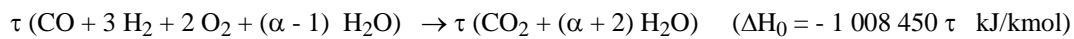
Let us call α the molar ratio of water and methane flows (α must be greater than 1 so that all methane can be processed).

At the anode, given the high operating temperature of SOFC, we can consider that the whole fuel is converted by the cracking reaction:
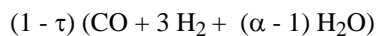
$$CH_4 + \alpha\, H_2O \rightarrow CO + 3\, H_2 + (\alpha - 1)\, H_2O \quad (\Delta H_v = 206\,140 \text{ kJ/kmol})$$
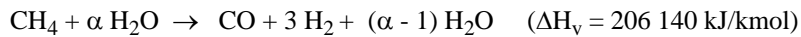
Then, only a fraction τ (rate of fuel use) is transformed in the cell, the rest coming out of it. The overall reaction giving the output species is written:
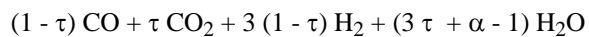
For the part used:

$$\tau\,(CO + 3\, H_2 + 2\, O_2 + (\alpha - 1)\; H_2O) \rightarrow \tau\,(CO_2 + (\alpha + 2)\, H_2O) \quad (\Delta H_0 = -\,1\,008\,450\,\tau \;\; \text{kJ/kmol})$$

Heat of reaction ΔH_0 is calculated here by considering that water remains in the gaseous state due to the temperature (LHV).

For the unused part:

$$(1 - \tau)\,(CO + 3\, H_2 + (\alpha - 1)\, H_2O)$$

We therefore get at the anode outlet:

$$(1 - \tau)\, CO + \tau\, CO_2 + 3\,(1 - \tau)\, H_2 + (3\,\tau + \alpha - 1)\, H_2O$$

Of the amount used, a fraction ε is directly converted into electricity, and $(1 - \varepsilon)$ is transformed into heat (some of which is used for steam cracking).

Moreover, λ being a parameter representing the incoming air, oxygen is removed from the oxidizer air at the cathode:

Intake air: $\lambda\,(O_2 + 3{,}76\, N_2)$

depleted air exiting: $(\lambda - 2\,\tau)\, O_2 + 3{,}76\,\lambda\, N_2$
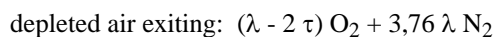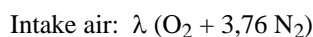
The model retained is the following (classes SOFCCH4inlet.java and SOFCCH4outlet.java):
- species composition is given by solving the equations above: we determine the molar flow rates of fuel and humidified air at the inlet, which provides values for α and λ, we deduce the molar flow at the output, the values of τ and ε being read on the screen;
- heat released by fraction $\tau\,(1 - \varepsilon)$ of the fuel is used to provide the energy needed to heat gas and by steam cracking.

The enthalpy released is equal to $\tau\, \Delta H0$. It is divided into electricity ($\varepsilon\,\tau\,\Delta H_0$), and heat required for steam cracking (ΔH_v) and heating of gas ($\tau\,(1 - \varepsilon)\,\Delta H_0 - \Delta H_v$).

Figure 3.14 shows the synoptic view of the fuel cell. The settings used are similar to that of the hydrogen-powered cell model: inlet gas temperature 500 °C, flow rate 10 g/s for fuel, and 80 g/s for air.
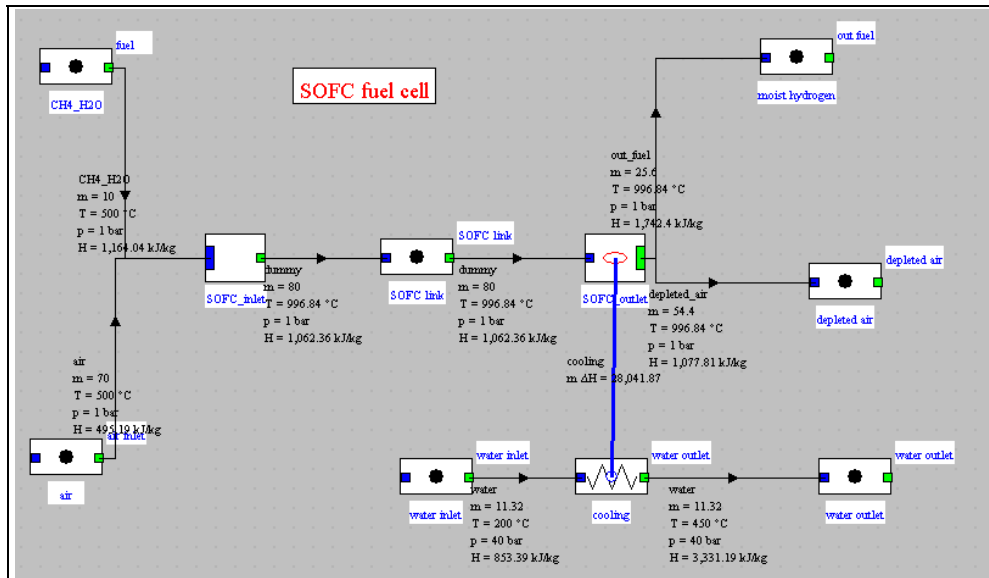
Figure 3.14: Synoptic view of the SOFC cell

Figure 3.15 shows the upstream mixer screen where appear the settings of the electric model, the fuel utilization rate and the fraction of the thermal power extracted by the thermocoupler.

Figure 3.15: Screen of the mixer upstream of the SOFC

The SOFC component screen is shown in Figure 3.16. We have taken a fuel utilization rate of almost 85%, corresponding to the figure announced by Siemens and Westinghouse for this type of cell operating with natural gas.

Figure 3.16: SOFC component screen

The gas compositions that are obtained are given in Figures below.

component name	molar fraction	mass fraction
H2O	0.52	0.5488451
CH4 ` methane	0.48	0.4511549

Figure 3.17: Fuel, flow-rate 10 g/s, LHV: 22,562 kJ/kg

component name	molar fraction	mass fraction
N2	0.781	0.7555302
Ar	0.009	0.01241636
O2	0.21	0.2320534

Figure 3.18: Air, flow-rate 80 g/s

component name	molar fraction	mass fraction
CO	0.03265306	0.0410301
CO2	0.2122449	0.4190309
H2	0.09795918	0.008858684
H2O	0.6571429	0.5310803

Figure 3.19: Fuel at the outlet, flow-rate 25.6 g/s, LHV: 1,477 kJ/kg

component name	molar fraction	mass fraction
N2	0.9782662	0.9721497
Ar	0.01127323	0.01597628
O2	0.01046053	0.01187401

Figure 3.20: O_2-depleted air, flow-rate 64.4 g/s

4) Variants

We propose a few variants, but many others can be imagined, depending on the time available, the level of the students, their number, and educational objectives pursued.

4.1 Coupling of the cell to a combined cycle

From the model developed section 3.5, it would be relatively easy to couple one or more steam cycle (s) to study the performance of the combined cycle

4.2 Modeling of the Siemens Westinghouse cell

Figure 4.1 shows the sketch of a fuel cell module proposed by Siemens and Westinghouse.

The fuel, natural desulfurized gas, enters at the right of the device in 1. It is directed to an ejector connected to a tube that sucks the gases leaving the anode, in 2, which are thus partly recycled.

The gases leaving the anode containing much water, this helps to humidify the fuel while preheating it. The mixture then enters the internal reformer, consisting of vertical tubes (3) heated by radiation from cell stack. The converted fuel then flows outside cells (4).

Air enters at the top left of the module, in 5, and warms up in 6 by exchange with the gases leaving the stack. It is then injected into the supply tubes at the bottom of the cells and then circulates in the annular space between the tubes and the cells. The depleted air is then mixed in 7 with the fraction of recirculated gas leaving the anode, further oxidation taking place due to high temperatures. The hot gases are then evacuated, after preheating the incoming air

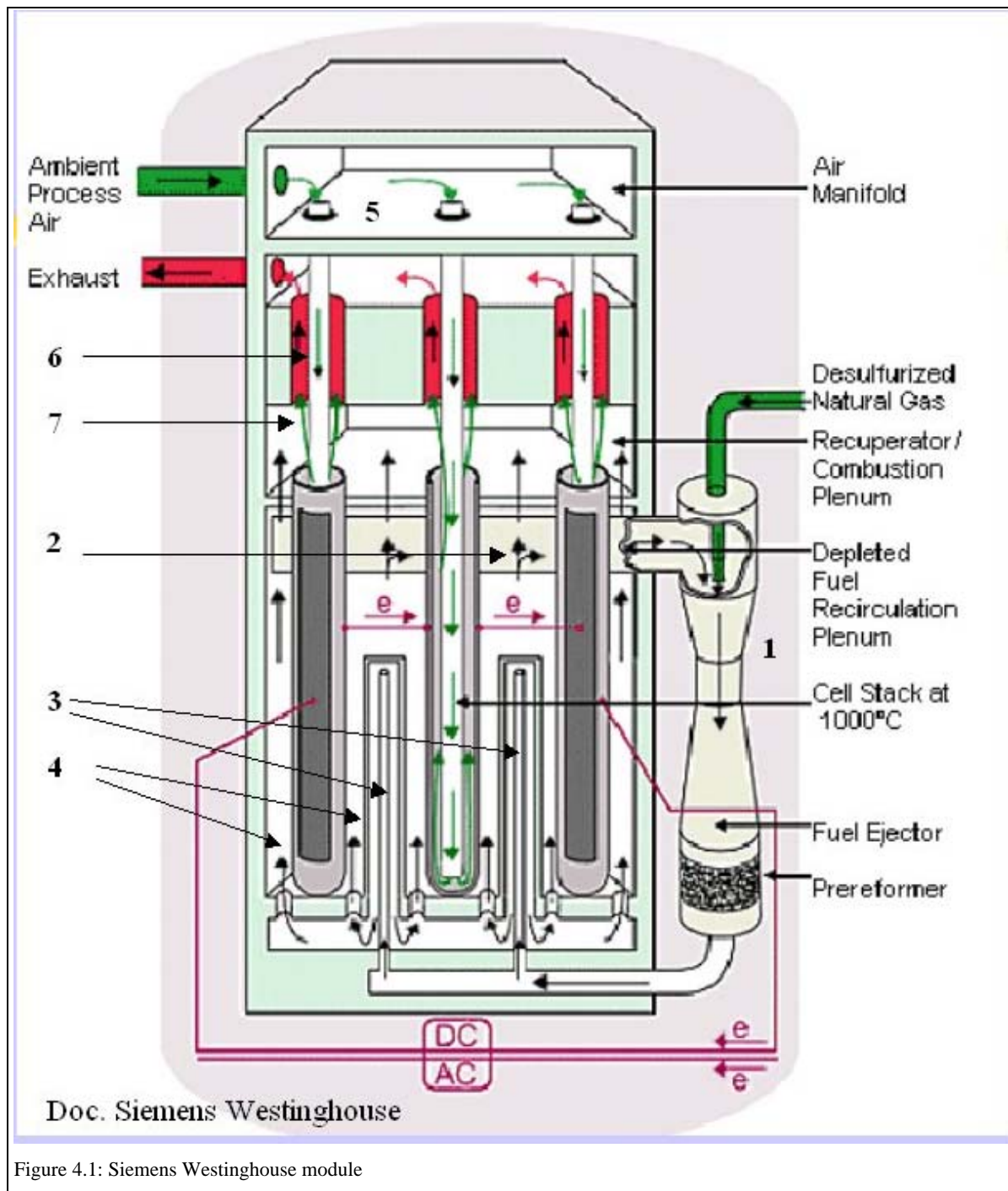Values are given in Diapason session S63En quoted above.

Figure 4.1: Siemens Westinghouse module

4.2.1 Model of the cell with recycling

The description just given of the operation of an industrial SOFC module shows that, to be realistic, our fuel cell model must be further refined, in particular so that it can accept as input a mixture of methane and gas leaving the anode
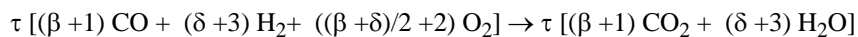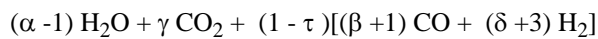
At the anode inlet, we get:

$$CH_4 + \alpha\ H_2O + \beta\ CO + \gamma\ CO_2 + \delta\ H_2$$

Steam cracking being supposed complete (with the condition $\alpha \geq 1$), the composition after cracking is:

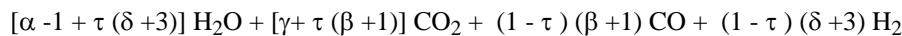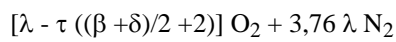$$(\alpha -1)\ H_2O + (\beta +1)\ CO + \gamma\ CO_2 + (\delta +3)\ H_2$$

For the part used:

$$\tau\ [(\beta +1)\ CO + (\delta +3)\ H_2 + ((\beta +\delta)/2 +2)\ O_2] \rightarrow \tau\ [(\beta +1)\ CO_2 + (\delta +3)\ H_2O]$$

For the unused part:

$$(\alpha -1)\ H_2O + \gamma\ CO_2 + (1 - \tau\ )[(\beta +1)\ CO + (\delta +3)\ H_2]$$

We therefore get at the anode outlet:

$$[\alpha -1 + \tau\ (\delta +3)]\ H_2O + [\gamma + \tau\ (\beta +1)]\ CO_2 + (1 - \tau\ )\ (\beta +1)\ CO + (1 - \tau\ )\ (\delta +3)\ H_2$$

At the cathode outlet, we get:

$$[\lambda - \tau\ ((\beta +\delta)/2 +2)]\ O_2 + 3{,}76\ \lambda\ N_2$$

4.2.2 Influence of pressure on the cell performance

As shown in the graph in Figure 4.2, cells developed by Siemens and Westinghouse are such that their performance improves with pressure, its influence is being felt mostly at the open circuit voltage E

We choose a model exponential in relation to pressure:

$$E = E_0 + E_1\ e^{E_2\ P}$$

The settings of this equation are defined in the inlet mixer.
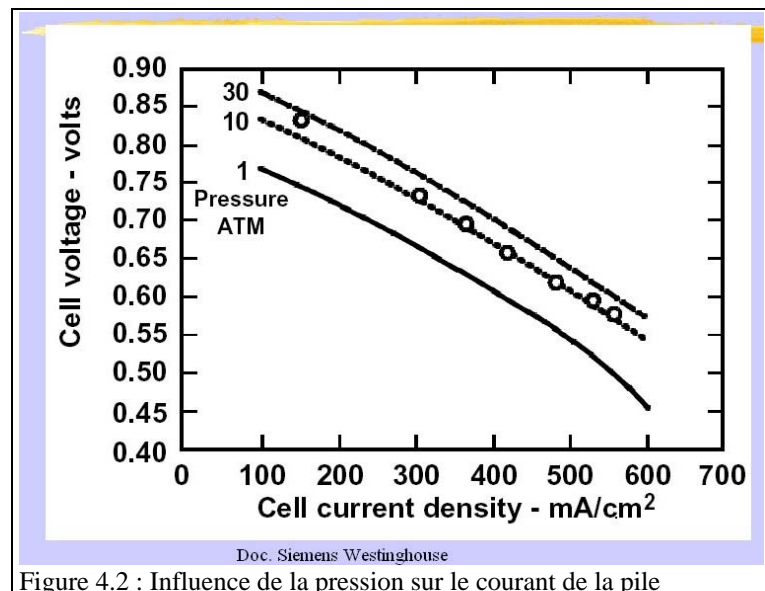
Figure 4.3 shows the diagram obtained.

Doc. Siemens Westinghouse

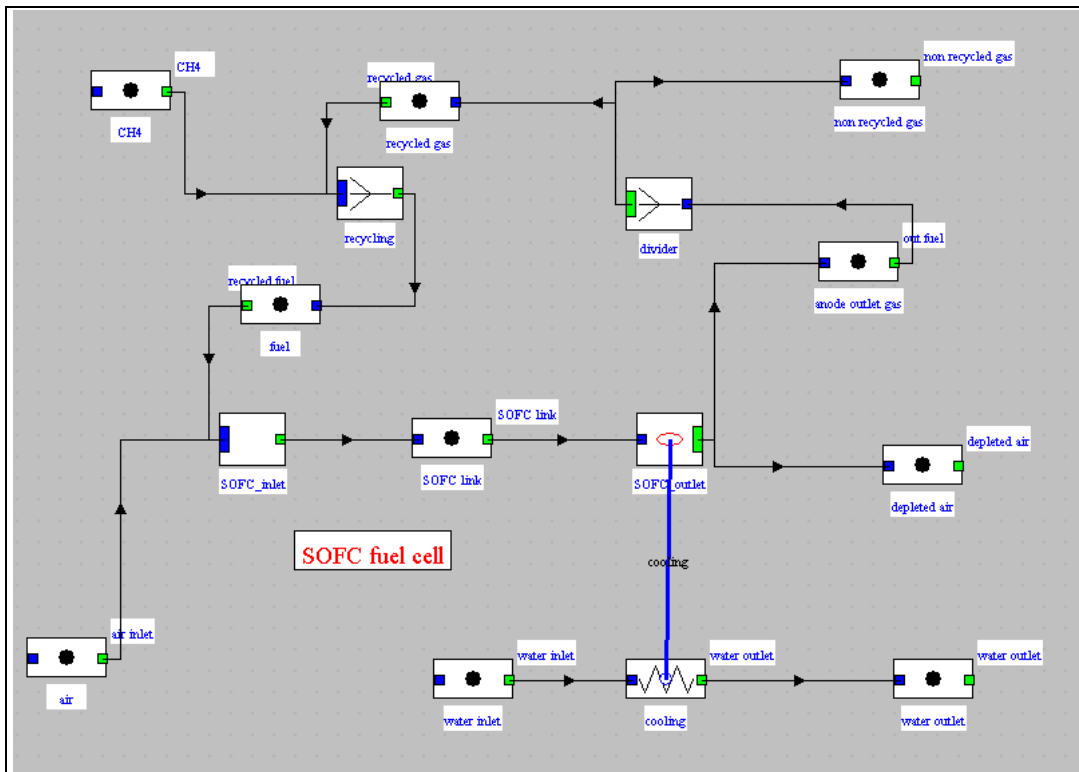Figure 4.2 : Influence de la pression sur le courant de la pile

Figure 4.3: Siemens Westinghouse cell diagram

5) Work files, recommendations

5.1 Work files

The following work files are attached in the archive SOFC.zip:
- code of external classes
- extUser.zip or extUser2.zip file containing external classes
- Project and diagram files of the Thermoptim models

5.2 Recommandations

It is necessary that the teacher checks that students have at their disposal in their work environment Thermoptim external classes they need.

The easiest way to this is to run Thermoptim, then open the external class viewer (menu Special of the simulator). Classes being grouped by type, SOFCInlet, SOFCOutlet and others must appear among the mixers and dividers, as shown in Figure 5.1

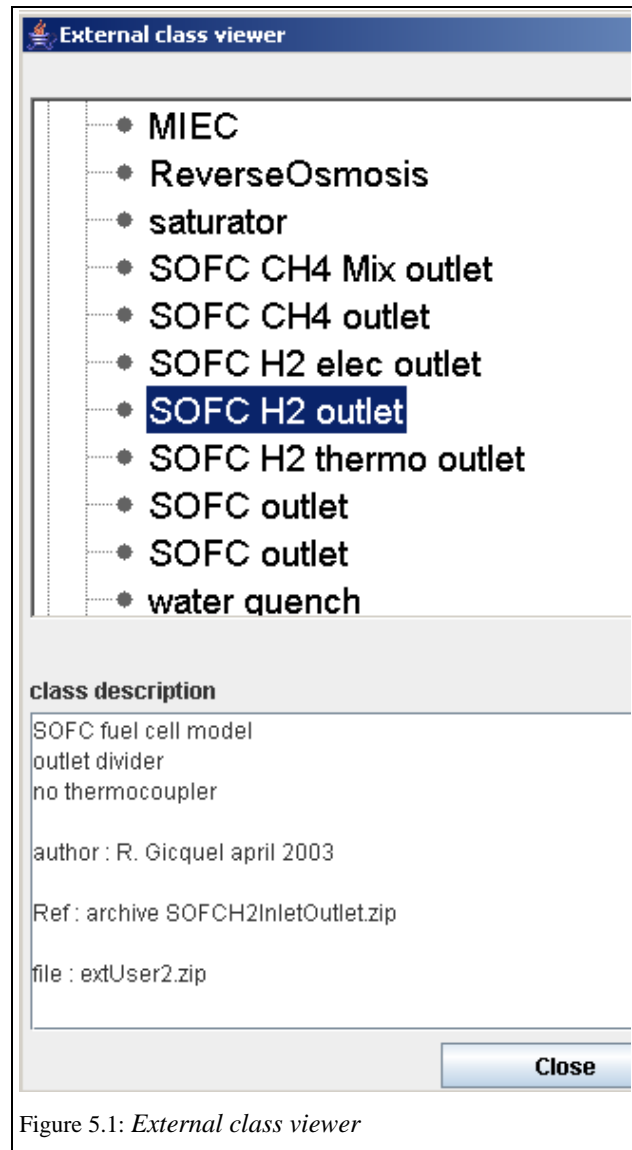If a class is missing, replace the extUser.zip file by that provided in the archive SOFC.zip. If present, it is unnecessary to make this change.

Figure 5.1: *External class viewer*