FAULT DETECTION BY TEMPERATURE BEHAVIOR ANALYSIS IN POLYMER ELECTROLYTE MEMBRANE FUEL CELLS

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Abstract. *This paper presents the method of fault detection by the temperature behavior analysis in polymer electrolyte membrane fuel cells. In order to avoid damages in other components of the stack due to the increase of operational temperature, a method for fault treatment is proposed. This method consists in the adjustment of the load demand reducing the operational temperature increase. These methodologies are applied in two types of faults: fault in the refrigeration system and sudden ruptures in the polymer electrolyte membrane. Tests show that the proposed fault treatment is applied successfully in case of refrigeration system faults; and, the optimal control of operational temperature (in which the operational temperature is the highest possible temperature preserving optimal conditions of operation) is a better choice to treat faults in case of ruptures in the electrolyte.*

Keywords. *Fault analysis, detection, and treatment; Membrane-electrode assembly; Polymer electrolyte membrane fuel cells; Temperature control.*

1. INTRODUCTION

Recent discussions about environmental issues (as greenhouse gas emissions, scarcity of fossil fuels, sonorous and visual pollutions) made increase the interest in renewable and clean energy sources. Fuel cells are a good choice of renewable and clean energy source and present several advantages over traditional energy technologies, as low pollutant gas emissions, higher efficiency and higher autonomy. Polymer electrolyte membrane fuel cells (also known as proton exchange membrane fuel cells – PEMFC) are the best option in the range 0 – 200 kW of power supply and presents additional advantages such as: no pollutant gas emissions (the only sub-products of its operation is water and residual heat), reduced size (permitting its application in portable electronics), low temperature operation and rapid start-up. Nevertheless, it is not viable the substitution of the traditional energy sources by fuel cells. Several researchers, nowadays, are working to improve this technology, increasing its efficiency and reliability, and reducing costs of fabrication and operation.

In a polymer electrolyte membrane fuel cell, hydrogen is supplied in the anode and reaches a catalytic layer, separating protons and electrons. The electrons feed an external electrical circuit and the protons pass through a polymeric membrane (the electrolyte). On the other side, oxygen is supplied from the air to the cathode and reaches a catalytic layer, reacting with protons and electrons, and generating water and residual heat as sub-products.

Two improvements on PEMFC technology permit to increase its efficiency and reliability. The first one is the optimal control of operational temperature, in which the stack operates at the highest possible temperature preserving minimum stoichometry and desired humidity in the membrane. It will be shown that the higher the temperature, the lower the energy losses, so the optimal temperature control increases the efficiency of the fuel cell stacks.

The second one is the concept of fault tolerant fuel cell, in which a supervisor system is able to recognize when some fault is occurring in the stack and, when possible, act in order to avoid failures in other components of the stack.

2. MATHEMATICAL MODEL OF PEMFC

The mathematical model of PEMFCs is composed by the electrochemical model (which calculates the output voltage of the stack) and the thermodynamic model (which calculates the operational temperature and output relative humidity of the cell).

2.1. Electrochemical model

The output voltage of the cell is calculated as (Larminie and Dicks, 2003):

$$V = n(E_{Nernst} - V_{act} - V_{ohmic} - V_{con}) \tag{1}$$

where n is the number of cells composing the stack, E_{Nernst} is the open-circuit voltage and V_{act} , V_{ohmic} and V_{con} are losses of voltage by activation of electrodes, resistance to proton and electron flow, and concentration of mass, respectively.

Figure 1 shows the polarization curves of a PEMFC for different temperatures. It can be noticed that the higher the temperature, the higher the output voltage. This is because the higher the temperature, the lower the activation losses, increasing the efficiency of the stack.

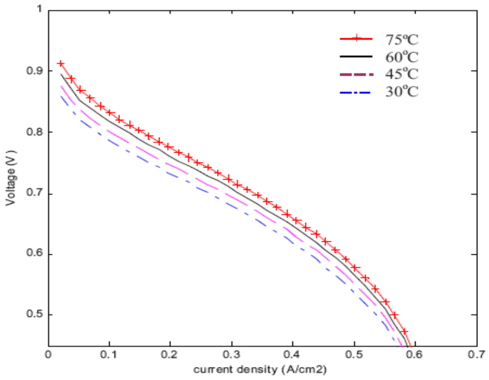

Figure 1. Polarization curves of a PEMFC

The generated power is given by the following expression:

$$Pow = V \cdot I_{FC} \tag{2}$$

where Pow is the generated power and I_{FC} is the electrical current of the stack.

2.2. Thermodynamic model

The operational temperature is calculated as follows:

$$T(k) = T(k-1) + \frac{\Delta\dot{Q}}{M \cdot C_S} \tag{3}$$

where T is the operational temperature, k is the discrete instant of operation, $\Delta\dot{Q}$ is the difference between generated and removed heat ($\Delta Q = Q_{gen} - Q_{rem1} - Q_{rem2} - Q_{rem3}$), M is the total mass of the stack and C_S is the average specific heat coefficient of the stack.

The generated heat is calculated by the following relationship (Larminie and Dicks, 2003):

$$\dot{Q}_{gen} = Pow\left(\frac{1.25}{V_{FC}} - 1\right) \tag{4}$$

where Q_{gen} is the generated heat and V_{FC} is the output voltage of a single cell ($V_{FC} = V/n$).

Three components of heat removal are considered: heat removed by the reaction air fan (Q_{rem1}), by the refrigeration system (Q_{rem2}) and by exchanges with the surround (Q_{rem3}). The heat removed is the sum of these three types.

The heat removed by the reaction air fan flowing inside the cell is calculated by the next equation:

$$\dot{Q}_{rem1} = \dot{m}_{air} \cdot C_{air} \cdot \Delta T \tag{5}$$

where $\dot{m}_{air}$ is the mass of used air ($\dot{m}_{air} = 3.57 \cdot 10^{-7} \cdot \lambda \cdot I_{FC}$ [kg/s]), λ is the input air stoichometry, C_{air} =1004 kJ/kg K is the air heating coefficient and ΔT is the difference between the operational and input air temperatures.

The heat removed by the refrigeration system is calculated by:

$$\dot{Q}_{rem2} = \eta_{cooler} \cdot Pow_{cooler} \cdot \Delta T \tag{6}$$

where η_{cooler} is the efficiency of the cooler, Pow_{cooler} is the power of the cooler and ΔT is the difference between the operational and environmental temperatures.

The heat removed by exchanges with the surround is given by:

$$\dot{Q}_{rem3} = Cap_{surr} \cdot \Delta T \tag{7}$$

where Cap_{surr} (W/K) is the capacity of heat removal characteristic of the surrounding, and ΔT is the difference between the operational and environmental temperatures.

In polymer electrolyte membrane fuel cells with optimal temperature control, the operational temperature is controlled be the highest possible, preserving a minimum air stoichometry and a desired output air relative humidity (which traduces the humidity on the polymer electrolyte membrane as well?). This theoretical temperature is defined as *limit temperature* (Riascos and Pereira, 2009) and is calculated as follows:

$$T_{limit} = 96.25 + 23.55 \ln\left[\frac{1}{RH_{des}}\left(\frac{0.421 \cdot P_{air}}{\lambda_{min} + 0.188}\right) + P_{w_{in}} + 0.01751\right] \tag{8}$$

where RH_{des} is the desired relative humidity, λ_{min} is the minimum input air stoichometry to ensure adequate amount of oxygen to the chemical reaction ($\lambda_{min} = 2$), P_{air} is the air pressure into the stack and Pw_{in} is the partial pressure of water of the input air.

In this research, it was considered a fuel cell equipped with polymer electrolyte membrane manufactured by Dupont, whose relative humidity should be between 85 % and 100 %. Below those limit, the membrane become dry, decreasing the proton conductivity and then increasing losses of voltage by ohmic resistance. Above those limits the membrane and the electrodes become flooded, blocking the passage of reactant gases and impeding the chemical reaction (Larminie and Dicks, 2003; Husar, Higier and Liu, 2008). In (Riascos, 2008), the output relative humidity is controlled by the reaction air fan. The stoichometry of reaction air to maintain the desired relative humidity (fixed as 85 % in this work) is calculated as follows:

$$\lambda = \frac{0.421 \cdot P_{air}}{RH_{des} \cdot P_{sat_{out}} - P_{w_{in}}} - 0.188 \tag{9}$$

where $P_{sat_{out}}$ is the saturated vapor pressure of the output air.

Figure 2 illustrates the behavior of electrical current (I_{FC}), voltage, load, temperature and output relative humidity in a normal operation. This stack is composed by 4 cells of 64 cm² each, with optimal temperature control and input air humidification. The stack is supplying a constant load demand of 10 W.

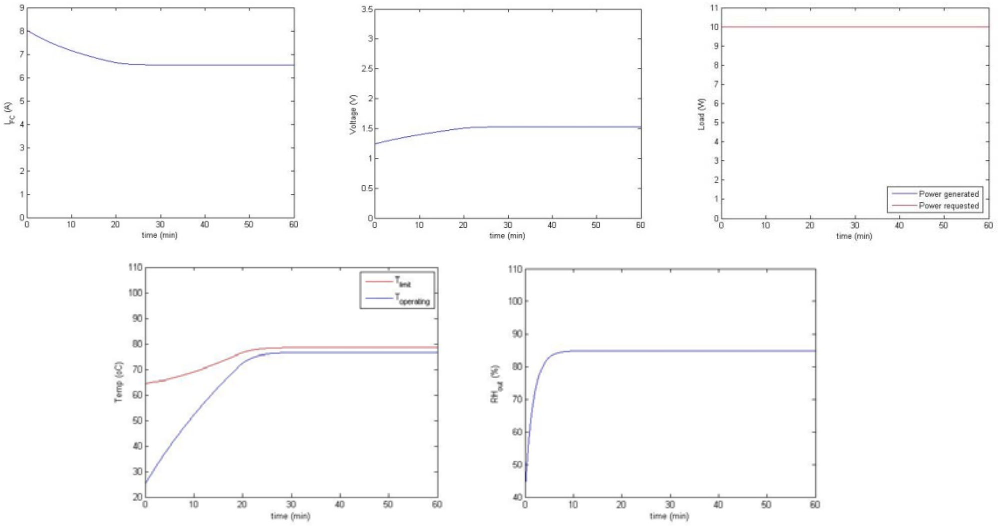

Figure 2. Behavior of variables in a PEMFC in normal operational conditions

3. FAULT DETECTION AND TREATMENT

In this chapter, the mathematical model of the analysis of temperature behavior will be presented. The method of load adjustment for fault treatment will be deduced based on the mathematical model presented in chapter 2.

3.1. Analysis of temperature behavior

Some faults in PEMFC affect the temperature. An option for detecting these faults is to search for changes in the temperature curve behavior. The goal of this analysis is to detect a temperature increase, in order to avoid the increase of operational temperature over the limit temperature – whose main consequence would be the drop of the relative humidity, decreasing the proton conductivity in the membrane and then decreasing the power generation (Riascos, Simões and Miyagi, 2007; Borup, Meyers, Pivovar, Kim, Mukundan, Garland, Myers, Wilson, Garzon, Wood, Zenelay, More, Stroh, Zawodzinski, Boncella, McGrath, Inaba, Miyatake, Hori, Ota, Ogumi, Miyata, Nishikata, Siroma, Uchimoto, Yasuda, Kimijima and Iwashita, 2007; Riascos, 2008). Also, the operation at temperature higher than the limit temperature compromises other components of the stack (Borup et al., 2008).

The analysis of temperature behavior can be performed in two different ways: first, the differential of the operational and limit temperature can be compared. If the differential of the operational temperature is higher than the differential of the limit temperature (in the same instant), then the operational temperature will overcome the limit temperature, and some component of the stack will fail. If some fault is detected by this method, this fault will be defined as fault type (f1). Mathematically,

$$\frac{dT}{dt} > \frac{dT_{limit}}{dt} \wedge E < E_{max} \Longrightarrow f = 1 \tag{10}$$

where $\frac{dT}{dt}$ is the differential of the operational temperature, $\frac{dT_{limit}}{dt}$ is the differential of the limit temperature, E is the error (difference) between the operational and limit temperature, E_{max} is the maximum error to be permitted (in this work, E_{max} = 1.6), and f is the type of the fault. The adoption of a maximum error avoids false fault detection while the process is in transitory state, when the differential of the operational temperature can be higher than the differential of limit temperature.

The second way to analyze the temperature behavior is to compare successive operational temperature differentials. In this case, the detection searches for abrupt changes in the operational temperature (which could be caused by a failure in the polymer electrolyte membrane or other component). If both operational and limit temperature are hugely affected by the fault, or if the PEMFC temperature is not optimally controlled, this method of fault detection should be applied. Faults detected by this method are defined as fault type (f2) and is simulated by the next equation:

$$varTemp > varTemp_{min} \Rightarrow f = 2 \tag{11}$$

where *varTemp* is the difference between the temperature at instant *t* and the instant *t* – *k* (*k* positive) and $varTemp_{min}$ is the minimum value of *varTemp* to be considered a fault detection (in this work, $varTemp_{min}$ = 0.6).

The treatment for a fault detected, especially by the first method (faults type *f1*) to avoid the temperature increase, may induce a decrease in the operational temperature. Even this decrease can be considered a fault: it is defined as fault type *f3* and is modeled mathematically as:

$$\frac{dT}{dt} < \frac{dT_{limit}}{dt} \Longrightarrow f = 3 \tag{12}$$

3.2. Load adjustment

The purpose of the load adjustment is to regulate the load in order to avoid the operational temperature increase overcoming the limit temperature, in case of fault detected.

According to eq. (3), the operational temperature increase is related to the difference between the generated and removed heat. Therefore, in case of excessive increase of the operational temperature, the generated heat should be controlled to avoid the overcoming of the limit temperature.

If the tax of heat is null ($\Delta Q = 0$), the operational temperature will remain constant. Then, a new variable can be defined: the referential generation of heat, $\dot{Q}_{gen_{ref}}$:

$$\dot{Q}_{gen_{ref}} \equiv \dot{Q}_{rem} \tag{13}$$

If the generated heat is equals to the removed heat, the tax of heat is null. Combining eq. (2), (4), and (14), a referential current can be defined as:

$$I_{FC_{ref}} \equiv {\dot{Q}_{gen_{ref}}} \Big/ {V \cdot \left(\frac{1.25}{V_{FC}} - 1\right)} \tag{14}$$

The referential load, which is the value of the load adjusted, can be then defined as:

$$Load_{ref} \equiv I_{FC_{ref}} \cdot V \tag{15}$$

Combining eq. (13), (14), and (15), a simpler form to the referential load equation is obtained:

$$Load_{ref} \equiv {\dot{Q}_{rem}} \Big/ {\left(\frac{1.25}{V_{FC}} - 1\right)} \tag{16}$$

If the fault detected by temperature analysis is type *f1* or *f2* (if the operational temperature is increasing too fast), the referential load is the *maximum* load permitted to avoid the overcome of the limit temperature; on the other hand, if the fault detected is type *f3* (if the operational temperature is tending to decrease), the referential load is the *minimum* load.

4. CASE STUDY: FAULTS IN THE REFRIGERATION SYSTEM AND RUPTURE IN POLYMER ELECTROLYTE MEMBRANE

In this section, the temperature behavior analysis and fault treatment by load adjustment will be applied for refrigeration system faults and ruptures in polymer electrolyte membrane. The load adjustment in case of ruptures in the polymer electrolyte membrane will be compared in two different PEMFC systems: in the presence and absence of optimal temperature control. The goal of this comparison is to appraise the optimal temperature control as a method of fault treatment (which is not possible in case of refrigeration system fault, once the temperature control is lost in this case).

4.1. Refrigeration system fault

In this work, the refrigeration system considered is composed by a fan which blows air from the surround to the stack, removing part of the generated heat. Also, this is the actuator of the temperature controller: the power of the fan is controlled by a proportional-integral temperature controller.

Figure 3 illustrates the temperature (Temp), relative humidity (RH_{out}), removed heat (Q_{rem}), and load behavior in case of refrigeration system fault. At t = 38 min, the refrigeration system stops totally (mathematically, $Q_{rem2} = 0$). As a consequence, the operational temperature starts to increase immediately, and overcome the limit temperature after 5 minutes later the fault occurrence. (Once the stack has extra humidification of the input air, the limit temperature is also affected by the fault, and is increased as a consequence of the raise of operational temperature. However, the operational temperature increases faster.) At t = 46 min, the output relative humidity decreases, because the high temperature vaporizes the water into the stack. The scarcity of water in the electrolyte membrane makes the proton conductivity to decrease drastically, and then, at t = 51 min, the stack is not able to attend the initial load demand of 10 W.

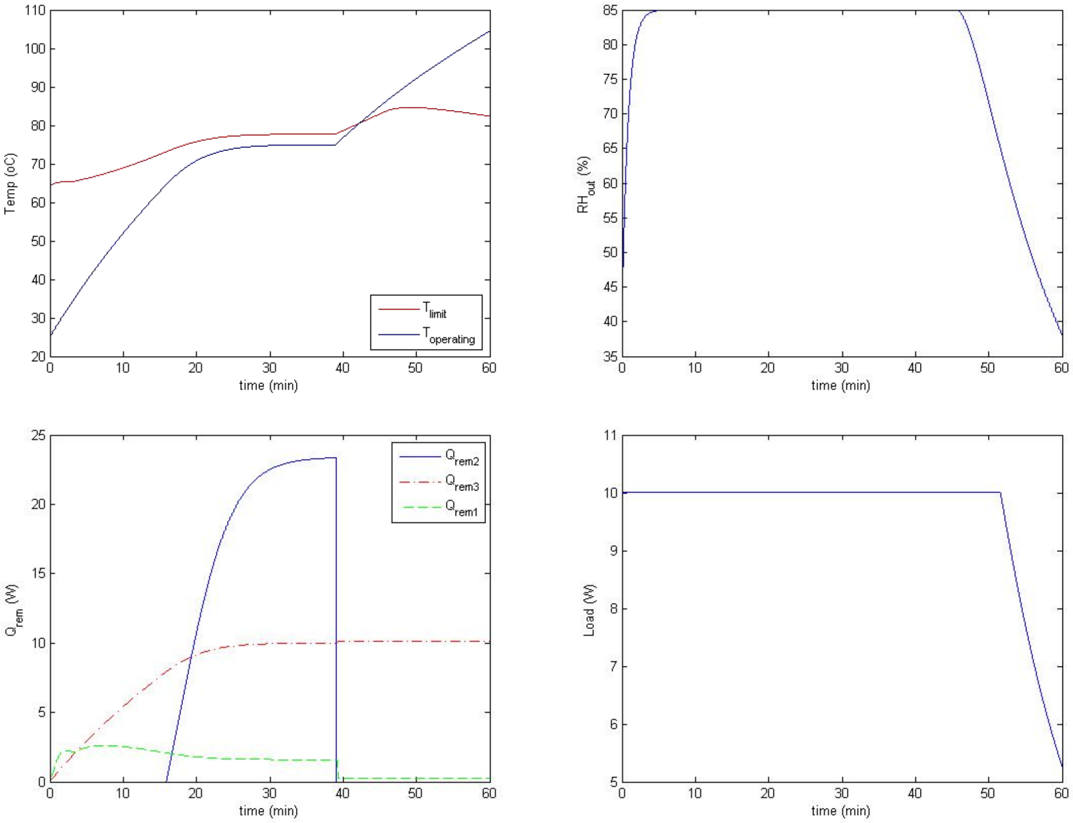

Figure 3. Behavior of the PEMFC variables in case of fault in refrigeration system

Applying the methodology proposed (fault detection by temperature analysis and fault treatment by load adjustment), the load is partially reduced and the operational temperature is maintained under secure limits, maintaining the humidity in secure limits, as well. Once the operational temperature is below the limit temperature, all the stack's components are kept in safe conditions. Fig. 4 shows the temperature, relative humidity, load, and heat in case of refrigeration system fault (similarly illustrated in fig. 3), but this time detected by temperature behavior analysis and treated by load adjustment. The fault was detected 30 seconds after the occurrence. The load generation was kept in 2.1 W (21 % of the initial load request) and the temperature is kept constant after the fault treatment, because the generated and removed heats are equals.

It is important to notice that, once the generated heat is equals to the removed heat after the fault treatment, the load adjusted would be higher if the refrigeration system did not stop totally. This fact is clearer in eq. (16): the higher the removed heat, the higher the referential load.

4.2. Ruptures in polymer electrolyte membrane

The polymer electrolyte membrane is composed by hydrophilic and hydrophobic regions. The conduction of protons is given by a repulsion-attraction phenomenon: the proton is attracted by the hydrophilic region and repulsed by the hydrophobic region. In this research was considered membranes Nafion, a perfluorinated sulfonic acid (PFSA) membrane.

In (Borup et al., 2007) the physical and chemical degradation of polymeric membranes (and other degradations in PEMFC) are reviewed. Basically, the polymeric membranes are submitted to compressive forces into the stack and undergo time-dependent deformation, and may creep as a consequence of long-time operation under compressive forces, high temperature, and inadequate humidification. Also, when the membrane gets thinner, the phenomenon of fuel crossover (fuel crossing the membrane without reacting) is increased.

In this work, is considered the failure occurred when the membrane (or the membrane-electrode assembly) suddenly creeps. The main characteristic of this failure is the reduction of current density by increase of fuel crossover (Jn [A/cm^2]), proportional to the rupture area.

Figure 5 illustrates the temperature, Jn, removed heat, and load behavior when the membrane suddenly creeps at t = 40 min. In this case, the fuel cell stack has no optimal temperature control; when the operational temperature reaches 50 ºC, the refrigeration system is activated with a constant power of 2 W. (In the figure, the limit temperature is calculated, but only for comparison). The current density loss (Jn) is increased from 0.022 A/cm^2 to 0.2 A/cm^2. Instantaneously, the power generation decreased from 10 W to 3.3 W because the rupture in the membrane; when the operational temperature overcome the limit temperature, the relative humidity decreased, decreasing the proton conductivity; then, at t = 58 min, the limit temperature begins to decrease constantly.

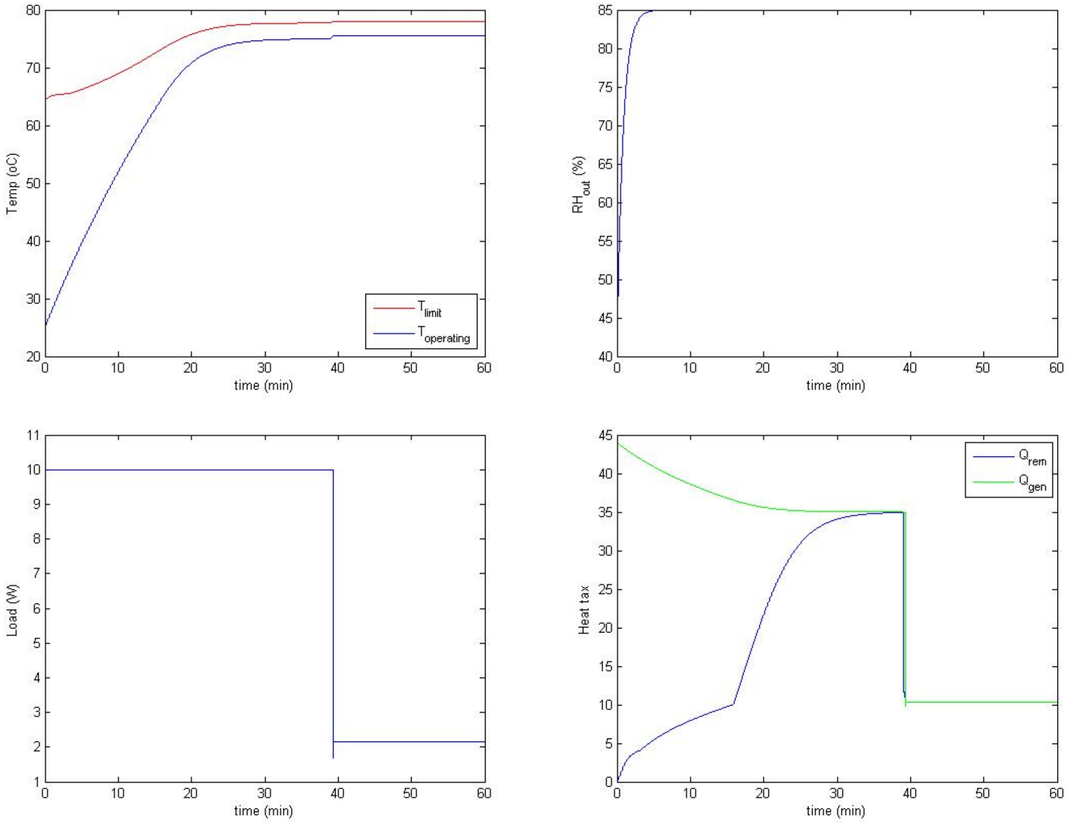

Figure 4. Behavior of the PEMFC variables in case of refrigeration system fault detected by temperature behavior analysis and treated by load adjustment

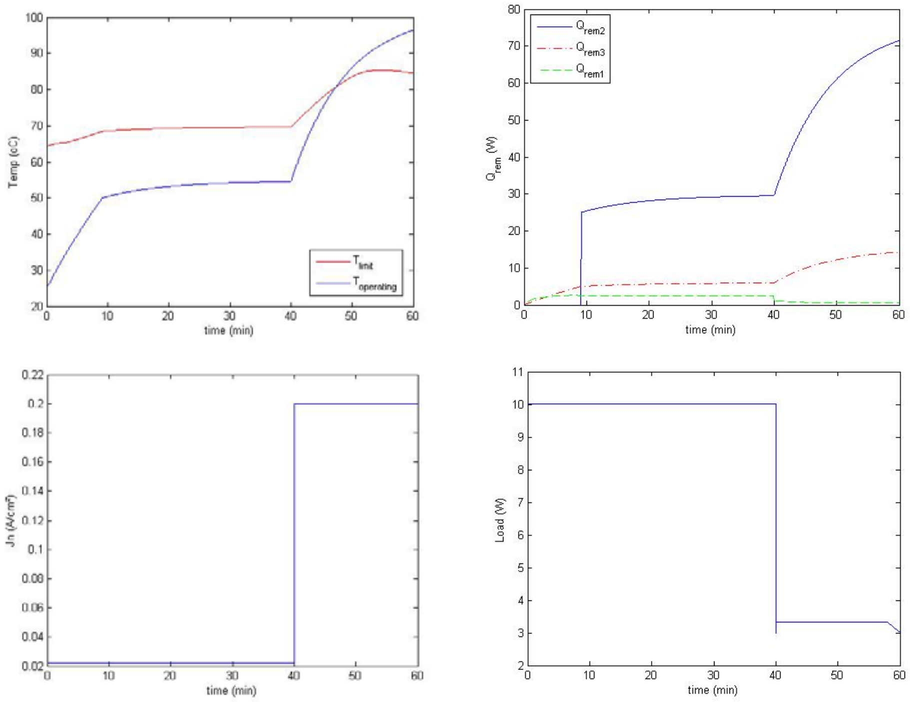

Figure 5 – Behavior of the PEMFC variables without optimal control of temperature in case of sudden ruptures in membrane

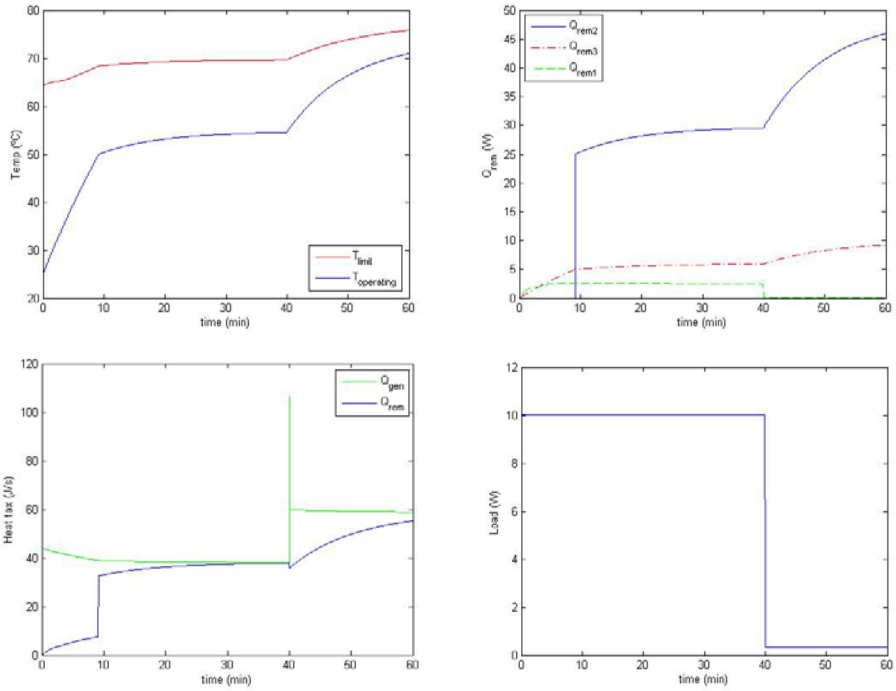

Figure 6. Behavior of the PEMFC variables in case of sudden ruptures in membrane. Fault detected by analysis of temperature behavior and load adjusted.

The temperature behavior analysis and load adjustment were applied in this fault and the results are shown in fig. 6. Once the temperature is not optimally controlled, the analysis was performed by eq. (11). In this case, the load adjustment was not enough to avoid the increase of operational temperature; load was limited to a minimum value of 0.5 W (in order to avoid the stop of the process), and the temperature increased anyway, although more slowly than expected.

In PEMFC systems with optimal temperature control, the fault is not detected, because the refrigeration system is adjusted in order to avoid the operational temperature increase. Nevertheless, the power generation is maintained in 3.3 W – a higher value than the value obtained in case of load adjustment (limited to 0.5 W).

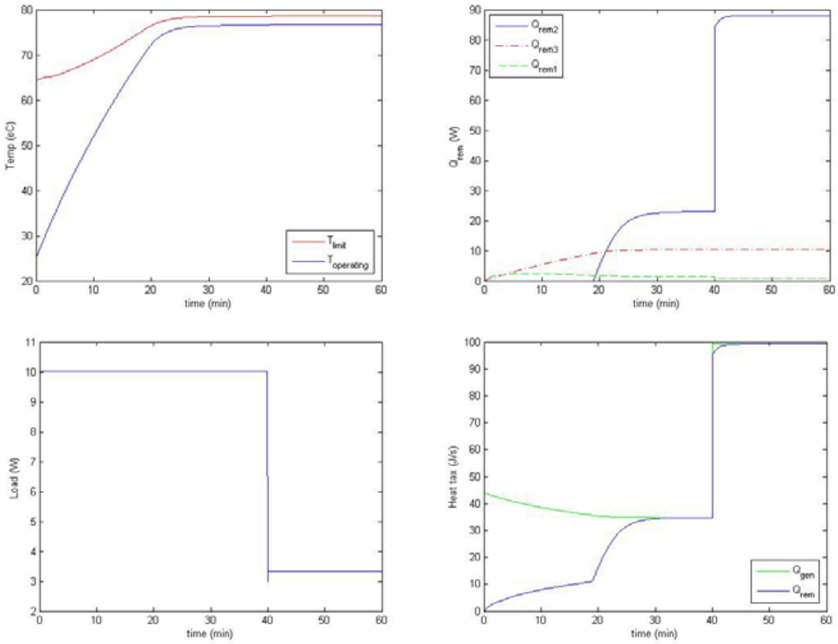

Figure 7. Behavior of the PEMFC system with optimal temperature control in case of sudden rupture in membrane.

In fig. 7, it is also important to notice that the generated heat (Q_{gen}), right after the fault occurrence, is not equals to the removed heat (Q_{rem}), proving that the fault is not effectively treated by load adjustment. In fact, the load adjustment ensures the drop of the generated heat, which becomes equals to the removed heat, guaranteeing a constant operational temperature. Then, the load adjustment is recommended only in case of refrigeration system fault, or in case of inefficacy of the refrigeration system to maintain the operational temperature under secure limits (for example, in case of rising temperature due to other faults, like creeps in the membrane).

5. CONCLUSIONS

As a clean and renewable energy source, the polymer electrolyte membrane fuel cells (PEMFC) are an interesting option: they are pollutant-emission free, efficient, low size and weight, quick start-up, and operate at low temperature. However, other researches are being performed in order to increase their efficiency and reliability, and to decrease their costs.

In this article, a new method for analysis of variable behavior was introduced: the temperature behavior analysis, which consists in searching for changes in temperature behavior, as changes in its tax of variation. It was also presented a methodology for fault treatment which affects the temperature behavior: the load adjustment, which is the adjustment of the reference load to avoid the operational temperature increase. The methodologies presented in this work were applied for two types of faults in polymer electrolyte membrane fuel cells: faults in refrigeration system and sudden creeps in the polymeric membrane.

When the refrigeration system fails, the first consequence is the operational temperature increase. The rise of temperature causes the relative humidity decrease in the electrolyte, reducing the proton conductivity. Because of those consequences, the power generation drops. When the temperature increase is detected (a few seconds after the fault occurrence), the load can be adjusted to make the generated heat equals to the removed heat. Then, the operational temperature is kept constant, and the other components of the fuel cell system are kept in safe conditions.

The main consequence of a sudden rupture in membrane is the sudden increase of fuel crossover. The power generation drops instantaneously because of the high fuel crossover. This fault is detected by changes in temperature only in fuel cell systems without optimal temperature control, but in this case, the application of the load adjustment does not avoid the increase of temperature. On the other hand, in fuel cell systems with optimal temperature control, the fault is not detected because the operational temperature is constant, but the power generation is kept higher than in case of load adjustment (in fuel cell systems with no optimal temperature control). Therefore, the load adjustment is recommended in case of inefficiency of the refrigeration system, when the operational temperature control is ineffective.

6. REFERENCES

Borup, R.; Meyers, J.; Pivovar, B.; Kim, Y.S.; Mukundan, R.; Garland, N.; Myers, D.; Wilson, M.; Garzon, F.; Wood, D.; Zenelay, P.; More, K.; Stroh, K.; Zawodzinski, T.; Boncella, J.; McGrath, J.E.; Inaba, M.; Miyatake, K.; Hori, M.; Ota, K.; Ogumi, Z.; Miyata, S.; Nishikata, A.; Siroma, Z.; Uchimoto, Y.; Yasuda, K.; Kimijima K.; Iwashita, N. *Scientific aspects of polymer electrolyte fuel cell durability and degradation.* American Chemical Society, pp. 3094 – 3951, 2007.

Husar, A.; Higier, A.; Liu, H. *In situ measurements of water transfer due to different mechanisms in a proton exchange membrane fuel cell*. Journal of power sources, pp. 240 – 246, 2008.

Larminie, J.; Dicks, A. *Fuel cell systems explained.* John Willey & Sons, 2nd ed., 2003.

Riascos, L.A.M. (Umidade relativa, 2008)

Riascos, L.A.M.; Pereira, D.D. *Limit operating temperature in polymer electrolyte membrane fuel cells.* Journal of electrochemical society, pp. 1051 – 1058, 2009.

Riascos, L.A.M.; Simões, M.G.; Miyagi, P.E. *A bayesian network fault diagnostic system for proton exchange fuel cells.* Journal of Power Sources, pp. 267 – 278, 2007.

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