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Abstract:
This deliverable depicts the prognostics approach developed on the SAPPHIRE project. This approach is based on a behavioral physics-based model.

Keywords:
Proton exchange membrane fuel cell, Prognostics and health management, Behavioral model, Static, Dynamic, Prediction

Revision History

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1.3	2015/07/21	Corrections	Elodie Lechartier (FCLAB)
1.4	2015/07/28	Corrections	Elodie Lechartier (FCLAB)

Table of Contents

Nomenclature

η_a	Voltage drop at the anode	$[V]$
η_c	Voltage drop at the cathode	$[V]$
τ_{Oc}	Time constante of the diffusion convection impedance	$[s]$
b_a	Tafel anode parameter	$[V^{-1}]$
b_c	Tafel cathode parameter	$[V^{-1}]$
b_{Oc}	Parameter of the variation law of R_{Oc}	$[V^{-1}]$
C_{dca}	Double layer capacity at the anode	$[F/cm^2]$
C_{dcc}	Double layer capacity at the cathode	$[F/cm^2]$
E_n	Nernst Potential	$[V]$
i	Number of EIS realized at each characterizations	
j_{0a}	Exchange current density at the anode	$[A/cm^2]$
j_{0c}	Exchange current density at the cathode	$[A/cm^2]$
j_{0Oc}	Parameter of the variation law of R_{Oc}	$[A/cm^2]$
J_{AC}	Dynamic current density	$[A/cm^2]$
J_{DC}	Static current density	$[A/cm^2]$
j_{Lc}	Limit current density at the cathode	$[A/cm^2]$
k	Number of characterizations	
k_{Oc}	Parameter of the variation law of τ_{Oc}	$[A.s/cm^2]$
L	Connectors' inductance	$[H.cm^2]$
R_m	Internal resistance	$[\Omega.cm^2]$
R_{Oc}	Module of the diffusion convection impedance	$[\Omega.cm^2]$
R_{ta}	Transfert resistance at the anode	$[\Omega.cm^2]$
R_{tc}	Transfert resistance at the cathode	$[\Omega.cm^2]$
U	Stack Voltage	$[V]$
U_{AC}	Dynamic stack Voltage normalised per cell	$[V]$
U_{DC}	Static stack Voltage normalised per cell	$[V]$
U_n	Stack voltage normalized per cell	$[V]$
W_{Oc}	Diffusion convection impedance	$[\Omega.cm^2]$

1 Introduction

In the frame of the SAPPHIRE project, a prognostics approach for PEMFC has to be developed. For that purpose, a behavioral model able to predict is described in this deliverable. It is based on an instantaneous behavioral model presented in [1] which present two main issues for the aim: the lack of ageing and the high number of parameter. This deliverable is composed of a quick description of the model used with a highlight of its limitations and the way they are overcome. In order to face the first issue, the high number of parameters, a sensitivity analysis is realized and described, in order to evaluate which parameters have big influences and then focus our attention on them. For the second issue,and with the results obtained thanks to the sensitivity analysis, the parameters are expressed with a time dependent function. Finally, this deliverable develops the progress from a simple instantaneous behavioral model to a model able to predict the behavior of the stack.

2 Model without ageing

2.1 Presentation of the model

In order to develop a model-based prognostics an efficient mean of reproduction of the behavior of the fuel cell is needed. To face this necessity, a model is presented here. It is composed of a static and dynamic part, as it can be seen on figure 1.

The input of this model is the current which is normalized as current density to be decomposed in alternative and continuous parts. These two current densities are the input of the static and dynamic models. The output of these models are recomposed in voltage per cell to finally be denormalized in voltage.

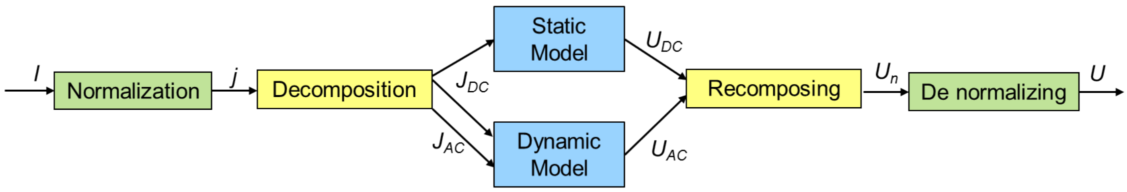

Figure 1: Scheme of the model

The aim of the dynamic part of the model is to link voltage variations with the current variation around a static operating point. This part of the model is based on an electrical equivalency. Indeed, the physical phenomena are represented by an impedance (Figure 2).

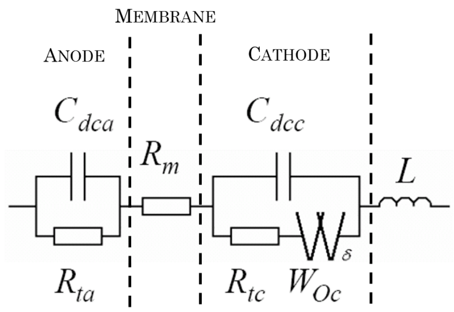

Figure 2: Electrical equivalency impedance of the dynamic model

The Warburg W_{Oc} is defined by its module R_{Oc} and its time constant τ_{Oc} which are finally defined thanks to sub parameters (also regressed on a later step).

$$R_{Oc} = \frac{1}{\left(b_{Oc}.2.j_{0Oc}.\sqrt{\left(\frac{J_{EIS}}{2.j_{0Oc}}\right)^2 + 1}\right)} \tag{1}$$

$$\tau_{Oc} = \frac{k_{Oc}}{J_{EIS}} \tag{2}$$

The static part of the model is based on a development of the Butler Volmer law with a difference made between the electrodes (eq. (3)) :

$$U_{DC} = E_n - R_m \cdot J_{DC} - \frac{1}{b_a} \cdot asinh\left(\frac{J_{DC}}{2 \cdot j_{0a}}\right) - \frac{1}{b_c} \cdot asinh\left(\frac{J_{DC}}{2 \cdot j_{0c} \cdot \left(1 - \frac{J_{DC}}{j_{Lc}}\right)}\right) \tag{3}$$

The parameters of the model are updated at each characterization phase thanks to experimental data: polarization curves and Electrochemical Impedance Spectroscopy. For the whole description of the parameter's updating process, please refer to complete description of the model [1].

The data used are based on experiments. A 5 cells stack of 100 square centimeters of active area is experimented with a ripple current of 70 A more or less 10% at a $5kHz$ frequency. The experiment is a long term test that lasted around one thousand hours. Some measures as current and voltage are monitored during the whole experiment. Each week, an experimental characterization is realized, which is composed of polarization curves (current - voltage curves) and Electrochemical Impedance Spectroscopies (EIS) at three DC current values.

The model developed is really satisfactory instantaneously (Figure3), indeed, it presents a good reproduction of the behavior during short amount of time, here around $200s$.

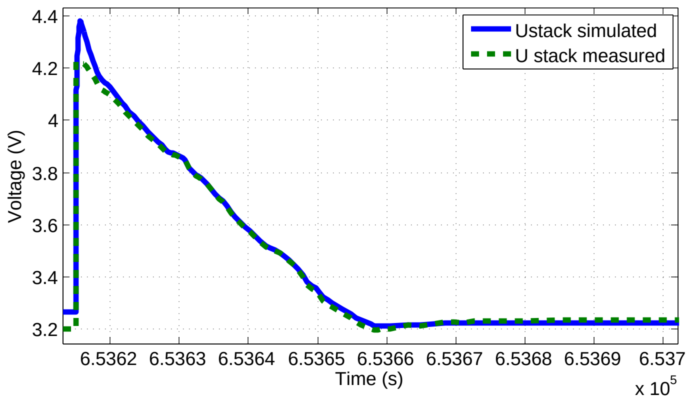

Figure 3: Evolution of the simulated voltage versus to the experimental one under the same solicitation

2.2 Discussion

2.2.1 Number of parameter

The global model has finally 13 parameters (Table 1) (as R_{ta} and R_{tc} are expressed thanks to b_a, b_c, j_{0a}, j_{0c} and j_{Lc}).

Parameter	Significance	Unit
b_a	Tafel anode parameter	$[V^{-1}]$
b_c	Tafel cathode parameter	$[V^{-1}]$
E_n	Nernst Potential	$[V]$
j_{0a}	Exchange current density at the anode	$[A/cm^2]$
j_{0c}	Exchange current density at the cathode	$[A/cm^2]$
j_{Lc}	Limit current density at the cathode	$[A/cm^2]$
j_{0Oc}	Parameter of the variation law of R_{Oc}	$[A/cm^2]$
k_{Oc}	Parameter of the variation law of τ_{Oc}	$[A.s/cm^2]$
b_{Oc}	Parameter of the variation law of R_{Oc}	$[V^{-1}]$
C_{dca}	Double layer capacity at the anode	$[F/cm^2]$
C_{dcc}	Double layer capacity at the cathode	$[F/cm^2]$
L	Connectors' inductance	$[H.cm^2]$
R_m	Internal resistance	$[\Omega.cm^2]$

Table 1: Parameters in the global model

As explained in [1], the different parts of the model are regressed on experimental data in order to obtain parameters values, in the tuning process. As there are numerous parameters, there are high chances to find local minima. Indeed, the numerical solution to the fitting issue can have no link with the physical sense.

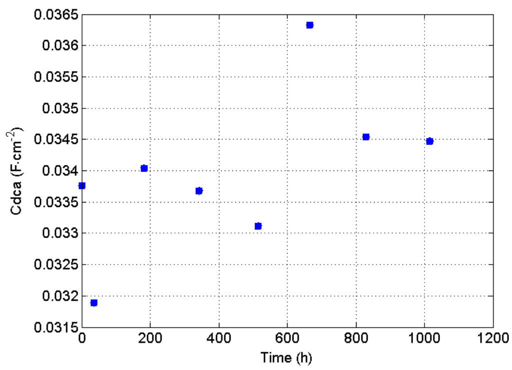

Figure 4: Evolution of C_{dca}'s value obtained at each characterization with the tuning process

Another aspect of this issue is the fact that, some parameters that do not show a clear evolution with the time as it can be seen on figure 4. It does not allow a smooth inclusion of the ageing effect on the evolution of the parameter with time. A crucial point here is the number of parameters which seems to be too large in relation to the number of data. Numerous local minima can be hit during the fitting process.

In order to face this issue, a sensitivity analysis is realized. It will allow to detect influential parameters with which extra caution will have to be taken.

2.2.2 Ageing

The model is instantaneously satisfactory, but since there is no evolution of the model with the time, the only means of evolving the model is to have a characterization phase and realize an updating procedure. Indeed, as it can be seen on figure 5, the simulated voltage does not match the experimental one. During these 1000 hours, the stack degraded, so its response to the same current solicitation evolve with the time: an ageing model is needed. Indeed, the final need being prognostics, it is necessary to have a prediction of the stack's behavior. For that, it is necessary to include a time dependency in the global model. In order to face this issue, the idea is to define the value of each parameter as a time dependent function (fig. 6).

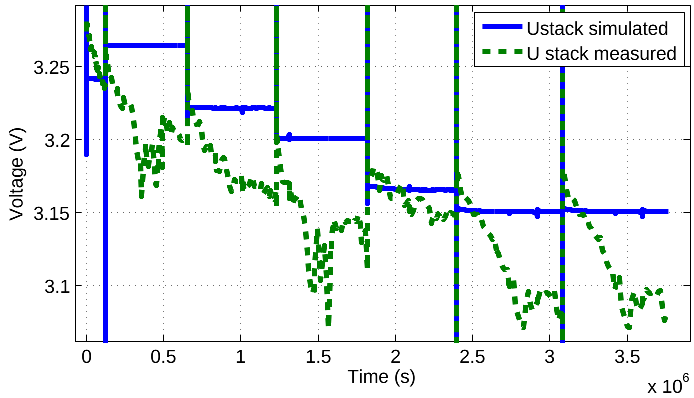

Figure 5: Evolution of the experimental voltage and simulated one under the same solicitation

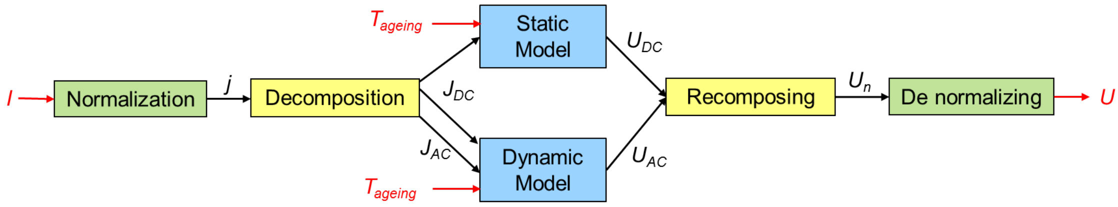

Figure 6: Inclusion of the time in the model

This step seems realizable: as it can be seen on figure 7, some parameters seems to have a clear evolution with time. This figure present the values of R_m obtained at each characterization with the tuning process versus to the time corresponding to the characterization.

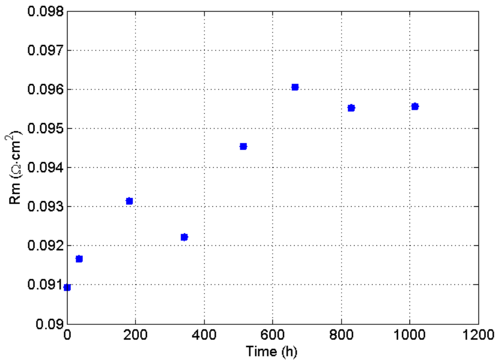

Figure 7: Evolution of R_m's value obtained at each characterization with the tuning process

However this step is related to the reliability of the identification of the parameters and the avoidance of local minima.

In conclusion, for facing these issues, a sensitivity analysis is realized on the static model that reproduce the polarization curve, on the dynamic model that can reproduce Nyquist plot obtained thanks to EIS and on the global model that can reproduce the voltage of the stack under the same current solicitation. It should allow pointing out which parameter has a big influence or not and compare it with the literature in order to decide if some should represent ageing or not.

3 Parameters Analysis thanks to ANOVA (ANalysis of VAriance)

3.1 The basics of ANOVA's calculation

The following presents the basics of the sensitivity analysis that has been applied independently on the three realized in our case (static part, dynamic part and global model). The following paragraph is presented with a general point of view as it can be applied to any study [2].

Lets Y be the results of the simulation that has to be studied, P the number of parameters that vary and A levels the number of levels for each p (parameter).

The experimental plan is realized with all the possible combinations of parameters that give a result Y. The total number of experiments is then expressed by :

$$N = A^P \tag{4}$$

The mean of all the simulation with Y_n being the results of the n^{th} experiment is:

$$\bar{Y} = \frac{1}{N} \cdot \sum_{n=0}^{N} Y_n \tag{5}$$

The total square summation is the basis for all of calculations and is defined with (eq. 6):

$$SCT = \sum_{n=0}^{N} \left(Y_n - \bar{Y}\right)^2 \tag{6}$$

3.1.1 Influence of one parameter

In the following the influence of each parameter p on its own is calculated.
Let Y_{p_a} be the result for the parameter p at the level a.

$$\bar{Y_{p_a}} = \left(\frac{A}{N}\sum_{a} Y_{p_a}\right) - \bar{Y} \tag{7}$$

The sum of the difference squared is calculated for each p:

$$SCE_p = \frac{N}{A}\sum_{a=0}^{A} \bar{Y_{p_a}}^2 \tag{8}$$

The influence of one parameter is then:

$$Inf_p = \frac{SCE_p}{SCT} \tag{9}$$

The influence can finally be expressed as:

$$Inf_p = \frac{\frac{N}{A}\sum_{a=0}^{A}\left(\left(\frac{A}{N}\sum_a Y_{p_a}\right) - \bar{Y}\right)^2}{\sum_{n=0}^{N}\left(Y_n - \bar{Y}\right)^2} \tag{10}$$

3.1.2 Interparametric influence of degree two

The details for the calculation of the influence of two parameters combined is given here.
On this second step, let $Y_{p_{1_{a_1}},p_{2_{a_2}}}$ be the result for the parameters p_1 at the level a_1 and p_2 at the level a_2.
The spectral radius, written $R2$ is defined as:

$$R2_{p_{1_{a_1}},p_{2_{a_2}}} = \left(\left(\frac{J^2}{N}\sum_{a1,a2} Y_{p_{1_{a_1}},p_{2_{a_2}}}\right) - \bar{Y} - \bar{Y_{p_{1_{a_1}}}} - \bar{Y_{p_{2_{a_2}}}}\right)^2 \tag{11}$$

The sum of the difference squared is calculated for each couple of parameters p_1, p_2 :

$$SCE_{p_1,p_2} = \frac{N}{A^2}\sum_{\substack{a_2=0\\a_1=0}}^{A} R2_{p_{1_{a_1}},p_{2_{a_2}}} \tag{12}$$

The interparametric influence is then:

$$Inf_{p_1,p_2} = \frac{SCE_{p_1,p_2}}{SCT} \tag{13}$$

3.2 Parameters' sensitivity analysis

3.2.1 Static model

For this ANOVA study, the Y taken is the error (MAPE) between the simulated polarization curve and the experimental one. This study was realized on each characterization. The static model is defined thanks to the parameters:

- R_m the resistance;
- E_n the Nernst potential;
- b_a, b_c the Tafel parameters;
- j_{0a}, j_{0c} the exchange current density;
- j_{Lc} the limit current density at the cathode only.

As explained in 3.1 a complete experimental plan is realized with all combinations of parameters possible. The table 3.2.1 presents the low value of each parameter and its high value, the number of levels taken being 3, there is one value added in the middle. The lower and upper bound of the variation for each parameters in the experimental plan is quite realistic.

Parameter	Minimum Value	Maximum Value	Unit
R_m	0.08	0.2	$\Omega.cm^2$
E_n	0.9	1	V
b_a	20	100	V^{-1}
b_c	20	100	V^{-1}
j_{0a}	0.001	1	A/cm^2
j_{0c}	0.001	1	A/cm^2
j_{Lc}	1.001	1.5	A/cm^2

Table 2: Static parameters extreme values for the experimental plan

The results for the static model are on figure 8. This figure shows the percentage of influence of each parameter on the error between the simulation and the experiment. There are 8 bars for each parameters, because the sensitivity analysis was realized on the 8 characterizations. The characterizations are numbered by the time they are happening, the first at time $0h$, the second at time $35h$ and the last at $1016h$. The results on the eight characterizations are similar, a convenient point as it shows that the parameters' influence on the difference between the simulation and the experiment is not drastically evolving.

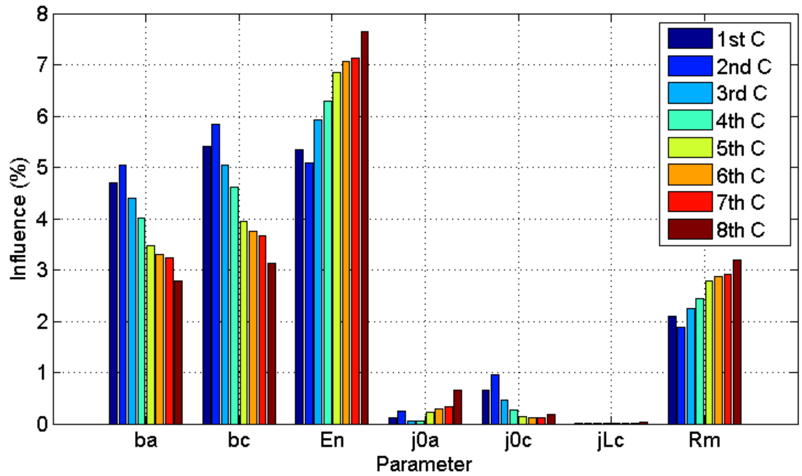

Figure 8: ANOVA's result for the static model

The parameters with the biggest influence are E_n, R_m, b_a and b_c that can be easily verified by the observation of the eq. (3). Indeed, a variation on the values of these parameters has direct impact on the voltage.

On table 3.2.1, the percentages of influence is given for the first characterization. It depicts the influence of one parameter on the diagonal, and the interparametric influence. A point has to be noted here, the total sum of the influences is low, around 18% (Table 3.2.1). The interparametric influences have values no higher than 0.1%.

The low value of the total sum could be explained by the range of values taken that is too short. Indeed the worst polarization curve given is not really a wrong one giving big error. The calculations are done between two values, the simulated polarization curve and the experimental one, finally too close.

This hypothesis can be confirmed by the realization of the same analysis with variations' range pushed to more extreme values. Such simulations give a sum growing with the increasing difference between the initial values.

The decision to take realistic values for the experimental plan is then bringing issues within the ANOVA calculation.

Influence (%)	b_a	b_c	E_n	j_{0a}	j_{0c}	j_{Lc}	r
b_a	4.69	0.0043	0.014	0.15	0.016	1.9 E^{-4}	0.0059
b_c		5.41	0.016	0.026	0,24	5.59 E^{-4}	0.0082
E_n			5.3547	0.040	0.038	1.58 E^{-4}	0.0019
j_{0a}				0.11	0.090	7.10 E^{-4}	0.016
j_{0c}					0.65	0.0016	0.015
j_{Lc}						0.0038	1.76 E^{-4}
r							2.10

Table 3: Results of the first sensitivity analysis of the static part of the model on the first polarization curve

3.2.2 Dynamic model

On this part of the model, the Y taken is the error (MAPE) between the simulated EIS and the experiment one at $70A$; as this is the solicitation of current during the experiment. This error is actually decomposed in two part, since the numbers on which it is calculated are complex impedance. So, there will be two different results for the sensitivity analysis of this model's part, the error on the real and the error on the imaginary.

The parameters on this model are:

- The Warburg impedance W_{Oc} which is decomposed in two impedances, R_{Oc} and τ_{Oc}.
- The double layer capacities C_{dca} and C_{dcc}.
- Two transfer resistances R_{ta} and R_{tc}.
- The ionic conductance of the membrane is modeled by an equivalent resistance R_m.
- The inductive behavior due to the connectors L.

The complete experimental plan can be seen on table 3.2.2, one should read it in the same way of the static experimental plan (3 levels with 2 extreme values and their middle).

Parameter	Minimum Value	Maximum Value	Unit
C_{cdca}	0.03	0.06	F/cm^2
C_{dcc}	0.02	0.05	F/cm^2
R_{Oc}	0.05	0.2	$\Omega.cm^2$
τ_{Oc}	0.1	0.6	s
L	0.8E-06	2E-06	H
R_m	0.08	0.2	$\Omega.cm^2$
R_{ta}	0.01	0.6	$\Omega.cm^2$
R_{tc}	0.01	0.4	$\Omega.cm^2$

Table 4: Dynamic parameters extreme values for the experimental plan

The results of the sensitivity analysis for the dynamic model are on figure 9. There are two figures as the sensitivity analysis is done on the imaginary and on the real part of the Nyquist plot. Indeed, the solicitation here is the frequency and permits to obtain the impedance expressed in a form of a complex number. These results can be seen in the figure 9, as one can see, the two parts present a complementary aspect on some parameter's influence. So the sum of the two influences have been realized, and is counted as a proportion face to two hundred.

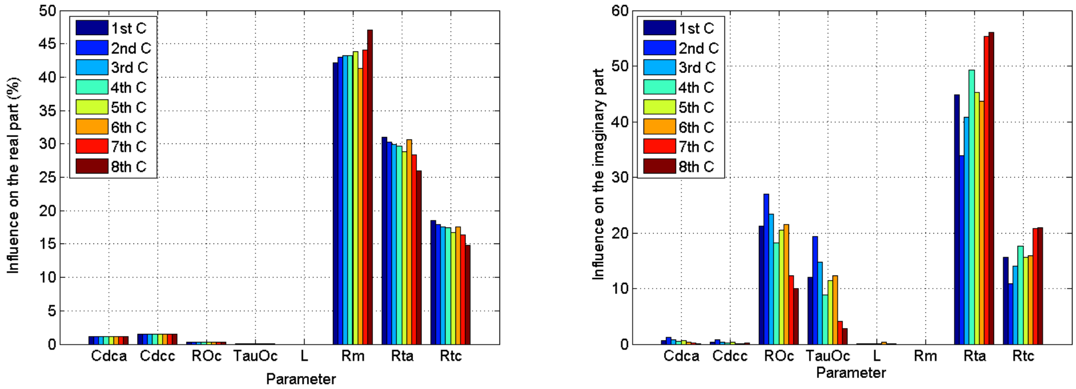

Figure 9: ANOVA's result for the dynamic real and imaginary part

The parameters with the biggest influence can be seen on figure 10. The sum here of all the influences and inter parametric influences is close to 100% for the two part of the impedance (Table 3.2.2 and 3.2.2).

Inf. (%)	C_{dca}	C_{dcc}	R_{Oc}	Tau_{Oc}	L	R_m	R_{ta}	R_{tc}
C_{dca}	1.10	1.76 E^{-5}	4.40 E^{-7}	1.83 E^{-7}	5.67 E^{-29}	9.04 E^{-4}	0.0061	8.20 E^{-5}
C_{dcc}		1.45	3.22 E^{-5}	1.50 E^{-5}	3.81 E^{-29}	0.0038	7.32 E^{-5}	0.075
R_{Oc}			0.35	3.16 E^{-4}	4.66 E^{-29}	4.42 E^{-5}	5.67 E^{-4}	9 E^{-5}
Tau_{Oc}				0.1189	1.85 E^{-27}	2.26 E^{-5}	1.82 E^{-4}	1.81 E^{-5}
L					3.27 E^{-27}	5.20 E^{-29}	5.45 E^{-29}	2.56 E^{-29}
R_m						42.1	0.0028	0.0064
R_{ta}							31.0	0.014
R_{tc}								18.5

Table 5: Influences of parameters on the real part of the dynamic model on the first characterization

Inf. (%)	C_{dca}	C_{dcc}	R_{Oc}	Tau_{Oc}	L	R_m	R_{ta}	R_{tc}
C_{dca}	0.71	5.49 E^{-5}	5.30 E^{-6}	2.82 E^{-6}	4.75 E^{-5}	4.40 E^{-28}	0.0075	2.35 E^{-4}
C_{dcc}		0.42	5.60 E^{-4}	1.46 E^{-5}	1.35 E^{-4}	5.69 E^{-28}	2.7 E^{-4}	0.0025
R_{Oc}			21.2	0.028	2.67 E^{-7}	5.20 E^{-28}	2.99 E^{-4}	0.0023
Tau_{Oc}				12.0	1.37 E^{-7}	6.34 E^{-28}	6.54 E^{-5}	1.62 E^{-4}
L					0.0017	5.50 E^{-28}	2.11 E^{-5}	5.07 E^{-5}
R_m						3.97 E^{-26}	5.26 E^{-28}	4.74 E^{-28}
R_{ta}							44.7	0.0090
R_{tc}								15.60

Table 6: Influences of parameters on the imaginary part of the dynamic model on the first characterization

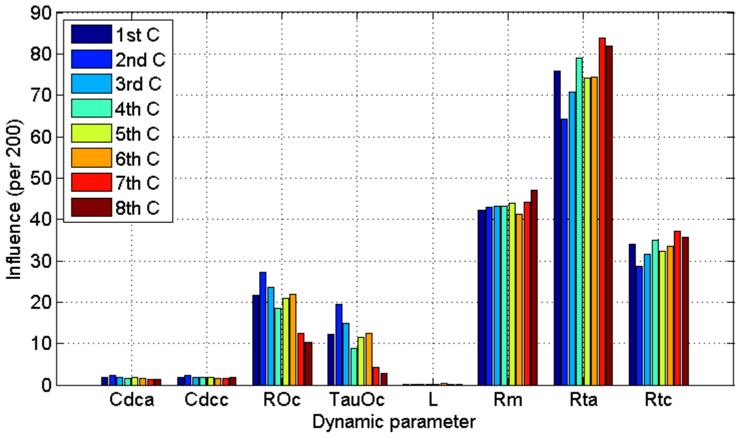

Figure 10: ANOVA's result for the static model

3.2.3 Global model

The global model present links between some dynamic and static parameters as exposed in 2.1. The parameters on the global model are:

- R_m the resistance;
- E_n the Nernst potential;
- b_a, b_c the Tafel parameters;
- j_{0a}, j_{0c} the exchange current density;
- j_{Lc} the limit current density at the cathode only;
- The double layer capacities C_{dca} and C_{dcc};

- The inductive behavior due to the connectors L;
- j_{0Oc} and b_{Oc} that are sub-parameters of R_{Oc};
- k_{Oc}, sub-parameter of τ_{Oc}.

There are here some dynamic parameters that are not present. As explained earlier, this can be explained by their decomposition in under parameters.

The experimental plan realized is supposed to be read like the two previous.

Parameter	Minimum Value	Maximum Value	Unit
E_n	0.9	1	V
b_a	20	100	V^{-1}
b_c	20	100	V^{-1}
j_{0a}	0.001	1	A/cm^2
j_{0c}	0.001	1	A/cm^2
j_{Lc}	1.001	1.5	A/cm^2
R_m	0.08	0.2	$\Omega.cm^2$
C_{cdca}	0.03	0.06	F/cm^2
C_{dcc}	0.02	0.05	F/cm^2
L	0.8E-06	2E-06	H
j_{0Oc}	0.01	0.5	A/cm^2
b_{Oc}	10	30	V^{-1}
k_{Oc}	0.01	0.5	$A.s/cm^2$

Table 7: Global model parameters extreme values for the experimental plan

The value taken for the ANOVA study is the mean of the difference taken between the experimental and simulation evolution during around $100s$. These $100s$ are chosen in the experiment as they present a solicitation evolving. There was 6 part of the experiment that met the previous requirement (i.e. around $100s$ and evolving solicitation), all around a characterization. The sensitivity analysis was then realized on those 6 parts.

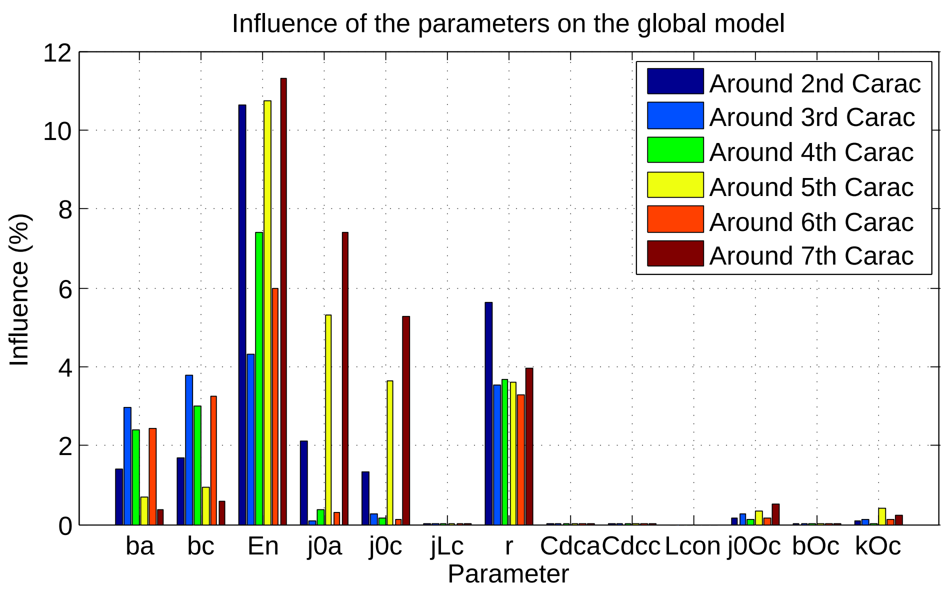

Figure 11: ANOVA’s result for the global model

Inf (%)	b_a	b_c	E_n	j_{0a}	j_{0c}	j_{Lc}	R_m	C_{dca}	C_{dcc}	L	j_{0Oc}	b_{Oc}	k_{Oc}
b_a	1.38	$7.3E^{-3}$	$1.6E^{-2}$	$7.7E^{-2}$	$2.9E^{-2}$	$8.1E^{-5}$	$9.8E^{-3}$	$3.31E^{-6}$	$4.6E^{-6}$	$1.8E^{-26}$	$7.6E^{-5}$	$2.7E^{-5}$	$4.2E^{-5}$
b_c		1.67	$1.7E^{-2}$	$3.6E^{-2}$	0.14	$6E^{-5}$	$1E^{-2}$	$1.8E^{-6}$	$4.2E^{-6}$	$2E^{-26}$	$6.8E^{-5}$	$2.5E^{-5}$	$4.5E^{-5}$
E_n			10.6	$3.1E^{-2}$	$3.2E^{-2}$	$5.3E^{-6}$	$4.9E^{-4}$	$7.9E^{-7}$	$5.3E^{-6}$	$1.9E^{-26}$	$8.5E^{-6}$	$7.2E^{-6}$	$2.2E^{-5}$
j_{0a}				2.12	0.11	$1.6E^{-4}$	$1.8E^{-2}$	$3.9E^{-5}$	$6.9E^{-5}$	$2.3E^{-26}$	$4.5E^{-4}$	$9.8E^{-5}$	$3.2E^{-4}$
j_{0c}					1.32	$6.8E^{-4}$	$1.9E^{-2}$	$2.5E^{-5}$	$1.8E^{-5}$	$2.2E^{-26}$	$3.2E^{-4}$	$6.9E^{-5}$	$2.1E^{-4}$
j_{Lc}						$1.1E^{-2}$	$5E^{-6}$	$1.7E^{-8}$	$4.2E^{-9}$	$2E^{-26}$	$7.5E^{-7}$	$4.5E^{-8}$	$1.5E^{-7}$
R_m							5.62	$9.2E^{-8}$	$1.4E^{-6}$	$2E^{-26}$	$1.6E^{-4}$	$1.5E^{-5}$	$8.4E^{-5}$
C_{dca}								$4.84E^{-5}$	$1.6E^{-7}$	$2.1E^{-26}$	$8.3E^{-8}$	$2.6E^{-8}$	$2.4E^{-7}$
C_{dcc}									$5.49E^{-4}$	$2.21E^{-26}$	$1.7E^{-7}$	$8.9E^{-7}$	$2.18E^{-6}$
L										$1.55E^{-24}$	$2.2E^{-26}$	$2.07E^{-26}$	$2.14E^{-26}$
j_{0Oc}											0.16	$1.3E^{-5}$	$1.06E^{-4}$
b_{Oc}												$5.3E^{-3}$	$1.58E^{-5}$
k_{Oc}													$7.6E^{-2}$

Table 8: Sensitivity analysis results in percentage for the global model around the second characterization

The figure 11 present the results on these 6 portions. The parameter with the biggest influence is E_n, a coherent point with the previous simulations of the model. Indeed, a wrong setup for the value of E_n directly implies an important error on the voltage at the open circuit voltage.

The static parameters are the ones having the most of influence. This may be explained by the data available. Indeed, the analysis was realized on the error between the experiment and the simulation. It is possible for the dynamic model to does not have a great influence because of the sampling that can be with a too low frequency.

However, the low influence of C_{cdca}, C_{dcc} can only be because they do not impact much the global model. Indeed, b_a, b_c, j_{0a} and j_{0c} are also present in the development of the dynamic model, so their great influence is coherent with the model developed.

3.3 Second version of the parameters' sensitivity analysis

A second sensitivity analysis was realized; only on the static and dynamic part of the model this time, but following the same process (i.e. experimental plan and influence calculation). The difference here, is that no data are taken into account. The idea is only to evaluate the influence of each parameter on the output of each part of the model.

3.3.1 Static

A second sensitivity analysis on the parameter was realized for the static part of the model. The Y taken here is the voltage obtained under a certain solicitation. This analysis was realized under three different solicitations: $0A/cm^2$, $0.5A/cm^2$ and $0.98A/cm^2$. The results are on figure 12. On the first point, the Nernst potential E_n is the only parameter influencing the output, indeed, if J_{DC} is null on the equation (3), the output take the value of E_n. The results for the second and third points are the same. Indeed, under these solicitations, this part models the same kind of behavior. This is also why the limit current density j_{Lc} has not an important influence. The range of solicitation tested does not go where this parameter allow to model another kind of behavior. However, based on the data used, it is not necessary to go over the solicitations proposed, indeed, on the data the current stays on the range proposed.

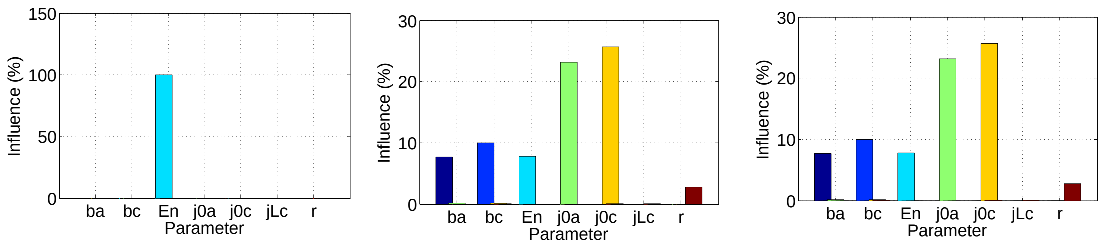

Figure 12: Influence of the static parameters on the output of the static part of the model under different solicitations(from left to right: $0A/cm^2$, $0.98A/cm^2$ and $0.5A/cm^2$)

3.3.2 Dynamic

On the dynamic part of the model, the second analysis lay on the output. The same experimental plan was followed, but the analysis is based on the impedance the model provide under specific solicitations. The points taken are spread on a Nyquist plot: $1.27E^3 rad.s^-1$; $280 rad.s^-1$;$39E^3 rad.s^-1$;$1.39 rad.s^-1$.

The points chosen are related to the data used. Indeed, it is unnecessary to exceed these values as they are not inputs of the stack during experiments. Almost every dynamic parameter has an influence on the output under defined solicitation, except the double layers capacities that has always the lowest influence (Figure 13).

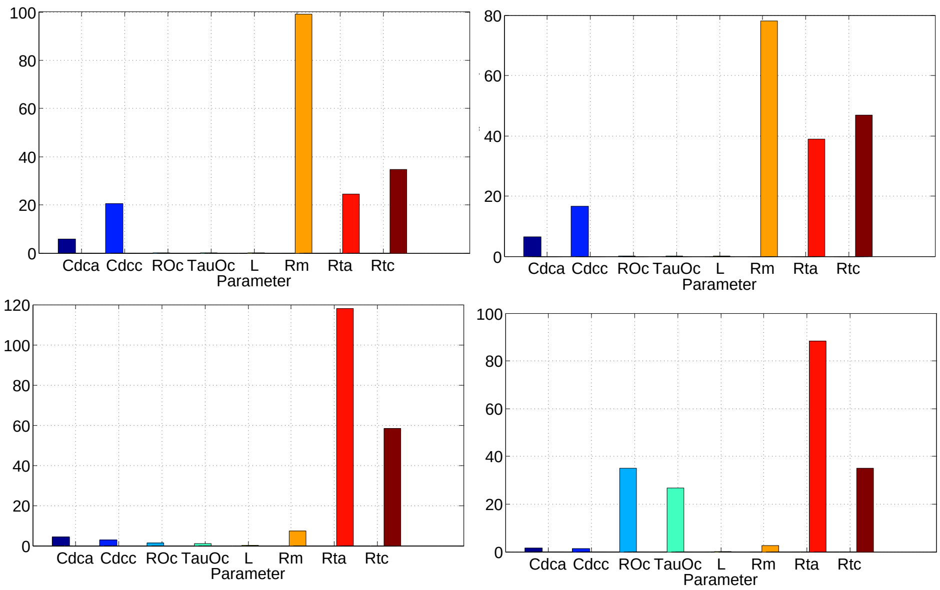

Figure 13: Sensitivity analysis on the output of the dynamic part of the model (from top left to bottom right: $1.27E^3 rad.s^-1$; $280 rad.s^-1$;$39E^3 rad.s^-1$;$1.39 rad.s^-1$)

3.4 Discussion

The two sensitivity analyses are not systematically giving the same results, but with their complementarity, they will allow to obtain a complete analyze. The objective was here to face a first issue, the excessive number of parameters. Indeed, the definition of the parameters' value thanks to data would be more like a numerical solution than one with physical meaning. The idea is then to detect which parameters have enough influence to model ageing, and represent a real ageing phenomena.

On the static part of the model, the great divergence is on the exchange current densities, indeed, these parameters have a great influence on the output, but they does not influence much the error between the model and the experiments. It means that these parameters are important for the instantaneous behavior as they are well influencing the output. But, their variations have no such influence on the error. This is why, they could be fixed, but based on the general knowledge of the fuel cell, only the anode current density, j_{0a} will be fixed.

The Tafel parameters have a great influence on the error but also a non-negligible influence on the output. They are thus important parameters.

The limit current density at the cathode j_{Lc} has no influence. This match the first assessment: the operating conditions does not allow the model to be on the behavioral state in which this parameter is expressed. As this parameter doesn't present much influence on either of the analysis, it is a parameter with a very low importance. This kind of parameters are necessary for the model, but seen their capability to influence the output or the error, it is not interesting to model their ageing. Indeed, their evolution would not bring a real difference in the output.

The Nernst potential E_n is shown to have a great influence on the first and second sensitivity analysis, on the static part of the model and on the global one. But this parameter has a true and drastic does not evolve much with the time but also because the model is too sensitive to it.

The internal resistance has some influence in a moderate way in all the analyses presented. But by the general knowledge of the fuel cell, it is known that the internal resistance R_m evolves with the ageing of the stack.

The double layer capacitances are parameters with a low influence. They are also known to evolve not much with the ageing. They are therefore also fixed.

The inductance of the connectors has no influence on any of our analyses. Following the same thought, it is a parameter to fix.

The diffusion convection impedance is expressed thanks to sub parameters. These parameters, which are directly defined in the global model are j_{0Oc}, b_{Oc} and k_{Oc}. The only parameter here that does not deserve a particular attention is b_{Oc} as it has a lower influence, this last parameter is also fixed for the same reason. A parameter with a low influence will not bring a drastic difference in the output of the model global.

4 Time ageing inclusion

The sensitivity analysis points out some parameters with low influence on the model. The idea is here to fix the values of some parameters with the time. It would allow to have less chances to find a local minimum during the numerous regressions in the updating procedure. Based on the previous conclusion, the following decisions are taken in regard to the ageing.

- Firstly, the double layer capacities C_{dca} and C_{dcc} will only be regressed with the first characterization's data and then fixed for the following and the ageing.
- Next, the connectors' inductance written L will not evolve as it is not exactly linked to the stack ageing itself and does not show a big evolution with the time.
- The limit current density at the cathode j_{Lc} is regressed on the first characterization and then fixed.
- The Nernst potential E_n and the exchange current density at the anode j_{0a} has their values set.
- The under parameter b_{Oc} of the resistance R_{Oc} in the diffusion convection impedance is also regressed with the first data and then fixed

The other parameters will evolve with time in the following.

4.1 Parameters functions

In a first step an exponential function is proposed for all the parameters evolving in the ageing model. This hypothesis will have to be improved with a closer analysis of stack ageing.

The idea is to have in the final model time-dependent exponential functions for the parameters. For that, it is necessary to have a sufficient number of characterizations in order to have enough values of each parameters. With these values and a regression function the variables of the exponential functions can be defined.

Let us take the example of the resistance R_m for the development of the process:

1. The complete updating process that allows defining its values is realized for the characterizations already obtained.

2. These values are memorized, as well as the time at which the characterizations are realized.

3. A regression is done in order to obtain the variables of the exponential function depending on time

4. This function is used for giving the value of R_m at the time considered in the model

The number of characterizations considered as already obtained is, here, 3, indeed, taking less than 3 points for an exponential regression is not a coherent approach as there would not be enough data. On the data available there are 8 characterizations and taking the first three (around time 0, $35h$ and $182h$) for the learning phase is acceptable, especially when compared with the number of hours needed for a standard data-based prognostics learning.

However, here, it can be noticed that 3 characterizations does not allow the fitted exponential function to follow the real trend of the parameters' value. Indeed, when the values obtained for all the characterizations are compared with the values taken with the exponential function, a difference of tendency is eventually obvious for some parameters. This would mean that the prediction of the parameters, does not have physical meaning.

Our model-based approach can now finally be considered as a hybrid-based approach. Indeed, when the parameter is replaced by the exponential function, at this stage, it cannot be assured that the value taken is really representative of the reality for the stack. This means that for example the prediction of R_m at the 6^{th} characterization is not the same than the value obtained with the data, so the physical meaning of this parameter can be lost (figure 14).

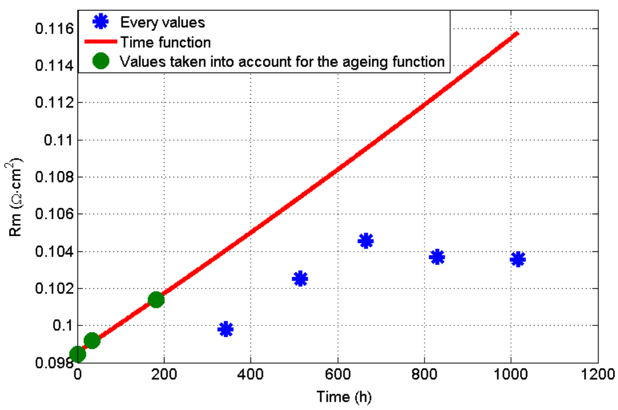

Figure 14: Exponential fitting of R_m

4.2 Validation

4.2.1 State of Health estimation

For validating the approach, the three first characterizations are used for the learning phase for the parameters. This means that on figure 15, the learning phase includes the second "peak" which is around after 182 hours, and the prediction phase start after. The exponential functions are then injected directly into the global model. It is finally simulated during the complete duration of the experiment. The solicitation used is the same as the one as in the experiment. That way, the simulation and the experiment can be compared (figure 15). The results are very satisfying with an answer very close to the real behavior of the stack. The mean error is under $0.2V$, corresponding to an error of around 5%. It is representative of the efficiency of the behavior prediction.

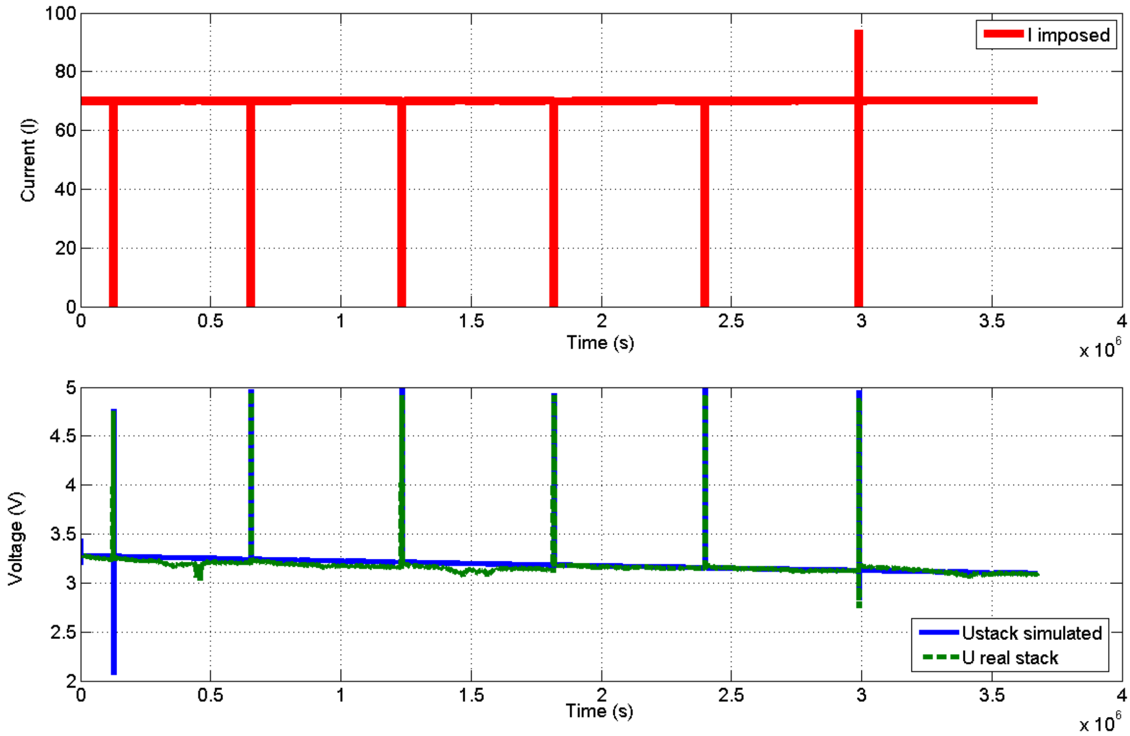

Figure 15: Simulation and experiment under the same solicitation during 1000 hours

More instantaneously, figure 16 represent the comparison during around $200s$ after 500 hours. The model reproduction of the behavior is really efficient. However, there is a small imperfection: the simulated voltage goes over the real data for a short amount of time. This is due to the decomposition block which is a simple low pass filter in the global model (figure 6).

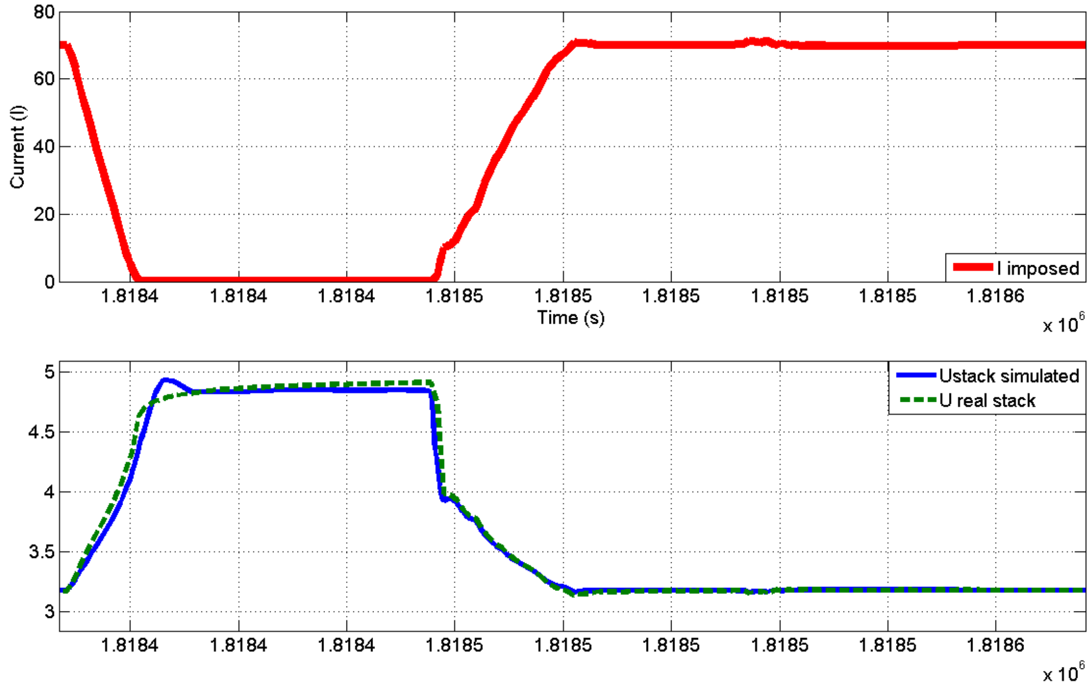

Figure 16: Simulation and experiment under the same solicitation during 1000 hours

Then, it is interesting to study the prediction of a polarization curve face to the experimental one. On figure 17, can be seen the comparison for the fifth characterization and the last one, the eighth.

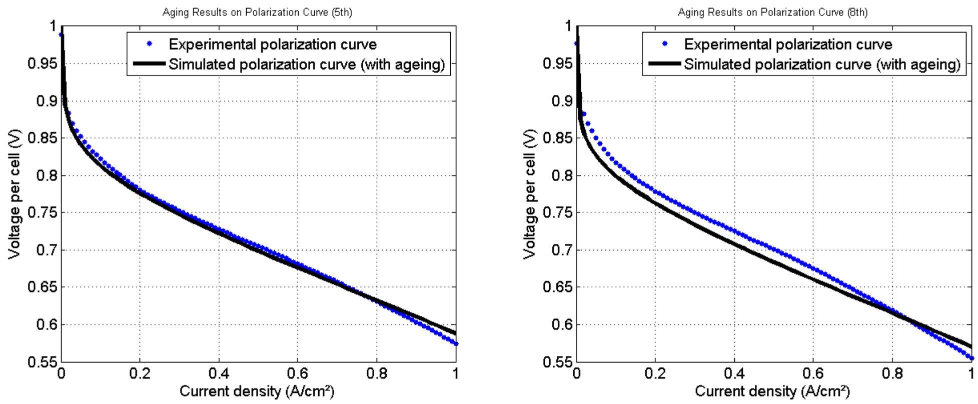

Figure 17: Comparison of the polarization curve predicted and the experimental one

A clear tendency can be observed, there is an aggravation of the difference between the simulation and the experimental data with the time. However, this is not extremely bad, indeed, the worst MAPE, on the eighth polarization curve is $1,9$ with an R^2 of $0,98$.

Finally, even though the model can now be considered as hybrid, its global performance is satisfying as the reproduction of the behavior of the real fuel cell is efficient.

4.2.2 Remaining Useful Life

Definition of the threshold: The definition of the end of life (EoL) for Dantherm is when the voltage reach $26.8V$ under a solicitation of $37A$. The stack concerned by this definition is a 46 cell stack, the voltage per cell is then $0.5826V$. It is then possible to adapt this threshold to the experimented 5 cell stack. At $37A$, when the stack's voltage is under $2.913V$, the system is considered at its EoL.

Remaining Useful Life prediction: With the resolution used for the simulation, the EoL of the stack tested is supposed to be between $5458h$ and $5597h$ (Figure 18). This prediction has no clear sense. Indeed, the system on the experiment on which the EoL is predicted is not running under $37A$ neither on the learning nor on the future.

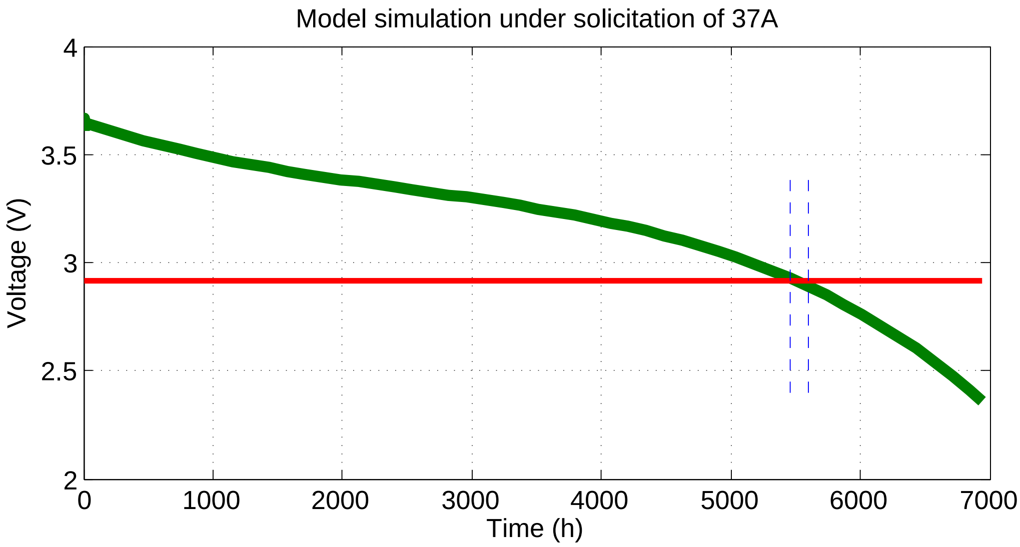

Figure 18: RUL

5 Conclusion

Finally the model presented is an efficient prognostic approach for the set of data used even with the evolution of the predicted parameters not linked with the evolution of the physic phenomenon they are supposed to represent.

The approach proposed is efficient as it can predict the behavior of the fuel cell, i.e. the voltage with the time. The prediction of the values of the parameters is however not satisfactory. This is certainly due to the first characterization which gives to some of them calendar variations with a wrong tendency. A few reasons can be considered, firstly, the parameters updating procedure on the first characterization may hit a local minimum. Secondly, the first characterization was maybe realized before the few hours of experiment necessary before the establishment of the regular experiment. For this issue, the same simulations presented here but with the exclusion of the first characterization will have to be realized.

This approach efficient with a constant load and has to be also experimented under a variable current. For that, the same simulations will be realized with the data gathered within the project.

A following part of the work, will consist in developing more accurate time functions for the parameters. The form developed should be more in agreement with the physics.

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