Towards an ageing model of a PEMFC for prognostics purpose

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ABSTRACT:

One of the main constraints of Proton Exchange Membrane Fuel Cell (PEMFC) in its breakthrough in the industrial world is its life duration [1], which is too short and not enough managed. From this point of view, the development of Prognostics and Health Management (PHM) technology [2] appears to be a relevant discipline; the estimation of the Remaining Useful Life (RUL) of a fuel cell system enables deciding for actions in order to try to mitigate the degradation and ensure longer life duration and availability.

This paper addresses this topic and aims at proposing a basic FC ageing model [3][4] that will serve for prognostics issues. Here, the proposed ageing model is based on the combination of a static model with a dynamical one. A physical based model is considered built on a Butler-Volmer law where the voltage is function of the current density and of fuel cell's physical parameters. This analytical static model allows the separation of cathode and anode contribution. The dynamical model is based on an electrical equivalence; on which different internal components can be distinguished. This model is expressed in a state-space representation and defines the voltage depending on the current. Moreover, the model also provides the possibility of modelling the ageing of the Polymer Exchange Membrane Fuel Cell. Indeed, different internal parameters can be represented using time-dependent functions. The limits of this model and its suitability for prognostics are discussed. The model validation is based on actual long-duration experimental tests.

KEYWORDS: Proton Exchange Membrane Fuel Cell; Prognostic and Health Management; Model; Ageing

1. Introduction

With the actual preoccupation about the global warming, the development of the fuel cell and more precisely the Proton Exchange Membrane Fuel Cell (PEMFC) seems to be a promising alternative. However, the PEMFC is limited by the production and the storage of dihydrogen, and also by its short life duration. The second point is addressed in this study.
The aim here is the improvement of the life duration of PEMFC. For this goal, the development of Prognostics and Health Management (PHM) seems to be a relevant solution. Indeed, this technology permits to detect, diagnostic and prognostic a failure then it enables to take the right decision at the good moment in order to avoid failure and optimize the use. The development of PHM for PEMFC is a new development in the scientific community of research.
The SAPPHIRE research project is financed by the European Commission and is the acronym for "System Automation of PEMFCs with Prognostics and Health management for Improved Reliability and Economy". This project has the goal of developing an advanced control system for PEMFC in order to improve the life duration based on the current technologies. Six partners from five different European countries are involved, research institutes (SINTEF, Norway and EIFER, Germany), academia (FCLAB, France and FESB, Croatia), a fuel-cell stack provider (ZSW, Germany).

2. Background and problematic

2.1. Prognostics and Health Management (PHM)

Every machine or system is getting deteriorate with the time until reaching the failure. It can happen at an inconvenient time and trigger negative consequences. PHM appears to be a solution to this kind of problem. Indeed among the aims of PHM, the principals are:

- Improve the availability and reduce the operational cost in order to optimize the maintenance,
- Improve the security of the system,
- Improve the decision making process in order to increase the life duration of the system.

The PHM is described as composed of seven layers that allow defining the different steps followed in the process.

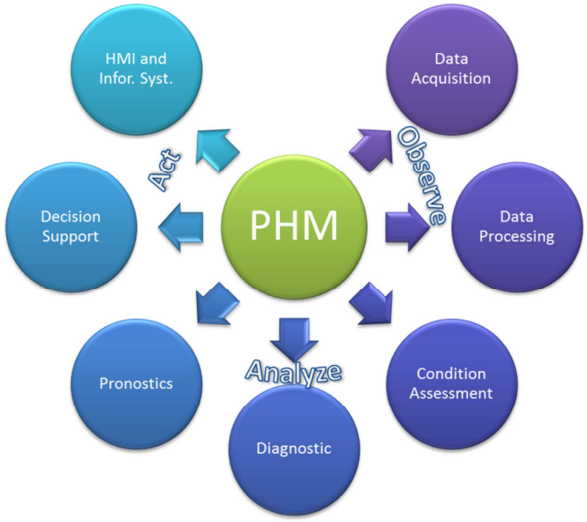

Figure 1 : PHM layers.

The study, here is focused on the prognostic part of PHM. The ISO definition of prognostic is: “estimation of the operating time before failure and the risk of existence or later appearance of one or more failure modes”. It allows defining the Remaining Useful Life (RUL) that is according to the ISO standard: “estimation of the time past between the current moment and the moment when the monitored machine is considered as failed”.

So, the prognostic aims to predict the time left for the system to be functional.

In this objective, the approaches can be distinguished as follow:

- The data-driven [7] approaches that are based only on the experience and so only on the data obtained. It is by learning (as neural network) that the state of health of the system can be predicted. This kind of approaches is generally simpler to implement but has no link with the internal phenomenon. It is then not possible to link the state of health observed or predicted with the real physic happening. For this kind of approach a large amount of data is needed.
- The physics-based approaches that describe the physics phenomenon happening. Indeed, the failure criterions developed in this approach are based on the description of the failure mechanisms. This approaches are reliable but require a precise knowledge of the physics phenomenon happening.
- The hybrid approaches are based on the two last kinds. The idea is, here, to try to combine the first two methods is order to associate their strength, and however, it also associates their weakness.

In a first work, we choose to develop a physic-based approach applied on a PEMFC stack.

3. Toward an analytical behavior model

The long term goal is to prognostic the RUL of the stack. For that purpose, we need to predict the RUL based on different data measured on the stack thanks to a stack model. This model will have to model dynamic phenomena at a macro scale in order to be more coherent with our final goal.

Numerous models of PEMFC already exist, but with different aims, like diagnostic [8], comprehension [9] or even control… This information is particularly difficult to decode inside the publications. It is however important because a model used for conception (for example [11]) would not be easily usable for another application.

Among these models, some concern the whole system. These models haven't been studied because the study is limited to the stack. Other concern a single cell [9,10,12,13,14,15]. Fouquet et al. introduce a cell model, but that seems easily applicable to a stack thanks to a repetition of the cell model. Shan et al. models' [16] is for a single cell and is finally extended to the stack. The criterion expressed regarding the object modeled can be softened, a single cell model easily extended to the stack can be considered. Another part of the literature presents models for the stack [3,17,18,19]. Asl et al. [20] introduce directly on the paper two models, one on a single cell and the other for the stack based on the first.
The definition of a dynamic or static model is not uniform inside the literature. Indeed, a model with a time dependency can be considered as a dynamic model with no regard to the value of the time constant. Even though that for some scientist a very small time constant would imply that the model is static. Some models are then told by the authors, as dynamic [15, 16, 19, 21] or static [8] but a lot do not define the kind of model that could appears to be static [9, 13] or dynamic [17].
We can also distinguished the models by the scale of the described phenomenon, that can be nano describing molecular phenomenon, micro with the description of phenomenon happening at the membrane. From this time scale follows the time characteristic carried by the model. The models with a description of too precise phenomenon were not studied. Indeed, we can't expect to project our model into a time scale of hundreds of hours if the time constant is too small. However, some analytical models describing physical and chemical phenomena can present a micro [9, 12, 14] or macro [8, 13, 17] scale.
In some papers, the degradations have been included. Fouquet et al. [8] characterize the drying and flooding of the membrane. He is trying to define the deteriorated states of the fuel cell; Robin et al. [18] model some degradations. The models are not built the same way; some can be characterized as data-driven with a learning phase [7]. These kinds of models were not studied regarding our wish of a physical-based model. Thus, some are formalized thanks to an electrical equivalency [3, 8, 13, 19, 22], other thanks to the equations expressing the physical and chemical phenomenon happening [9, 12, 14, 15, 22].
The different authors validate their model thanks to experimental data [17, 11], thanks to other papers [20], or even thanks to comparison with the results of resolved equations [10]. Lee et al. [13] don't really validate the model, it is only the parameter evaluation that is validated as only the comparison between the real curve and the curve obtained by the simulation is shown. Hou et al. [17] validate the evaluation of the parameters thanks to experiments and then validate it on another experiment done on another stack. Chevalier et al. [14] validates the model thanks to a comparison with data extracted on other papers.
However, generally, the inputs and outputs of the model are, respectively the current (or current density) and the voltage.
The model fitting the most our needs is the one of E. Laffly et al. [3]. Indeed, this model is the one presenting the most of common point with our criteria.

This model is a combination of a static and a dynamic model. First the current is normalized in the current density which is decomposed on its static and dynamic part. Then the model expresses the cell voltage responses to the DC and AC current densities that are recomposed in the cell voltage to be de normalized in the stack voltage.

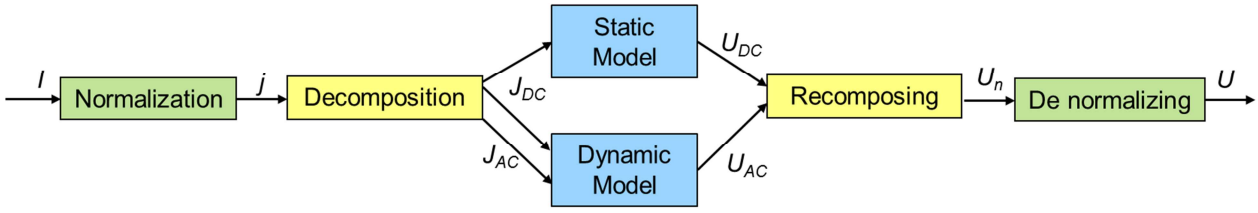

Figure 2 : Ellie Laffly's model

In this paper, the static and dynamic models are validated.

4. Static model

The static model is based on the Butler-Volmer law. It gives us a variation law that takes into account the activation phenomenon at the anode and at the cathode by the two voltage drops η_a et η_c.

$$U_{DC} = E_0 - r.J_{DC} - \eta_a - \eta_c \qquad (1)$$

With *r* the internal resistance of the fuel cell, J_{DC} the static current density and E_0 the open-circuit voltage of the stack normalized per cell.
If the system is supposed to be symmetrical, the voltages drops are expressed thanks to the following laws:

$$\eta_a = \frac{1}{b_a}.asinh\left(\frac{J_{DC}}{2.j_{0a}}\right) \qquad (2)$$

$$\eta_c = \frac{1}{b_c}.asinh\left(\frac{J_{DC}}{2.j_{0c}}\right) \qquad (3)$$

With:
– b_a, b_c the Tafel parameters at the anode and cathode.
– j_{0a}, j_{0c} the exchange current densities at the anode and cathode.

In this case, the phenomenon of limit current due to species diffusion is not taken into account by the authors. This is solved by integrating a limit current at the anode and at the cathode in the variation law of the voltage drops (equation (4) and (5)).

$$\eta_a = \frac{1}{b_a}.asinh\left(\frac{J_{DC}}{2.j_{0a}.\left(1-\frac{J_{DC}}{j_{La}}\right)}\right) \qquad (4)$$

$$\eta_c = \frac{1}{b_c}.asinh\left(\frac{J_{DC}}{2.j_{0c}.\left(1-\frac{J_{DC}}{j_{Lc}}\right)}\right) \qquad (5)$$

With j_{La} the limit current density at the anode and j_{Lc} the limit current density at the cathode.
Actually, the authors are only taking into account the diffusion at the cathode. Indeed, during the measurements, the diffusion on the air side was detected as more important than on the dihydrogen side [3]. It is the equations (2) and (5) that are considered for the voltage drops η_a et η_c in the voltage variation law of the stack (equation (6)).

$$U_{DC} = E_0 - r.J_{DC} - \frac{1}{b_a}.asinh\left(\frac{J_{DC}}{2.j_{0a}}\right) - \eta_c \frac{1}{b_c}.asinh\left(\frac{J_{DC}}{2.j_{0c}.\left(1-\frac{J_{DC}}{j_{Lc}}\right)}\right) \qquad (6)$$

The static model has only one input: the current density, and one output: the voltage per cell. However, the parameters on the equation (6) need to be initialized.

5. Dynamic model

Here, the aim is to link the voltage variation to the current variation, with the hypothesis is that the variations are around a static operating point. We consider that the current density is well separated in its static and dynamic part.
The dynamic model has got two inputs, the dynamic and the static current density, the last one permit to define the operating point.
The model is an electrical impedance that can be expressed in the Laplace space:

$$\frac{U_{AC}(p)}{J_{AC}(p)} = Z_{pem}(p) \qquad (7)$$

The authors have tried to model the phenomenon that can be observed by the electrochemical impedance spectroscopy. The phenomena are multi-physical; they proposed to model them by electrical impedances with the same behavior. The diffusion convection of the different gases at the cathode and anode are modeled by diffusion-convection impedances. The double layer capacities at the interface electrode-electrolyte on the anode and cathode are simulated by capacitor C_{dca} and C_{dcc}. Two transfer resistances R_{ta} and R_{tc} demonstrate the electrons transfer at the electrodes. The ionic conductance of the membrane is modeled by an equivalent resistance R_m. And finally, the inductive behavior due to the connectors is taken into account by an inductance L_{con}.
However, during the measurements the authors have noticed that the influences of the diffusion-convection impedance at the anode fades faced to the one of the dioxygen at the cathode. The diagram is then the one on figure 4.

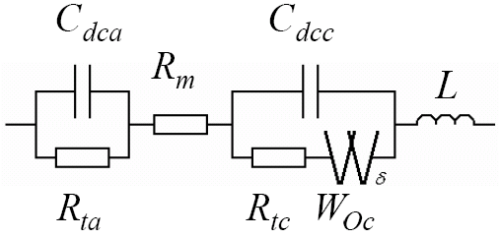

Figure 3 : Dynamic model [3]

The electrical diagram of each electrode is then modeled thanks to a state space representation, that won't be developed here, with *U(p)* representing the current density and *Y(p)* the voltage.
The dynamic model is composed by an equivalent electrical diagram expressed thanks to a state space representation. This electrical diagram gives the value of the dynamical part of the voltage U_{AC} depending of the dynamic part of the current J_{AC}. The parameters of this electrical diagram are dependent of the operating point defined by the static part of the current density J_{DC}. The model obtained is described on the figure 6.

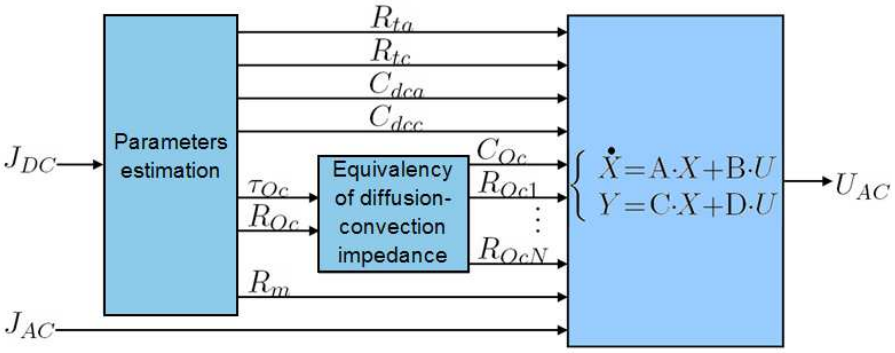

Figure 4 : State space representation of the model [3]

6. Validation

6.1. Experimental setup

The model was validated thanks to two long-term tests carried out. The experimentations were realized on two different stack of similar kind (PEMFC composed of 5 cells with an active surface of 100cm²).
A first stack (named FC1) was operated in stationary regime, with a constant load expressed by a current of 70A, at roughly nominal operating conditions during 1000 hours.
A second stack (named FC2) was operated under dynamic current testing conditions, i.e. with high-frequency current ripples. The current is 70A with a ripple part of more or less 10%. The operating conditions are set constant. The test lasted 1000 hours.
For both tests, characterizations were carried out once per week (around every 160 hours) according to an identical protocol: polarization curve test (i.e. measuring the static I/V curve of the fuel cell stack), global historic curves (i.e. evaluating the evolution over time of voltage levels), and Electrochemical Impedance Spectroscopy (EIS) measurement (i.e. measuring the "Nyquist" plot of the fuel cell stack over a frequency range from 50 mHz to 10 kHz).

6.2. Validation process

The aim here is to validate the fitting of this model with the experimental data. For that purpose, at each characterization, an evolution of the equation (6) parameters is done following the process on figure 4.

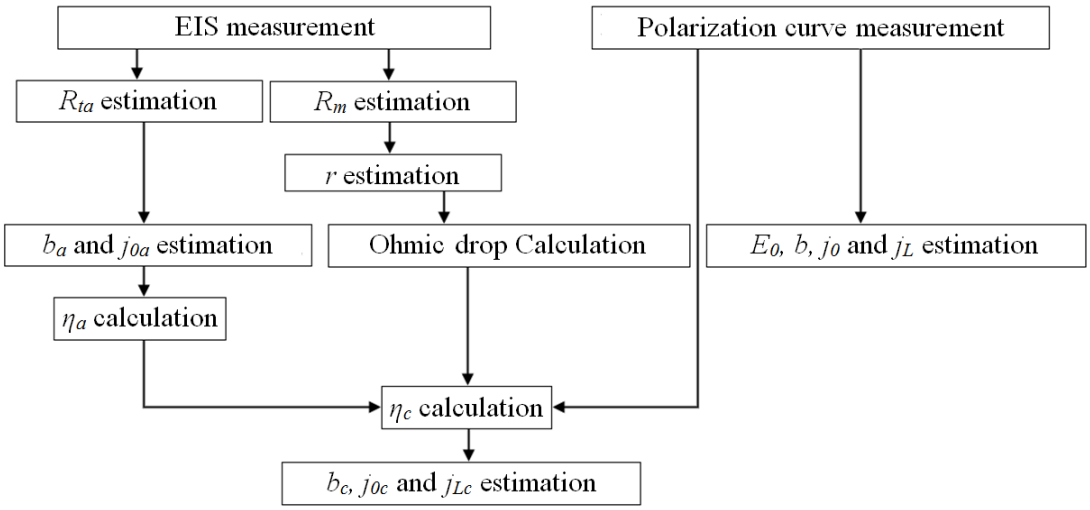

Figure 5 : Static parameters initialization process

R_{ta} is the transfer resistance at the anode expressed as a function of j_{0a} et b_a.
j_0 is the exchange current density for the cell that is evaluated in a first step without separating the anode and cathode.
R_m is the membrane resistance.
At each characterization, three Nyquist plots are obtained at three different current densities, and a polarization curve is also obtained. From these data, and thanks to nonlinear regression on each curve, the different values of the parameters can be deduced.
Some parameters are estimated thanks to only one curve. Others, like the membrane resistance are estimated with the three EIS of the characterization, but also with all the EIS realized before the considered characterization.
The dynamic parameters are initialized following the same type of reasoning, but it is too complex to be described here.
Following these estimations, the values of the parameters are injected in the model, and the ability of the model to adjust with the experimental data is evaluated.

6.3. Results

6.3.1. Polarization curve

In a first step, the match between the experimental polarization curve and the simulated one is evaluated. The fitting appears to be successful.

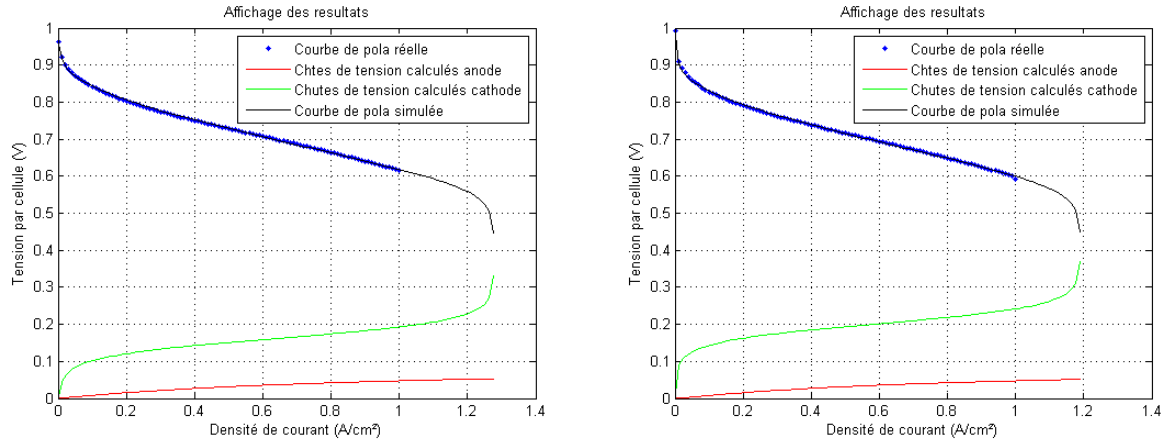

Figure 6 : Example of a fitting of the polarization curve at t=0 FC1 and FC2

The errors MAPE (Mean Absolute percent error) and RMSE (Root Mean Square Error) have been calculated in order to study if the model is still adapted when the stack ages (figure 6). We can see a small evolution with the time; it would mean that the model is less adapted to an old stack.

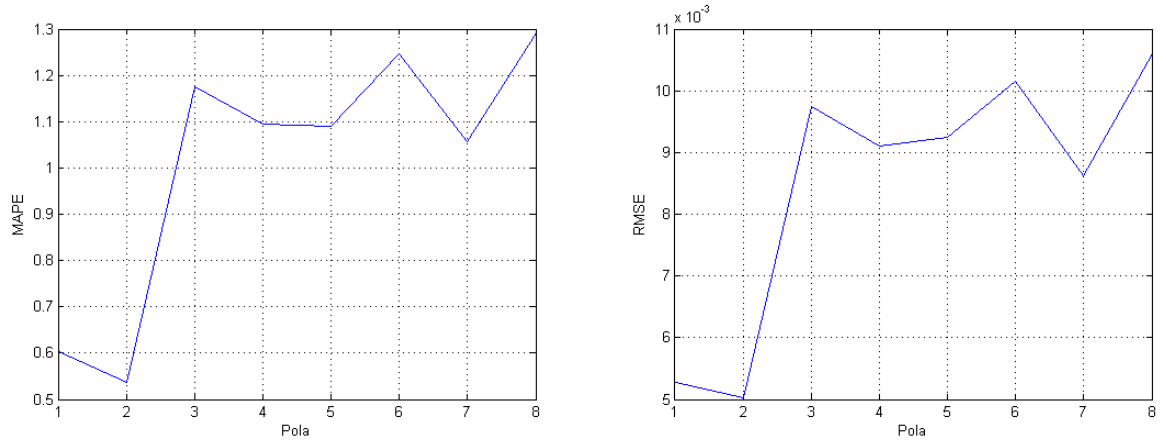

Figure 7 : MAPE and RMSE evolution of the fitting of the polarization curve for the FC2

The mean results are gathered in the table 1. The errors are low and confirm the accuracy of our model.
The fitting of our model to the experimental data stay accurate on the 1000 hours of the two tests and on each polarization curve of each test.

Table 1. Mean errors of the simulations

	Stationary current	Ripple current
Mean MAPE (%)	1,07	1,01
Mean RMSE	9,62 e-03	8,47 e-03

6.3.2. Nyquist plot

The accuracy of the model with the dynamic part is evaluated qualitatively with the comparison of the experimental curve and the simulated one. As it can be seen on the figure 8, the model is giving good results.

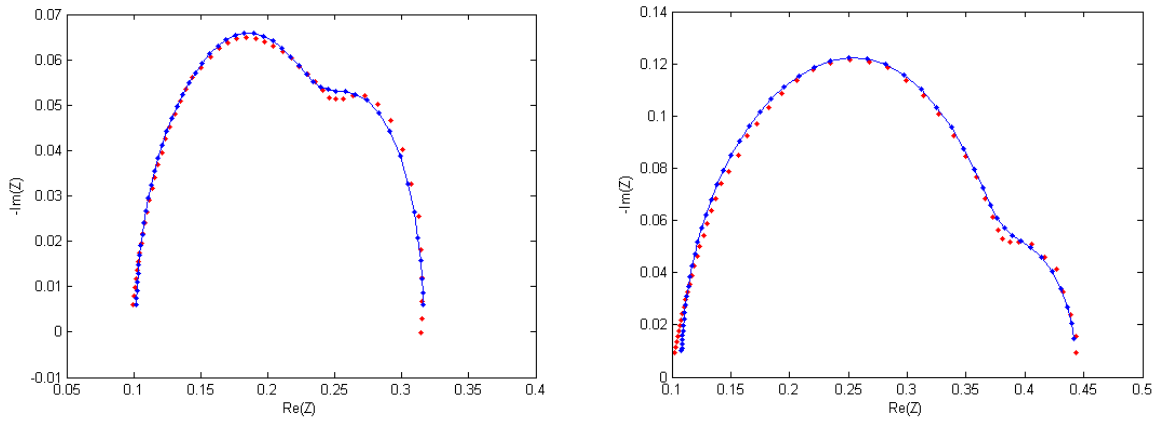

Figure 8 : Example of a fitting of Nyquist plot at t=0, I=20A and I=70A for the FC1

The study of the evolution of the curves with the time is not showing any degradation of the accuracy.

7. Conclusion

The model introduced here is applied to experimental data, and gives satisfying results. Indeed, the fitting between the experimental data and the simulated data obtained validate the model used. The model is really accurate for this PEMFC stack, thanks to a good parameters initialization.
The following of work will consist in the validation of the complete proposed model [3]. Some critical steps have to be optimized as the decomposition of the current density in a DC and AC components. As a matter of fact, in [3] a simple low pass filter is proposed.
The application of the model to prognostics will consist in including the ageing in the model. For that purpose, the integration of a time dependent function for defining the variation of some relevant parameters seems to be a solution to dig. Thus, the simulation of the state of health of the stack starting from an initial characterization should be possible. In the nominal ageing conditions, that should allow to predict the state of health of the stack, or even, to predict the RUL.

AKNOWLEDGEMENTS:
The work performed was done within the SAPPHIRE project, funded by the European Commission through the Fuel Cells & Hydrogen Joint Undertaking.
This work has been performed in cooperation with the Labex ACTION program (contract ANR-11-LABX-01-01).

References:

[1] Jinfeng Wu, Xiao Zi Yuan, Jonathan J. Martin, Haijiang Wang, Jiujun Zhang, Jun Shen, Shaohong Wu, and Walter Merida. “A review of pem fuel cell durability : Degradation mechanisms and mitigation strategies”. Journal of Power Sources, 2008, pp. 1735 – 1746.

[2] R. GOURIVEAU. “Intelligent approaches for phm : overview and challenges”. Aerospace Program Workshop – SIMTech, 13 October 2011.

[3] E. LAFFLY, “Modélisation d’une Pile à Combustible de Type PEMFC Intégrant les Phénomènes de Vieillissement”. PhD thesis, Universite de Franche-Comté, 2008.

[4] E. Laffly, M.C. Péra, D. Hissel, “PEM Fuel Cell Modeling with Static-Dynamic Decomposition and Voltage Rebuilding”, IEEE-ISIE’08 International Symposium on Industrial Electronics, pp. 1519-1524, Cambridge, UK, 2008

[5] h. gauthie. “Piles à combustibles” : support de présentation. 2002.

[6] AFNOR. Iso 13381-1 :2004 surveillance et diagnostic des machines - pronostic - partie 1 : Lignes directrices générales.

[7] Zhi-Dan Zhong, Xin-Jian Zhu, and Guang-Yi Cao. “Modeling a pemfc by a support vector machine”. Journal of Power Sources, 160 :293–298, 2006.

[8] N. Fouquet, C. Doulet, C. Nouillant, G. Dauphin-Tanguy, and B. Ould-Bouamama. “Model based pem fuel cell state-of-health monitoring via ac impedance measurement”. Journal of Power Sources, 159(2) :905 – 913, 2006.

[9] N.P. Siegel, M.W. Ellis, D.J. Nelson, and M.R. von Spakovsky. “A two-dimensional computational model of a pemfc with liquid water transport”. Journal of Power Sources, 128(2) :173 – 184, 2004.

[10] Melika Hinaje, Stéphane Raël, Panee Noiying, Dinh An Nguyen, and Bernard Davat. “An equivalent electrical circuit model of proton exchange membrane fuel cells based on mathematical modelling”. Energies, 5(8) :2724–2744, 2012.

[11] Sang-Kyun Park and Song-Yul Choe. “Dynamic modeling and analysis of a 20-cell pem fuel cell stack considering temperature and two-phase effects”. Journal of Power Sources, 179 :660–672, 2008.

[12] L.S. Martins, J.E.F.C. Gardolinski, J.V.C. Vargas, J.C. Ordonez, S.C. Amico, and M.M.C. Forte. “The experimental validation of a simplified pemfc simulation model for design and optimization purposes”. Applied Thermal Engineering, 29 :3036–3048, 2009.

[13] Ju hyung Lee, Jong-Hak Lee,Woojin Choi, Kyung-Won Park, Hee-Young Sun, and Jae-Hyuk Oh. “Development of a method to estimate the lifespan of proton exchange membrane fuel cell using electrochemical impedance spectroscopy”. Journal of Power Sources, 195 :6001–6007, 2010.

[14] S. Chevalier, D. Trichet, B. Auvity, J.C. Olivier, C. Josset, and M. Machmoum. “Multiphysics dc and ac models of a pemfc for the detection of degraded cell parameters”. International Journal of Hydrogen Energy, 38(26) :11609 – 11618, 2013.

[15] M.Ceraolo, C. Miulli, and A. Pozio. “Modelling static and dynamic behaviour of proton exchange membrane fuel cell on the basis of electro-chemical description”. Journal of Power Sources, 113(1) :131 – 144, 2003.

[16] Yuyao Shan and Song-Yul Choe. “Modeling and simulation of a pem fuel cell stack considering temperature effects”. Journal of Power Sources, 158(1) :274 – 286, 2006.

[17] Yongping Hou, Zhihua Yang, and Gang Wan. “An improved dynamic voltage model of pem fuel cell stack”. International Journal Of Hydrogen Energy, 35(20) :11154 – 11160, 2010.

[18] Christophe Robin, Mathias Gerard, Alejandro A. Franco, and Pascal Schott. “Multi-scale coupling between two dynamical models for pemfc aging prediction”. International Journal Of Hydrogen Energy, 38(11) :4675 – 4688, 2013.

[19] U. Reggiani, L. Sandrolini, and G.L. Giuliattini Burbui. “Modelling a pem fuel cell stack with a nonlinear equivalent circuit”. Journal of Power Sources, 165 :224 – 231, 2007.

[20] S.M. Sharifi Asl, S. Rowshanzamir, and M.H. Eikani. “Modelling and simulation of the steady-state and dynamic behaviour of a pem fuel cell”. Energy, 35 :1633 – 1646, 2009.

[21] S.P. Philipps and C. Ziegler. “Computationally efficient modeling of the dynamic behavior of a portable pem fuel cell stack”. Journal of Power Sources, 180 :309 – 321, 2008.

[22] Stavros Lazarou, Eleftheria Pyrgioti, and Antonio T. Alexandridis. “A simple electric circuit model for proton exchange membrane fuel cells”. Journal of Power Sources, 190 :380 – 386, 2009.