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Fault tree analysis for PEM fuel cell degradation process modelling

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ABSTRACT

For transportation applications, Proton Exchange Membrane fuel cells (PEMFC) are considered to be the most promising fuel cell technology due to their low operating temperature and pressure resulting in a possible quick start-up. However, to implement them in transportation systems, their reliability should be improved. In the present work, a single fuel cell is considered. It is composed of a membrane, catalyst layers (anode and cathode electrodes) and diffusion layers (anode and cathode electrodes). Those layers are considered as the critical components of the cell. Modelling the process degradations of those components is a great issue. In this work, Fault Tree (FT) is used for this modelling for two main reasons. At first, FT helps to model clearly and intuitively the different causal relations of the degradation mechanisms. Secondly, FT allows quantifying components specific degradations, and their effects on the global degradation of the cell. The cell is considered non repairable. Degradation modelling needs knowledge about mechanisms involving components failures. For 1000 simulations of 100 h operation in cycling conditions, the results of the FT show the most important degradations effects on the global degradation of the cell. This work also proposes degradation probability estimates for some specific events.

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1. Introduction

Reliability is one of the most important issues to be solved before successful commercialisation of Proton Exchange Membrane fuel cells (PEMFC).

There are many methods to model reliability: Fault Tree (FT) analysis, Markov chains and Petri Nets [1]. FT analysis is a deductive, top–down method aimed at analyzing the effects of initiating faults and events on a complex system. A Markov chain is a random process with the property that the next state depends only on the current state and not on the past one called “Markov property”. Petri nets have an exact

mathematical definition of their execution semantics, with a well-developed mathematical theory for reliability analysis. More details of those methods can be found in Ref. [1]. In the PEMFC field, M. Gerbec et al. [2] used FT analysis to make operational and process-safety on a commercial system. FT analysis does not consider dependence between components degradations. In addition, the order of appearance of degradations cannot be taken into account. To remedy it, M. Taniroven and M.S. Alam [3] developed a Markov chain state-space generation model for a stand-alone Proton Exchange Membrane (PEM) fuel cell. V. Mangoni et al. [4] proposed also a Markov chain reliability model of fuel cell by using

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a probabilistic approach, considering lack of data and uncertainties of design. Markov chains cannot model reliability of systems with more than two states. For that modelling, Petri nets are used. Wieland et al. [5] modelled through Petri nets PEMFC stacks reliability data.

To model reliability, it is necessary to understand degradation processes of PEMFC components. R. Borup et al. [6] and F.A. de Bruijn et al. [7] reviewed scientific aspects of PEMFC components degradations. For specific components degradations: N. Yousfi-Steiner et al. [8] made a review on PEMFC catalyst degradations and C. Chen [9] studied membrane degradations.

To understand causes and mechanisms of fuel cell components degradations and their influence on long term performance, W. Schmittinger et al. [10] presented an overview and J. Wu et al. [11] made a review of degradation mechanisms and mitigation strategies of PEMFC.

The present work is a contribution to degradations process modelling of a single PEM fuel cell using FT analysis.

This paper is organised as follows: Section 2 introduces the scope of the work, the method, and the data used for the analysis. Next, fuel cell components FTs are presented in Section 3. Then, results of FT applications are presented in Section 4. Finally, a conclusion is made in Section 5.

2. Scope of the work, the method and the data used

2.1. The single PEM fuel cell considered

The single PEM fuel cell considered is composed of five layers: one membrane, two catalyst layers (anode and cathode sides) and two diffusion layers (anode and cathode sides). Those layers are the critical components of the fuel cell. Their degradations lead to a loss in the cell performance.

Membrane is the most critical component because of its structure and its functions. Although there are a variety of membranes, the Nafion® type is studied in this work. It is a perfluorosulfonic acid (PFSA) which is widely used as a fuel cell membrane. Its failure mechanisms can be classified as mechanical (pinhole and crack formation), thermal (dryout, solvolysis, and desulfonation), and chemical (peroxide initiated free radical degradation) degradations [8].

Catalyst layers (CL) are the second most critical component. They are composed of anode and cathode electrodes. Platinum (Pt) or Pt alloy with particles of nanometer size is the material usually used for catalysts [10]. Degradation mechanisms of Pt/C catalysts used in CL have been the aim of many research works [6,9–12]. On the cathode side, the oxygen reduction can be observed on the carbon supports covered by a catalyst layer (platinum, palladium). The anode side is mostly degraded by carbon monoxide (CO) poisoning. CO quickly takes place on the catalyst particles sites. Consequently, sites are no longer available for hydrogen adsorption and subsequent oxidation.

Gas Diffusion Layers (GDL) are the interface between bipolar plates and CL. They are frequently made of carbon paper or cloth. Pt catalyst formed into very small particles, is applied on the carbon surface [10]. The carbon paper facilitates the diffusion of reactants onto the catalyst. There is little

research work on the GDL carbon corrosion. W. Schmittinger et al. [10] reported that carbon corrosion of the GDL has a negative influence on the catalyst properties and subsequently on the performance of the cell. Since carbon paper serves as the catalyst support, its corrosion directly affects lifetime of the cell. In addition, polytetrafluoroethylene (PTFE) and carbon of GDL are vulnerable to chemical attacks such as peroxide radicals. PTFE losses involve GDL physical properties modification: drop of electron conductivity and hydrophobicity, leading to a decrease of the cell performance.

2.2. The method and the approaches used

A general introduction to reliability analysis can be found in Refs. [1,13,14]. Implementing a reliability analysis consists of following a structured procedure in order to meet robust objectives. In this work, the reliability analysis is carried out with the following procedure (Fig. 1).

The definition of the system/components, its functional analysis and the components degradation modes has been introduced in Section 2.1. System modelling, probabilistic analysis and discussion (results) are presented in Section 3. FT is used for system modelling. It is widely used in reliability science [14]. It is a graphical representation of the relationship between an undesirable event (called “top event”) and all its potential causes. It is a top–down approach starting with the top event and determining all the causes that can lead to it. FT analysis helps to determine combinations of component level faults that could result in the occurrence of the top event.

To perform FT analysis, quantitative data (components degradation rates) is necessary. The data used in this work, is presented in the next section.

2.3. PEMFC components data used

To enable a quantitative assessment of probabilities, degradation-rate data for basic events is necessary. Basic events are any kind of component degradation during normal operation conditions of the fuel cell.

Related to the components degradation rate, the same difficulties as in previous studies [2,4], were encountered: a lack of specific data available for fuel cell component degradation rates. Like with the approach of M. Gerbec et al.

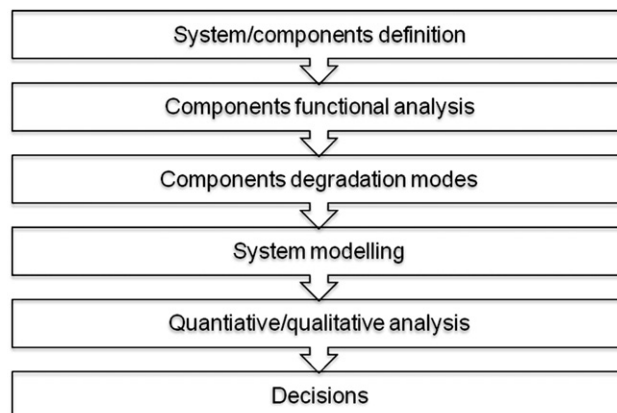


Fig. 1 – Procedure used for the reliability analysis.

[2], compiled data was used from the literature sources [6–8,10,11], and is presented in Tables 1–5.

Components degradation rates were supposed to follow a Weibull distribution as in Ref. [2]. Unavailable data were estimated as in Ref. [2].

Finally, a calculation of probabilities was carried out using the software Aralia WorkShop™ from ARBoost [15].

3. Proton Exchange Membrane fuel cell fault tree

The top event of the fault tree is the “degradation of the cell”. It can result from degradations of the membrane, CL or GDL.

The global cell fault tree (Fig. 2) is an “OR” gate that brings about the three critical components degradations (CL, GDL, and membrane).

FT of membrane, CL and GDL components are presented in the next section.

3.1. Membrane fault tree

Fig. 3 shows the FT of the membrane component. As presented in Section 1.1, membrane degradations are classified as mechanical, thermal, and chemical [8]. Every type of degradation is decomposed from causes to causes until the basic events that are responsible of the undesirable event (degradation of the membrane).

Table 1 – Basic events of membrane degradations.

Basic events	Test conditions	Degradation rate ($V\ h^{-1}$)	Source
Improper membrane electrodes assembly (MEA) fabrication processes	RH at 20% of H_2 and air, potential cycling, 1000 h test period in normal conditions	10^{-8}	[7]: page 4, Table 1, line 12 (Gore 5510)
Congenital membrane defects	RH at 20% of H_2 and air, potential cycling, 1000 h test period in normal conditions	4×10^{-8}	[7]: page 4, Table 1, line 12 (Gore 5510)
Mechanical degradation due to long-term operation	1000 h test period in normal conditions	10^{-6}	[11]: page 105, Table 1, line 2
Pinholes production (mechanical degradation)		10^{-8}	Proposed
Increasing gas crossover	20 000 potential cycles, crossover after 2500 h test	10^{-8}	[6]: page 3911, Table 5 and also page 3925
Rapid start-up degradation	55 temperature cycles	10^{-9}	[6]: page 3914, Section 2.2.1
Severely impaired mechanical strength	4000 RH cycles of more than 200 h	10^{-6}	[6]: page 3921, Table 9, last line (RH cycling for Nafion®)
Severely impaired gas impermeability	385 temperature cycles between $-40\ ^\circ C$ and $+80\ ^\circ C$ during 1000 h test period	10^{-6}	[11]: page 107, Section 3.1.1.2 (McDonald et al.)
Severely impaired ionic conductivity	385 temperature cycles between $-40\ ^\circ C$ and $+80\ ^\circ C$ during 1000 h test period	10^{-6}	[11]: page 107, Section 3.1.1.2 (McDonald et al.)
Glass transition temperature of PFSA polymers		2.5×10^{-9}	Proposed
Production of sulphur dioxide OH radicals		2.5×10^{-9}	Proposed
Drop of protonic conductivity	RH at 100%	10^{-5}	[10]: page 4, Table 2 and page 5, Fig. 2
Formation of amid acid structure	1200–3000 h tests durations	10^{-6}	[6]: page 3924, Section 3.3.2 (S. Faure et al. and C. Perrot et al.)
Formation of amine and diacid terminal groups	1200–3000 h tests durations	10^{-6}	[6]: page 3924, Section 3.3.2 (S. Faure et al. and C. Perrot et al.)
Destruction of the MEA due to exothermal combustion between H_2 and O_2		10^{-5}	Proposed
Pinholes (due to exothermal combustion between H_2 and O_2)	50 h accelerated tests of 120 cells with 50 ppm of CO	4×10^{-6}	[6]: page 3921, Table 9, 1st line
Formation of H_2O_2	720 h accelerated tests with humidity and OCV as accelerating parameters	10^{-7}	[6]: page 3921, Table 9, 6th line
Formation of OH and OOH radicals		2.5×10^{-9}	[10]: page 7, Section 3.3 (G. Escobedo et al. and D.E. Curtin et al.)
Formation of COOH radical	50 h accelerated tests	10^{-9}	[6]: page 3923, section dégradation mechanisms of PFSA membranes (Curtin et al.)
Présence of foreign cationic ions		5×10^{-7}	[10]: page 9, Section 4.2 (B. Kienitz et al. and X. Cheng et al.)
Formation of pinholes (due to contamination by trace metal ion)		4×10^{-6}	Proposed
Acceleration of membrane thinning	H_2/N_2 pressure of 1 atm, temperature at $75\ ^\circ C$	10^{-8}	[10]: page 8, Fig. 3

Table 2 – Basic events of anodic side catalyst layers degradations.

Basic events	Test conditions	Degradation rate (V h ⁻¹)	Source
Nafion® Degradation	900 h test, RH at 26% for H ₂ and air in cycling conditions	10 ⁻⁶	[7]: page 2, Table 1, line 11 (Toray)
Long-term operation (involving Pt dissolution)	0.5–1.5 V, 100 V/s, 1 M H ₂ SO ₄ , 40 °C	1 × 10 ⁻⁹	[6]: page 3933, Table 12, last line of the 2nd column
Long-term operation (involving C degradation)	150 h test at low humidity and at OCV	1 × 10 ⁻⁹	[6]: page 3921, Table 9, 7th line (Flemion)
Control strategy involving insufficient reactant		10 ⁻¹¹	Proposed
Transients involving insufficient reactant		10 ⁻¹⁰	[6]: page 3937, paragraph 4.5.1
Water or ice formation		10 ⁻¹⁰	Proposed
Manufacture anomaly		10 ⁻¹¹	Proposed
Contamination	Impedance tests with anode poisoning with CO at 50 ppm and 100 ppm	10 ⁻⁸	[10]: page 9, Fig. 5
Leached impurity existence		10 ⁻¹⁰	[8]: page 138, Fig. 8(b)
Reactant crossover	Pressure of H ₂ /N ₂ at 1 atm temperature of 75 °C	10 ⁻⁸	[10]: page 8, 4Fig. 3

Table 3 – Basic events of cathodic side catalyst layers degradations.

Basic events	Test conditions	Degradation rates (V h ⁻¹)	Source
Nafion® degradation	900 h test, RH at 26% for H ₂ and air in cycling conditions	10 ⁻⁶	[7]: page 2, Table 1, line 11 (Toray)
Long-term operation (involving Pt dissolution)	0.5–1.5 V, 100 V/s, 1 M H ₂ SO ₄ , 40 °C	3 × 10 ⁻⁹	[6]: page 3933, Table 12, last line of the 2nd column
Cycling	300 000 potential cycling during 5500 h operation	2.8 × 10 ⁻⁸	[8]: page 136, Section 3 (Mathias et al.)
Long periods at OCV	10 000 cycles of 2000 h	10 ⁻⁸	[11]: page 109, Fig. 2
Low stoichiometry		10 ⁻⁸	[8]: page 138, Fig. 8(c)
Hinderance of gas access to the catalyst access		10 ⁻⁹	[6] page 3915 (He et Mench)
Long-term operation (involving C degradation)	150 h test at low humidity and at OCV	10 ⁻¹⁰	[6]: page 3921, Table 9, 7 ^{ème} ligne (Flemion)
Control strategy involving insufficient reactant		10 ⁻¹¹	Proposed
Transients involving insufficient reactant		10 ⁻¹⁰	[6]: page 3937, Section 4.5.1

Table 1 shows the basic events considered for the degradation of the membrane, their degradation rates and tests conditions in which those degradation rates were obtained.

Due to the different experimental conditions of the degradation rates provided in the literature, it is necessary to

consider a common basis for exploiting them. Potential cycling and number of cycles are the most influential factors on the fuel cell degradation [16,17]. Moreover, potential cycling corresponds to real operation conditions of the fuel cell for transport applications. A fuel cell that can support

Table 4 – Basic events of anodic side gas diffusion layers degradations.

Basic events	Test conditions	Degradation rates (V h ⁻¹)	Source
OH radicals formation (PTFE degradation)	Potential cycling	2.5 × 10 ⁻⁹	[10]: page 7, Section 3.3 (G. Escobedo et al. and D.E. Curtin et al.)
Long-term operation (PTFE degradation)		10 ⁻¹⁰	Proposed
Long-term operation (C degradation)		10 ⁻¹⁰	Proposed
OH radicals formation (C degradation)	Potential cycling	2.5 × 10 ⁻⁹	[10]: page 7, Section 3.3 (G. Escobedo et al. and D.E. Curtin et al.)
Flooding		10 ⁻¹¹	Proposed
Voltage oxidation		10 ⁻⁸	Proposed

Table 5 – Basic events of cathodic side gas diffusion layers degradations.

Basic event	Test conditions	Degradation rates (V h ⁻¹)	Source
Long-term operation (PTFE degradation)		10 ⁻¹⁰	Proposed
OH radical (PTFE degradation)		2.5 × 10 ⁻⁹	[10]: page 7, Section 3.3 (G. Escobedo et al. and D.E. Curtin et al.)
Low reactant RH (PTFE degradation)	26 000h tests at 0.8 A/cm ² , T = 70 °C	4 × 10 ⁻⁸	[7]: page 13, Section 4.4.1 (Gore)
OH radical (C degradation)	HR = 100%	2.5 × 10 ⁻⁹	[10]: page 7, Section 3.3 (G. Escobedo et al. and D.E. Curtin et al.)
Flooding		10 ⁻¹¹	Proposed
Voltage oxidation		10 ⁻⁸	Proposed
Long-term operation (C degradation)		10 ⁻¹⁰	Proposed

a thousand potential cycling of 100 h reaches an acceptable durability [16]. It is the common basis hypothesis for this research work.

Basic events in Table 1 are from Refs. [18–35]. Degradation rates corresponding to those basic events in Table 1 are:

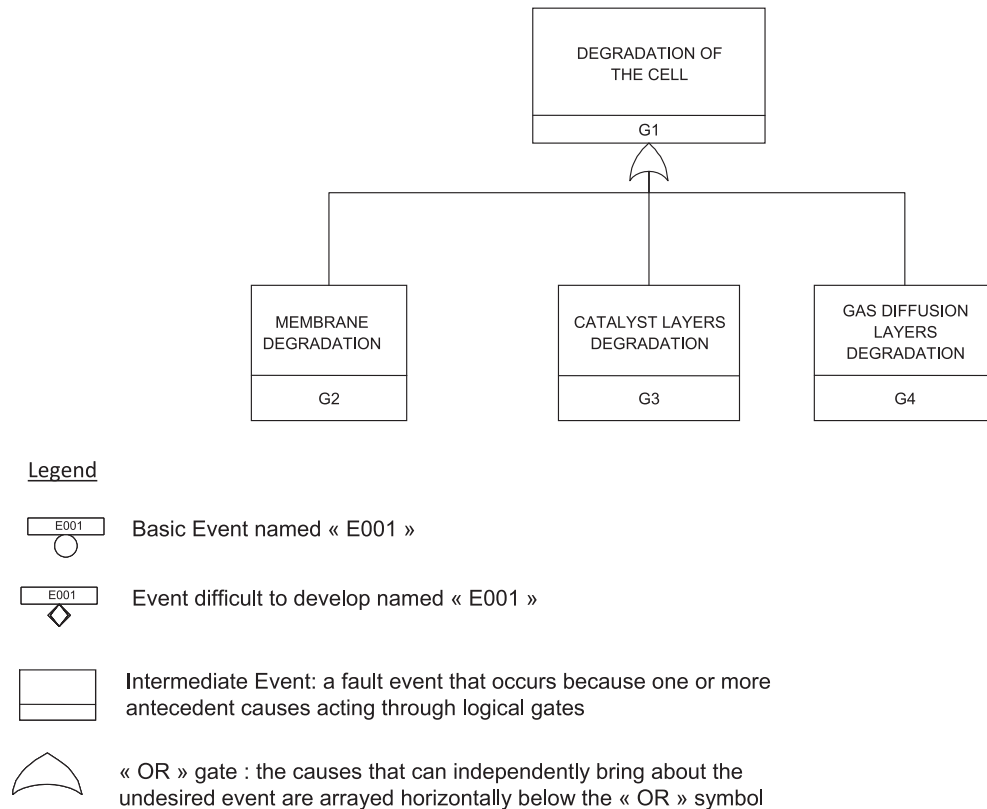
- Either proposed taking into account experts/experimenters judgements: in this case, in the 4th column (sources) of the table, they are “proposed”.
- Either estimated from references of the last column of Table 1.

In the 2nd case, degradation rates are deduced from tables (example 1), figures (example 2), or estimated from

recommendations of researchers on the effect of those rates (example 3).

3.1.1. Example 1: Deduction from a table of the degradation rate

Considering the 1st two basic events of Table 1, in Ref. [7], on page 4, in the 1st table, at the 12th line, there is 45 μV h⁻¹ voltage loss for 1000 potential cycling (common basis hypothesis). A degradation rate equals to (45/1000) μV h⁻¹ can be deduced. It leads to a value of 4.5 × 10⁻⁸ V/h, which can be rounded to 5 × 10⁻⁸ V/h. In fact, the 2nd basic event (membrane congenital defects) has a higher degradation rate than the 1st event (improper MEA fabrication processes) [11].

**Fig. 2 – Global cell fault tree.**

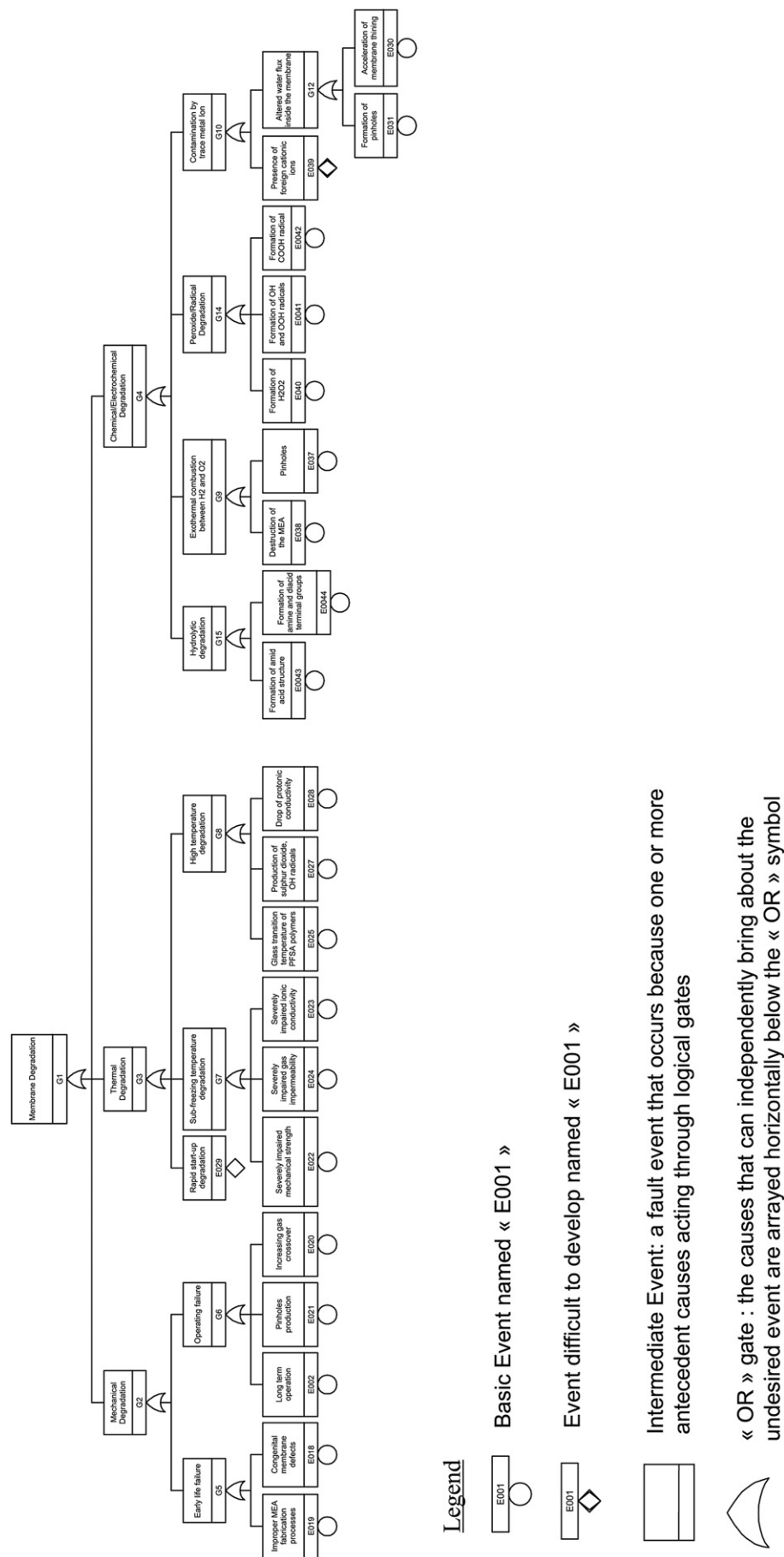


Fig. 3 – Membrane fault tree.

The 2nd event is supposed to be 4 times more degraded than the 1st one. Thus, degradation rates values of those two 1st events of Table 1 are in the 3rd column.

3.1.2. Example 2: Deduction of the degradation rate from a figure

Considering the 12th event of Table 1 (drop of protonic conductivity), on the Fig. 2 of page 5 in Ref. [10], for a current density of 0.4 A/cm², a fall of cell potential from 0.725 down to 0.700 V is observed during a period of time of 0–37 min. It equals to a loss of potential of 0.025 V. The degradation rate can be computed: (0.025/(37/60)). It equals to 4.05×10^{-2} V/h. This value is very high. It is supposed to correspond to 1000 potential cycling (common basis hypothesis). This rate becomes 4.05×10^{-5} V/h. The order of magnitude (10^{-5}) is considered for this degradation.

3.1.3. Example 3: Deduction from experts recommendations

For the 14th basic event “formation of amine and diacid terminal groups”, the Section 3.3 of Ref. [6], on page 3924, shows a lifetime between 1200 and 3000 h. A voltage loss of 0.7 V is supposed during 1200 h operation [6]. In addition, considering 1000 potential cycling (common basis hypothesis), the degradation rate is: $(0.8/(1200 \times 1000)) = 6.67 \times 10^{-7} \sim 10^{-6}$

The order of magnitude of 10^{-6} is considered as the degradation rate for this 14th basic event of Table 1.

Membrane degradation rates estimates illustrated with the three previous examples are also used to determine the degradation rates of CL (Tables 2 and 3) and GDL (Tables 4 and 5).

3.2. Catalyst layers fault tree

Fig. 4 shows the FT of the CL. CL degradations are separated into anode and cathode degradations.

Every electrode degradation is decomposed in constitutive materials of the electrode (platinum, carbon, Nafion®). Basic events considered are from Refs. [6,10,12].

3.2.1. Anodic side

Table 2 shows basic events considered for anodic side catalyst layers degradations, the corresponding degradation rates, and test conditions in which those rates were obtained.

3.2.2. Cathodic side

Table 3 shows basic events considered for cathodic side catalyst layers degradations, the corresponding degradation rates and test conditions in which those rates were obtained.

3.3. Gas diffusion layers fault tree

Fig. 5 shows the FT of the GDL. As for CL, GDL degradations are separated into anode and cathode degradations.

Every electrode degradation is decomposed in constitutive materials of the electrode (carbon and PTFE). Basic events considered are from Refs. [7,10].

3.3.1. Anodic side

Table 4 shows basic events considered for anodic side Gas Diffusion layers degradations, the corresponding degradation rates and test conditions in which those rates were obtained.

3.3.2. Cathodic side

Table 5 shows basic events considered for cathodic side Gas Diffusion layers degradations, the corresponding degradation rates and test conditions in which those rates were obtained.

4. Fault tree applications

Degradation rates are introduced in fault trees as varying over time following a Weibull law. The fuel cell is supposed to support a thousand potential cycling of 100 h. To ensure the quality of statistical results, 1000 simulations are performed. Thus, each simulation corresponds to a cycle. Simulations results are presented for 1000 potential cycling of 100 h.

In the present work, the global fault tree of the fuel cell is simulated 1000 times in potential cycling conditions.

Aralia WorkShop™ software [15] helps to determine the probability degradation of fuel cell components through fault tree events. The probability degradation is linked to the reliability function (R(t)) by Equation (1).

$$P(\text{degradation on } [0, t] \text{ period of time}) = 1 - R(t) \quad (1)$$

The different degradation rates are supposed to follow a Weibull law. In the next section, the parameters of the Weibull distribution are introduced.

4.1. Weibull parameters used for degradation rates of basic events

In this work, the location parameter γ is supposed to be equal to 0 because degradations start at the beginning of life of the fuel cell. The shape parameter β is chosen according to component operating period of time (early life, useful lifetime, end of life...). The scale parameter η is deduced from the degradation rates $\lambda(t)$ of Table 1–5 using Equations (2) and (3).

$$\eta = \frac{\mu(t)}{\Gamma\left(1 + \frac{1}{\beta}\right)} \quad (2)$$

where:

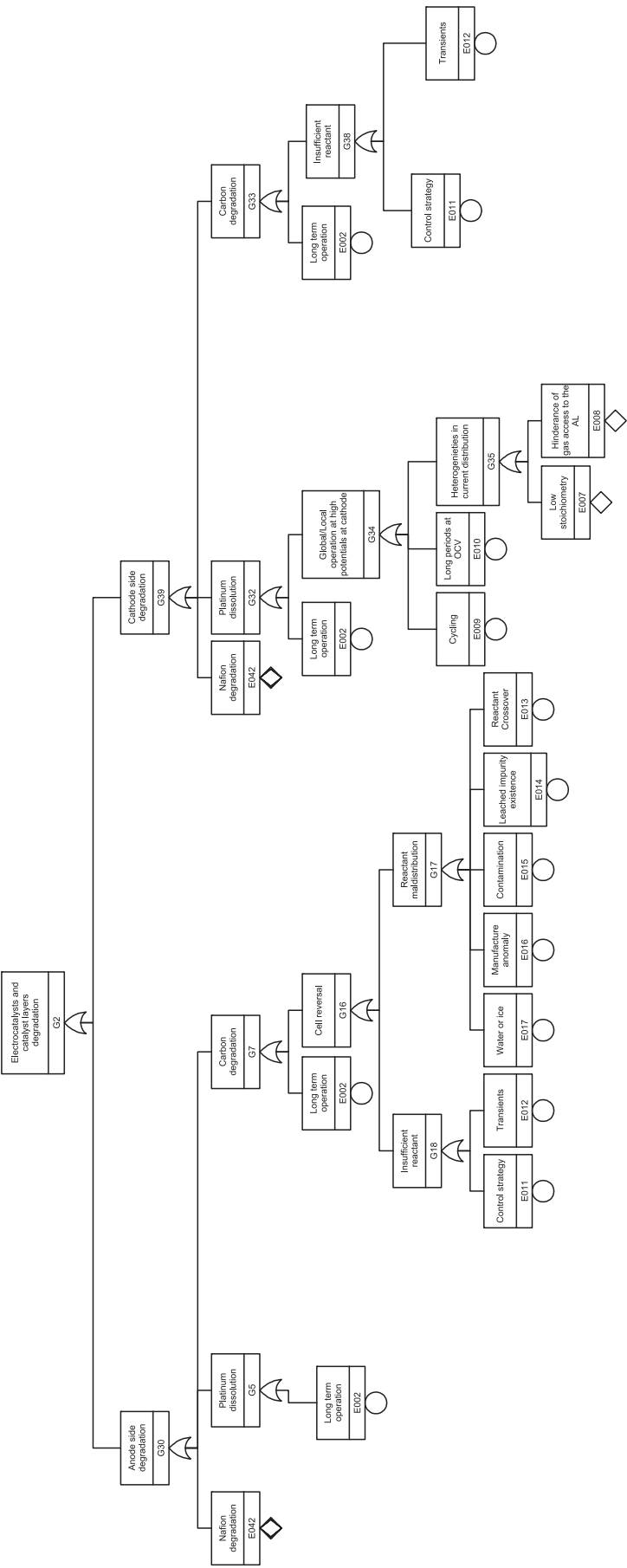
$$\mu(t) = \frac{1}{\lambda(t)} \quad (3)$$

and

$$\Gamma(\alpha) = \int_0^{\infty} x^{\alpha-1} e^{-x} dx \text{ (Gamma function)} \quad (4)$$

From the membrane fault tree, basic events “improper MEA fabrication processes”, “membrane congenital defects”, and “start-up degradation” have their $\beta = 0.8$ (early life) [7]. Basic event “end of life” of the membrane has a $\beta = 3.5$ [11]. All other basic events correspond to a period where $\beta = 2.5$ (increasing degradation rate due to long-term operation) [6] [10].

From the CL fault tree, there is no basic event that corresponds to early life period of time. Basic events “Long-term operation (involving Pt dissolution)” and “Long-term operation (involving C dissolution)” correspond to an end of life period of time with $\beta = 3.5$ [6]. All other basic events correspond to a period where $\beta = 2.5$ [8,10].



Legend



Basic Event named « E001 »



Event difficult to develop named « E001 »



Intermediate Event: a fault event that occurs because one or more antecedent causes acting through logical gates



« OR » gate : the causes that can independently bring about the undesired event are arrayed horizontally below the « OR » symbol

Fig. 4 – Catalyst layers fault tree.

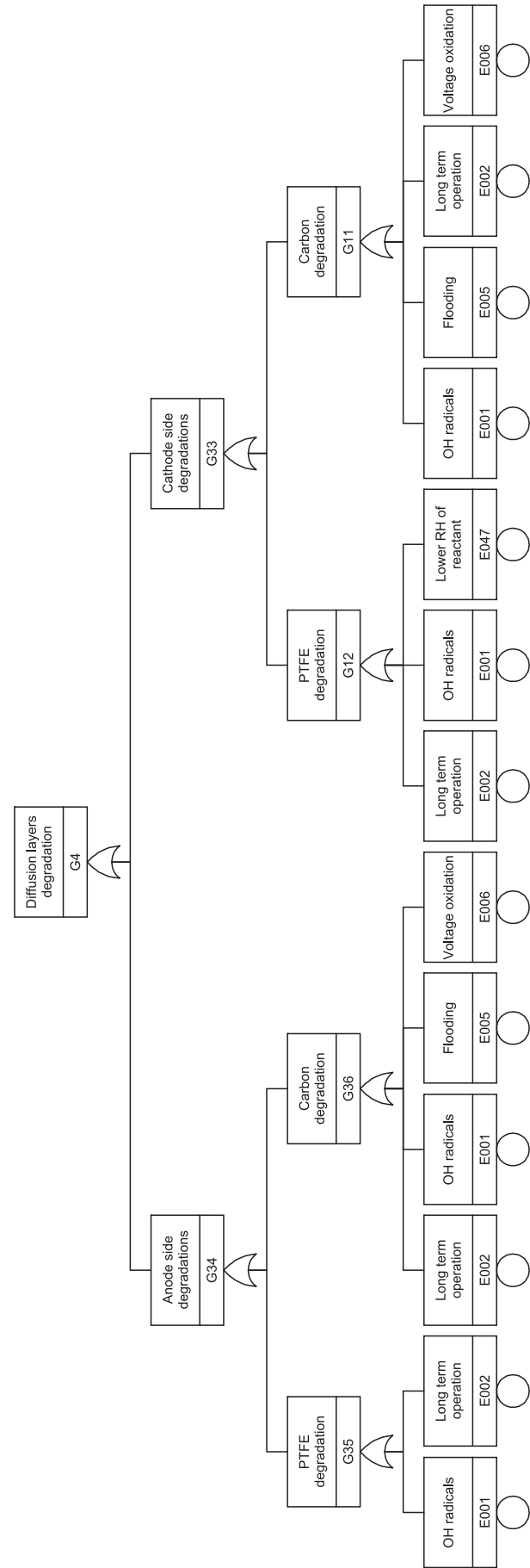


Fig. 5 – Gas Diffusion layers fault tree.

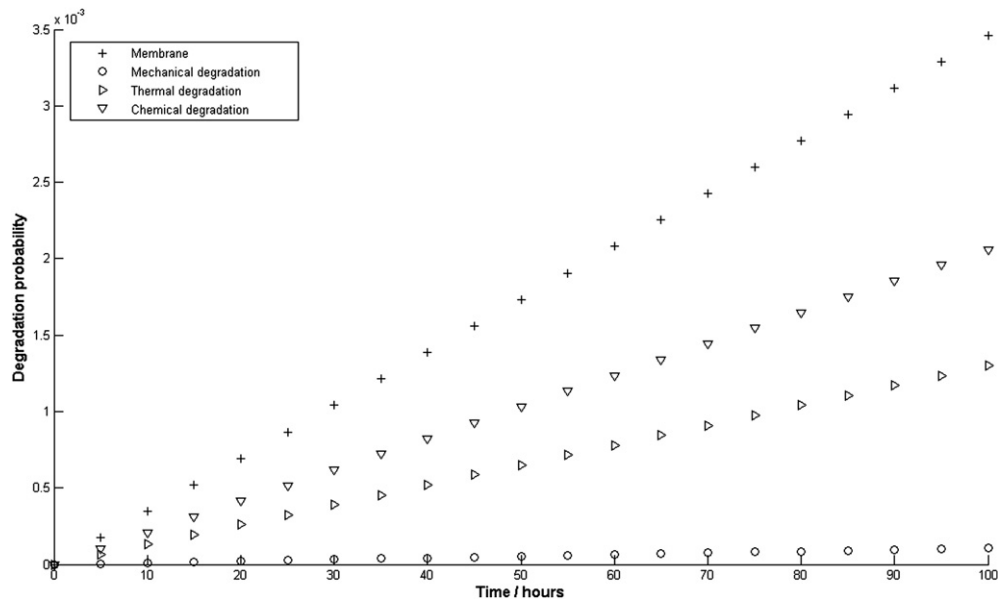


Fig. 6 – Membrane degradation probability versus time.

From the GDL fault tree, there is no event that corresponds to early life period of time. Basic events “Long-term operation (involving PTFE degradation)” and “long-term operation (involving C degradation)” correspond to an end of life with $\beta = 3.5$. All other basic events correspond to a period where $\beta = 2.5$ [8,36].

4.2. Membrane process degradation modelling

Fig. 6 shows the membrane degradation probability versus time. Mechanical degradations have the highest probability to occur, followed by thermal and chemical degradations. After

1000 simulations of 100 h operation in cycling conditions, the probability is 7×10^{-5} for mechanical degradations, 2.8×10^{-6} for thermal degradations and 2.8×10^{-8} for chemical degradations. It results a probability of 7.3×10^{-5} for the membrane degradation. This value is nearly the 10^{-4} probability encountered in Refs. [6–10].

4.3. Catalyst layers process degradation modelling

Fig. 7 represents catalyst layers degradation probability versus time. Cathode and anode sides' degradation probabilities are similar. After 1000 simulations of 100 h operation in cycling

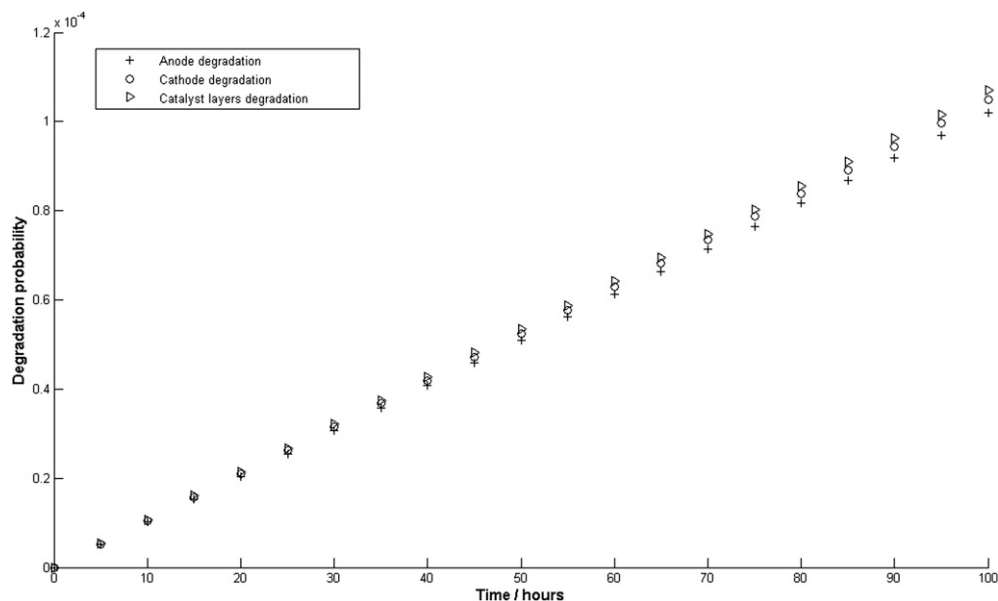


Fig. 7 – Catalyst layers degradation probability versus time.

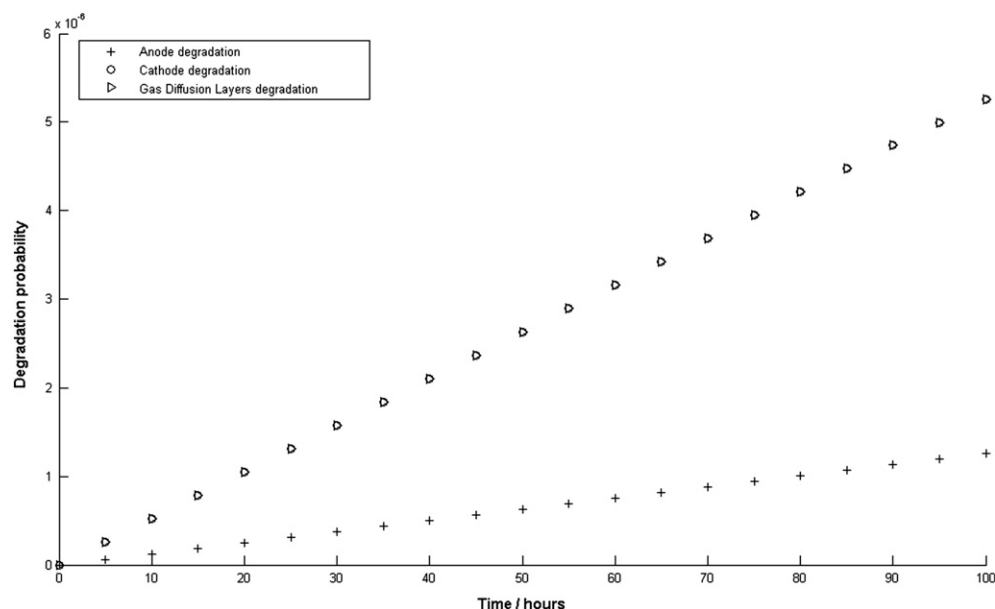


Fig. 8 – Gas Diffusion layers degradation probability versus time.

conditions, cathode side degradation probability is 7.415×10^{-11} and anode side one, is 7.415×10^{-11} . For the catalyst layers, that probability is 7.416×10^{-11} . The degradation probability of catalyst layers is very low compared to membrane one.

4.4. Gas diffusion layers process degradation modelling

Fig. 8 shows the GDL degradation probability versus time. Cathode side degradation probability is more important than the anode side one. In fact, it is similar to GDL degradation

probability. Anode side degradation is thus negligible. After 1000 simulations of 100 h operation in cycling conditions, the cathode side degradation has a probability of 2.45×10^{-14} to occur, whereas the anode side has 7.80×10^{-14} degradation probability.

4.5. Fuel cell process degradation modelling

Fig. 9 represents the degradation probability of the whole cell versus time. As expected from Fig. 6–8, the most important

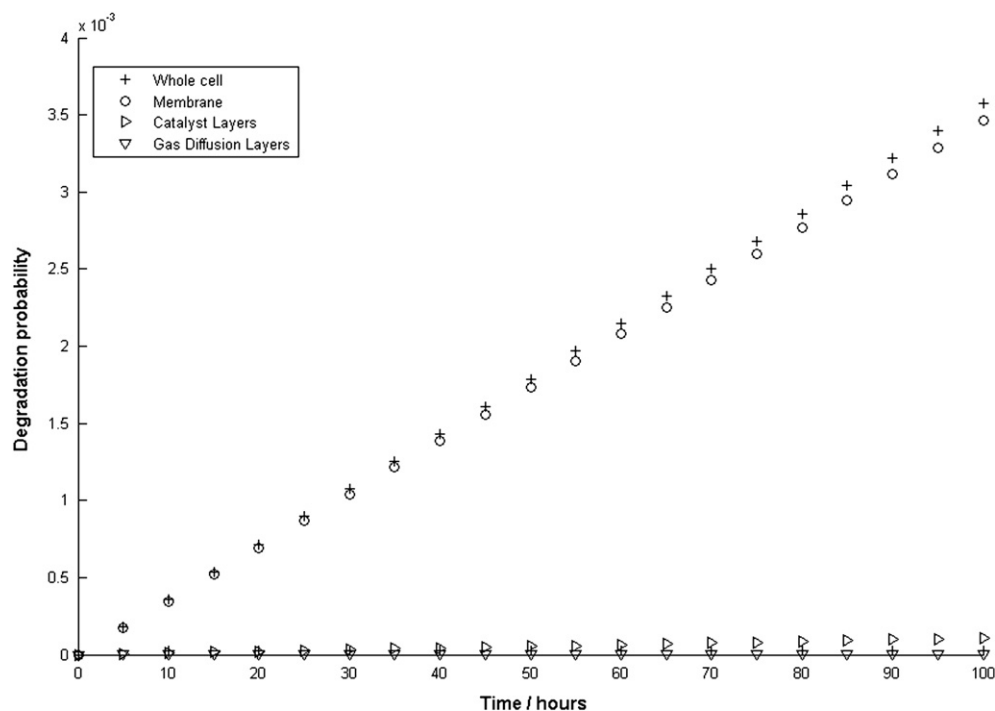


Fig. 9 – Whole cell degradation probability versus time.

probability comes from the membrane, followed by the catalyst layers and then, the GDL. After 1000 simulations of 100 h, the degradation probability is 7.34×10^{-5} for the membrane, 7.416×10^{-11} for catalyst layers and 2.45×10^{-14} for GDL.

The results are similar to those reported in the literature [6–10].

5. Conclusion

Fault Tree analysis contributes on a very efficient way to the fuel cell degradations process modelling. It helps to identify components with highest degradation rates and their effects on the global degradation of the cell. The results show that membrane degradations are the most important ones with two severe basic events: the drop of protonic conductivity and the destruction of the MEA.

The results of this work are interesting to quantify probabilistically fuel cell degradation and also for diagnostic purposes.

5.1. Possible future work

Degradation rates used in this work are subject to uncertainties. For instance, they came from different operation conditions and tests methodologies. As a possible future work, it may be good to estimate uncertainties on those degradations, to study their propagation and their effects on the global degradation of the cell.

REFERENCES

- [1] Rausand M, Hoyland A. System reliability theory, models, statistical methods, and applications, Wiley, ISBN 0-471-471 33-X.
- [2] Gerbec M, Jovan V, Petrovic J. Operational and safety analyses of a commercial PEMFC system. *Int J Hydrogen Energy* 2008;33:4147–60.
- [3] Tanrioven M, Alam MS. Impact of load management on reliability assessment of grid independent PEM fuel cell power plants. *J Power Sources* 2006;157:401–10.
- [4] Mangoni V, Pagano M, Velotto G. Fuel cell reliability model based on uncertain data. International Conference on Clean Electrical Power, 2007. ICCEP '07. 21–23 May 2007, IEEE, 1-4244-0632-3/07; 2007. pp. 730–735.
- [5] Wieland C, Schmid O, Meiler M, Wachtel A, Linsler D. Reliability computing of polymer-electrolyte-membrane fuel cell stacks through Petri nets. *J Power Sources* 2009;190:34–9.
- [6] Borup R, Meyers J, Pivovar B, Kim YS, Mukundan R, Garland N, et al. Scientific aspects of polymer electrolyte fuel cell durability and degradation. *Chem Rev* 2007; 3904–51.
- [7] de Bruijn FA, Dam VAT, Janssen JM. Review: durability and degradation issues of PEM fuel cell components. *Fuel Cells* 2008;08(1):3–22.
- [8] Yousfi-Steiner N, Moçotéguy Ph, Candusso D, Hissel D. A review on PEM fuel cell catalyst degradation and starvation issues: causes, consequences and diagnostic for mitigation. *J Power Sources* 2009;194:130–45.
- [9] Cheng Chen. Membrane degradation studies in PEMFCs. PhD dissertation, School of Chemical and Biomolecular Engineering, Georgia Institute of Technology, USA, August 2009.
- [10] Schmittinger W, Vahidi A. A review of the main parameters influencing long-term performance and durability of PEM fuel cells. *J Power Sources* 2008;180:1–14.
- [11] Wu J, Yuan XZ, Martin JJ, Wang H, Zhang J, Shen J, et al. A review of PEM fuel cell durability: degradation mechanisms and mitigation strategies. *J Power Sources* 2008;184:104–19.
- [12] Wu Bi. PEM fuel cell catalyst degradation mechanism and mathematical modeling. PhD dissertation, School of Chemical and Biomolecular Engineering, Georgia Institute of Technology, USA, August 2008.
- [13] Ireson WG, Coombs CF, Moss RY. Handbook of reliability engineering and management. McGraw-Hill, ISBN 0-07-012750-6; 1995.
- [14] Vesely WE, Goldberg FF, Roberts NH, Haas DF. Fault tree handbook. Washington, DC 20555: Systems and Reliability Research Office of Nuclear Regulatory Research, US Nuclear Regulatory Commission; January 1981. NUREG-0492.
- [15] <http://www.arboost.com>.
- [16] Hinds G. NPL Report DEPC-MPE 002; 2004. pp. 25–42.
- [17] Borup RL, Davey JR, Garzon FH, Wood DL, Inbody MA. Proceedings of the fuel cells durability. Washington, DC. 1st ed.; 2006. pp. 21–42.
- [18] Meyer Gilles, Perrot Carine, Gebel Gerard, Gonon Laurent, Morlat Sandrine, Gardette Jean-Luc. Ex situ hydrolytic degradation of sulfonated polyimide membranes for fuel cells. *Polymer* 2006;47:5003–11.
- [19] Meyer Gilles, Gebel Gerard, Gonon Laurent, Capron Philippe, Marscaq Didier, Marestin Catherine, et al. Degradation of sulfonated polyimide membranes in fuel cell conditions. *J Power Sources* 2006;157:293–301.
- [20] Luo Z, Li D, Tang H, Pan M, Ruan R. Degradation behavior of membrane-electrode-assembly materials in 10-cell PEMFC stack. *Int J Hydrogen Energy* 2006;31:1831–7.
- [21] LaConti AB, Hamdan M, McDonald RC. In: Vielstich W, Lamm A, Gasteiger HA, editors. Handbook of fuel cells: fundamentals, technology and applications, vol. 3. Chichester: John Wiley & Sons Ltd; 2003. p. 647.
- [22] Healy J, Hayden C, Xie T, Olson K, Waldo R, Brundage M, et al. Aspects of the chemical degradation of PFSA ionomers used in PEM fuel cells. *Fuel Cells* 2005;5(2):302–8.
- [23] Knights SD, Colbow KM, St-Pierre J, Wilkinson DP. Aging mechanisms and lifetime of PEFC and DMFC. *J Power Sources* 2004;127:127–34.
- [24] Endoh E, Terazono S, Widjaja H, Takimoto Y. Degradation study of MEA for PEMFCs under low humidity conditions. *Electrochem Solid State Lett* 2004;7:A209–11.
- [25] Huang C, Tan KS, Lin J, Tan KL. XRD and XPS analysis of the degradation of the polymer electrolyte in H₂–O₂ fuel cell. *Chem Phys Lett* 2003;371:80–5.
- [26] Liu W, Ruth K, Rusch G. Membrane durability in PEM fuel cells. *J New Mater Electrochem Syst* 2001;4:227–32.
- [27] Taniguchi A, Akita T, Yasuda K, Miyazaki Y. Analysis of electrocatalyst degradation in PEMFC caused by cell reversal during fuel starvation. *J Power Sources* 2004;130:42–9.
- [28] Wilkie CA, Thomsen JR, Mittleman ML. The interaction of poly(methyl methacrylate) and nations. *J Appl Polym Sci* 1991;42:901–9.
- [29] Yu J, Matsuura T, Yoshikawa Y, Islam MN, Hori M. In situ analysis of performance degradation of a PEMFC under nonsaturated humidification. *Electrochem Solid State Lett* 2005;8:A156–8.
- [30] Samms SR, Wasmus S, Savinell RF. Thermal stability of Nafion® in simulated fuel cell environments. *J Electrochem Soc* 1996;143:498–1504.

-
- [31] McDonald RC, Mittelsteadt CK, Thompson EL. Effects of deep temperature cycling on Nafion®112 membranes and membrane electrode assemblies. *Fuel Cells* 2004;4(3): 208–13.
- [32] Scherer GG. *Ber Bunsenges. Phys Chem* 1990;94(9):1008–14.
- [33] Panchenko A, Dilger H, Möller E, Sixt T, Roduner E. In situ EPR investigation of polymer electrolyte membrane degradation in fuel cell applications. *J Power Sources* 2004; 127:325–30.
- [34] Panchenko A, Dilger H, Kerres J, Hein M, Ullrich A, Kaz T, et al. In-situ spin trap electron paramagnetic resonance study of fuel cell processes. *Phys Chem Chem Phys* 2004;6(11):2891–4.
- [35] Kundu Sumit, Simon Leonardo C, Fowler Michael W. Comparison of two accelerated Nafion™ degradation experiments. *Polym Degrad Stabil* 2008;93:214–24.
- [36] Takeuchi N, Fuller TF. Modeling and investigation of design factors and their impact on carbon corrosion of PEMFC electrodes. *J Electrochem Soc* 2008;155:B770.