Journal of Power Sources 190 (2009) 34–39

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Reliability computing of polymer-electrolyte-membrane fuel cell stacks through Petri nets

C. Wieland, O. Schmid, M. Meiler*, A. Wachtel, D. Linsler

Department of MEA and Stack Technology, Daimler AG, Neue Str. 95, D-73230 Kirchheim/Teck, Germany

ARTICLE INFO

Article history:
Received 10 June 2008
Received in revised form
30 September 2008
Accepted 1 October 2008
Available online 17 October 2008

Keywords:
PEM (polymer-electrolyte-membrane) fuel cell
Simulation
Petri net
Degradation
Reliability

ABSTRACT

In this paper a model is introduced which computes reliability data of PEMFC (polymer-electrolyte-membrane fuel cell) stacks, especially the average lifetime of a single stack or the reliability of stacks of a whole fuel cell vehicle fleet within a given timing. The stack and its behaviour over time is modelled by a Petri net. The behaviour is divided into degradation, spontaneous and reversible events. Through the worsening over time the characteristics voltage, internal and external leakages, which are assigned to the components MEA (membrane electrolyte assembly) and BIP (bipolar plate), are changed. Thresholds for every characteristic monitor the operating ability of the whole stack.

1. Introduction

For several years, PEM stacks are used as a part of powertrain in the automotive industry. But the practical experiences picked up until now only apply for prototypes and small series production. For the preparation of large-scale production of fuel cell vehicles, tools are needed that model the reliability of a whole vehicle fleet. The operation of a fuel cell vehicle fleet is connected to an increased logistic support. Reliability models are able to estimate the number of spares that have to be in stock or to set appropriate maintenance intervals. The latter is inevitable to save customers from breakdowns and achieve customer satisfaction. High reliability of fuel cell vehicles will lead to high customer satisfaction, which is the crucial factor for the success of the product.

There are many analyses (e.g. [1] or [2]) which are engaged in durability of the MEA (membrane electrolyte assembly) or parts of the MEA in case of different influences. Very rarely the complete stack or furthermore a production run of stacks is regarded.

The ambition of the developed model is to determine, how single components and special events under operating conditions influence the lifetime of the entire stack and the reliability of PEM stacks in a fleet of fuel cell vehicles. Therefore every MEA and every BIP (bipolar plate) of a stack is imaged with its characteristics voltage and leakage. The various influences on the characteristics in terms of degradation and mechanical, chemical and physical mechanisms are mapped. This theoretical approach is supported by the use of expert knowledge and experimental data, extracted from publications that focus on the topic of degradation mechanisms, to reach real conditions as accurate as possible.

2. Theory

2.1. PEM fuel cell

A rough understanding of the operations is necessary to comprehend the further dividing of the influences on the fuel cell. For detailed information about PEMFCs we refer to Larminie and Dicks [3].

2.2. Monte Carlo simulation

In this special case, the Monte Carlo simulation maps the temporal changes of the stacks concerning the reliability. Monte Carlo simulation is reduced to the Weak Law of Great Numbers, saying that the median of a series of independent, identically distributed random numbers approximates the mean arbitrarily close taking only enough random numbers [4].

---

* Corresponding author. Tel.: +49 7021 89 35 20; fax: +49 711 30 52 19 35 20.
E-mail address: markus.meiler@daimler.com (M. Meiler).

0378-7753/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.jpowsour.2008.10.010

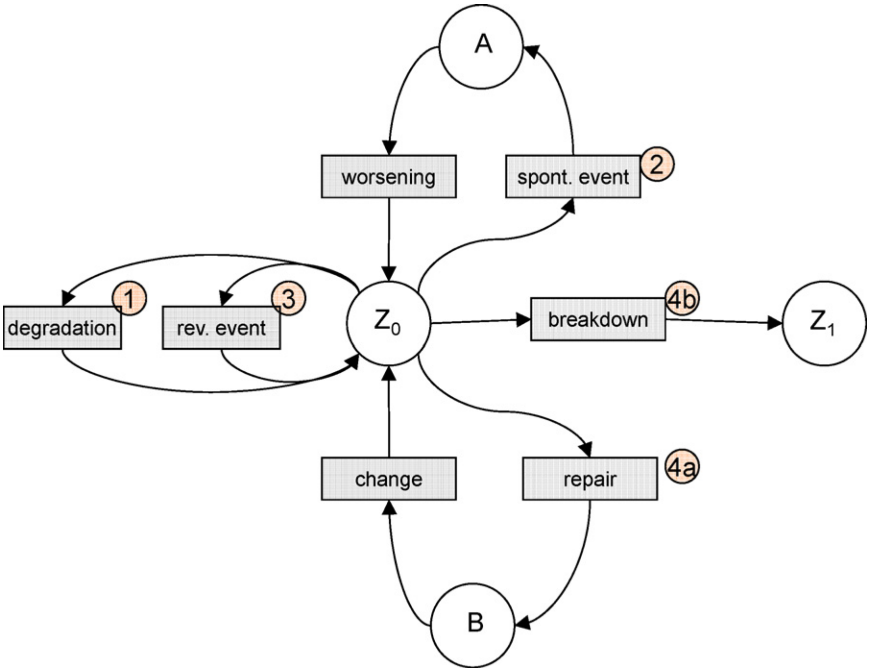

Fig. 1. Developed Petri net model.

Asking for the average lifetime of a stack, a defined number of simulations is done and afterwards the median lifetime over all simulations is calculated.

2.3. Petri nets

Petri nets are directed graphs which consist of two different kinds of knots: places and transitions. Places can be interpreted as events and transitions as conditions. In the developed model the Petri net organizes the worsening of the characteristics of the components and the components themselves. The formal definition is [5]:

Definition. A Petri net is a structure (P, T, F, B) with

- a finite set of places $P = \{p_1, \ldots, p_{|P|}\}$,
- a finite set of transitions $T = \{t_1, \ldots, t_{|T|}\}$ with $P \cap T = \{\}$,
- a $|P| \times |T|$-matrix F with elements out of $\{0,1\}$, and
- a $|P| \times |T|$-matrix B with elements out of $\{0,1\}$.

The terms F and B refer to "forward" and "backward" and show the perspective of the places. It follows from the definition that places can only be connected with transitions and transitions can only be connected with places as the matrices F and B only provide such combinations. If Petri nets are drawn the places are represented by circles and transitions by rectangles. Marks (black points) are moving through Petri nets, which can only take a position on places. Marks belonging to one Petri net need not be identical and every mark can have different properties.

If a transition fires, the marking of the net can be changed. Transitions fire, if certain net-dependent rules for firing are met. In the following model there will be three kinds of transitions, which are derived from Pedrycz and Gomide [6].

- The first kind of transition fires in any case. It will represent degradation later as it occurs without exception in every step for all marks.
- The second kind fires, if a random number falls below a given value. It is used to image spontaneous and reversible events.
- The last kind of transition is needed to realize repair and breakdown. These transitions fire, if certain characteristics of the marks fall below particular thresholds.

3. Modelling

3.1. Marks and their characteristics

A Petri net is used, as it is a flexible model with a lot of expansion and adaptation possibilities. Every single BIP and every single MEA can be mapped, modified and exchanged. A MEA and a BIP together build a cell and each of the cell components is represented by a mark. The one which is representing the i-th MEA to time t, carries the characteristic of MEA voltage $U_{MEA}(t,i)$, the internal leakage of fuel to air $L_{MEA}(t,i)$ and the external leakage $L_{out}(t,i)$. The BIP carries the characteristic of voltage loss $U_{BIP}(t,i)$ and the coolant-gas-leakage $L_{BIP}(t,i)$. Additionally, each mark stores its age $a_{MEA}(t,i)$ and $a_{BIP}(t,i)$.

In Fig. 1 the Petri net is shown which describes the behaviour of the stack over time. In state Z_0 the cell of a stack is operational. State Z_1 stands for "cell is out of order", which is equal to "stack is out of order". Place A is the "state of spontaneous events" where the influences of an occurred spontaneous event on the cell characteristics are calculated. In the "state of repair" B damaged cells are designated to be replaced by new ones. For this special Petri net it is considered that at the end of every time step all marks have to be in state Z_0 or Z_1; the states A and B have to be left within one time step. Transitions 4a and 4b except each other. Regarding the reliability of a vehicle fleet transition 4a fires, considering the average lifetime of a single stack transition 4b fires.

3.2. Initialisation

At the beginning of each simulation the characteristics are set up with reasonable values which will be explained in the following.

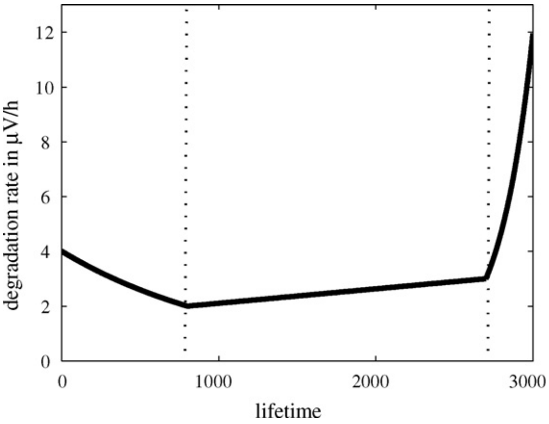

Fig. 2. Example for a run of degradation rate.

3.2.1. *Voltage*

The voltage of a single cell is computed by the MEA voltage and the loss of voltage of the BIP (Eq. (1)):

$$U_{Cell}(t, i) = U_{MEA}(t, i) - U_{BIP}(t, i). \tag{1}$$

The MEA voltage at time 0 is generated by a normal distributed random variable $N(\mu_V, \sigma_V^2)$ with mean μ_V and standard deviation σ_V while the loss of voltage of the BIP $U_{BIP}(0,i)$ is zero. Under normal operation the histogram of all cell voltages of a stack may be assumed as normally distributed [7], as there are some cells working better or worse than other cells. The effect of cells behaving different according to their positions along the stack is not taken into consideration.

3.2.2. *Leakage*

At the beginning of a stack life the internal leakages do not have to be zero, but there must not be an external one.

For the whole simulation, the influence of current density is not explicitly calculated, because the degradation mechanisms resulting from current density variation are taken into account by using spontaneous events and other degradation mechanisms.

3.3. *Degradation*

The degradation is the first transition in the Petri net and fires for every mark and in any case. For every characteristic of every mark, it calculates the worsening which is caused by the natural ageing of the stack. For all five characteristics a mean and a standard deviation to every age is saved separately. This mean and this standard deviation build a random number depending on the age of the component computing the worsening of the characteristic.

As an example, the run of the mean for the degradation rate of the MEA voltage is given in Fig. 2. For this run interpolation between four points is done: first exponentially decreasing, then linearly, and finally exponentially increasing.

Experimental tests have shown that the standard deviation is linearly increasing with the age of the components. The corresponding standard deviation is saved to its mean. Altogether the MEA voltage is given by Eq. (2):

$$U_{MEA}(t+1, i) = U_{MEA}(t, i) - N(\mu_{U,MEA}(a_{MEA}(t, i)),$$
$$\sigma^2_{U,MEA}(a_{MEA}(t, i))). \tag{2}$$

After computation of the degradation for every characteristic, the age of each component is increased by one.

3.4. *Spontaneous events*

The state *A* takes care about the spontaneous events occurring during fuel cell stack operation. Unlike degradation, spontaneous events *j* do not occur at every time step. Spontaneous events do not take effect on the whole fuel cell stack, rather, only affect one or a few selected cells.

1. Firstly, it is determined if a spontaneous event *j* is happening to time *t*. Every spontaneous event *j* occurs with a certain probability $p(j,a_{stack})$. Here a_{stack} is the stack age, which is defined by the age of the oldest component. The spontaneous event takes place if a uniformly distributed random variable $U(0,1)$ is less than or equal to the given probability $p(j,a_{stack})$.
2. After deciding whether the spontaneous event *j* is occurring, the number of affected cells next to a randomly chosen start cell z_s is determined. Some mechanisms affect weak cells in favour. In such cases the start cell z_s is the cell with the lowest voltage or the cell with the greatest leakage. The number of cells that are affected by the event *j* is generated by normal distribution. For every event a mean $\mu_{j,num}$ and standard deviation $\sigma_{j,num}$ is saved. The number num_j of affected cells is specified by Eq. (3):

$$num_j = N(\mu_{j,num}, \sigma^2_{j,num}). \tag{3}$$

3. At last, the actual worsening of the components can be defined by normal distribution again. So exemplary for the MEA the following is given by Eq. (4):

$$\text{for } i = z_S : z_S + num_j - 1$$

$$U_{MEA}(t', i) = U_{MEA}(t, i) - N(\mu_{j,U}, \sigma^2_{j,U}),$$
$$L_{MEA}(t', i) = L_{MEA}(t, i) + N(\mu_{j,L}, \sigma^2_{j,L}). \tag{4}$$

It is $t' = t$ as the ageing is done by the degradation transition already.

3.5. *Reversible events*

Reversible events are treated similarly to spontaneous events: a random number defines whether the event happens or not. If the reversible event occurs, the number of attacked cells is defined. With certain probability, the system will break down due to too low voltage. If this happens, it will be noted in a protocol. Though there are no further actions, as the process is reversible and recovers itself, the breakdown caused by a reversible event is an impairment of serviceability and therefore has to be included in the reliability analysis. After that, the cells return in the state Z_0 as there is no need for repair just for a restart.

Table 1
Different simulations with lifetime and error.

Component	Standard deviation of starting voltage	Linear increase of standard deviation	t	e
MEA	0 mV	$0\,\mu\mathrm{V\,h^{-1}}$	2901	0
MEA	$1/\sqrt{2}$ mV	$0\,\mu\mathrm{V\,h^{-1}}$	2481.93	18.41
MEA	1 mV	$0\,\mu\mathrm{V\,h^{-1}}$	2304.7	24.88
MEA, BIP	$1/\sqrt{2}$ mV	$0\,\mu\mathrm{V\,h^{-1}}$	1248.27	8.68
MEA	$1/\sqrt{2}$ mV	$\sqrt{0.05}$ – $\sqrt{0.1}\,\mu\mathrm{V\,h^{-1}}$	2048.93	13.67
MEA	$1/\sqrt{2}$ mV	$\sqrt{0.08}$ – $\sqrt{0.2}\,\mu\mathrm{V\,h^{-1}}$	1838.33	15.99
MEA	$1/\sqrt{2}$ mV	$\sqrt{0.1}$ – $\sqrt{0.3}\,\mu\mathrm{V\,h^{-1}}$	1738.3	14.37

Table 2
Parameters used in simulation; all values in μV h^{-1} cell^{-1}; otherwise indicated.

No.	Input parameter x	Lower limit	Value	Upper limit	Source
1	Starting voltage	650 mV cell^{-1}	850 mV cell^{-1}	900 mV cell^{-1}	[8]
2	Natural ageing	1	40	70	[9,10]
3	Dry operation	5	14	60	[11]
4	High temperature operation	5	16	40	[12][a]
5	Start below 0 °C (SBZ)	9 μV start h^{-1} cell^{-1}	15 μV start h^{-1} cell^{-1}	100 μV start h^{-1} cell $^{-1}$	[13]
6	Contamination	0.2	1	2	[14][b]
7	Idle operation	83	110	146	[15]

[a] By assuming the cell to be half of the operating time above a potential of 0.6 V.

[b] By assuming a linear relation between voltage degradation and concentration of impurities.

Table 3
Spontaneous events; all values in μV h^{-1} cell^{-1}; otherwise indicated.

No.	p in %	c in %	Parameter	Lower limit	Value	Upper limit	Source
8	6.6	100	Spontaneous contamination	7	10	12	[14]
9	10	75	Fuel starvation	50	120	180	[a]
10	7	100	High temperature operation	10	20	30	[a]
11	1	30	Contamination with particles	10	30	50	[a]
12	1	50	High potentials	700	1000	1300	[15]

[a] Own presumption.

3.6. *Repair or breakdown*

All characteristics of the components are changed in every step at least through degradation. For every characteristic a threshold exists which forces the system to be repaired or to break down if it is hurt. The transitions 4a or 4b check these specific boundary values. There are thresholds for a single component, for a cell row or for the complete stack and they are set depending on the application. In the case of simulating the lifetime of a single stack, a breakdown marks the end of life of the stack. In the case of regarding the reliability of a vehicle fleet, damaged stacks get repaired by replacing injured components. Repairs and breakdowns are noted in a protocol. In the Petri net components are changed by means of getting their marks new characteristics as described in Section 3.2.

4. Verification

Verification is done to check the logical consistency of the reliability model. Validation of the reliability model is impossible, as there is no large-scale production of fuel cell vehicles existing yet. The values used for verification have no relation to reality, they are chosen that way, that they lead to failure during the simulation time of 3000 h of operation, so that different effects on the mean lifetime and their influence on the error e can be seen. The mean lifetime t can be found in the confidence interval $[t-e; t+e]$ with a probability of 95%.

Verification has been done for voltage and internal leakage because these properties contain all possible variations of degradation. Spontaneous and reversible events have been verified, too. Here, verification is exemplified for voltage degradation: 30 simulations of a stack with several hundred cells in two rows working 3000 h were run (Table 1).

A fixed and identical degradation of MEA and BIP is given so that influence of the components on the voltage is equal. When the standard deviation of the starting voltage of each cell is set to zero, the stack fails at the same time for all simulations, e equals zero. The next step is to vary the starting value of MEA voltage with a standard deviation. As a stack fails as soon as one cell falls below a certain limit, lifetime depends on the voltage variation. Variations through BIP are correctly integrated as lifetime halves when the BIP degradation has the same values as MEA degradation. Additionally, three different progresses of standard deviation are simulated. Deviation values during the simulation result from linear interpolation.

5. Example

5.1. *Simulation parameters*

The introduced Petri net including the Monte Carlo simulation is implemented in MATLAB using a standard PC with dual core processor 2*2.2 GHz. For this publication, the parameters in Tables 2 and 3 – taken from various publications [8–15] and from expert knowledge – are chosen to be analyzed concerning their influence on the voltage degradation of a stack of two rows with several hundred cells running 2000 h.

Primary goal of the following investigation is to find the parameters that have to be upgraded to achieve a better stack performance. This kind of analysis may be helpful for establishing component-level durability requirements.

The Petri net is able to account for spontaneous events. Their probabilities, the expectation of affected cells c in percent and the degradation values are listed in Table 3.

The used example drive cycle is described in Table 4. Stack running in smog is reflected in the spontaneous event catalyst contamination, and the input parameter “contamination” mirrors normal city traffic. The degradation values of idle, dry and high temperature operation modes correspond to the input parameters with the same name. Highway driving is the mode with the lowest voltage degradation; here only the natural ageing is taking place, which is independent of the operation mode and occurring at every time step. Several hundred starts below 0 °C (SBZ) are assumed to take place in 2000 h of vehicle operation.

Table 4
Used drive cycle.

Operation mode	In %	In h
City drive	39.8	796
Highway drive	19.9	398
Idle operation	14.3	286
Dry operation	13.3	265
Smog	6.6	133
High temperature operation	6.1	122
Total	100	2000

5.2. Analysis of simulation results

In order to make a Pareto analysis to find the parameters degrading the cell voltage most severely, an upper and a lower limit of possible input parameters is defined. By multiple regression, a linear model for the target variable, voltage degradation, is gained. The linear model is not taken out of the simulation itself to have a further verification and to depict the influence of the single parameters clearly. The optimal parameters b of the linear model, as given in Eq. (5), with the vector of estimated voltage degradation $\hat{y}$ and the design matrix X, are needed:

$$\hat{y} = Xb. \tag{5}$$

The design matrix X consisting of 96 rows corresponding to 96 different input parameter combinations which are given by an D-optimal experimental design (DoE) using the 12 inputs in Tables 2 and 3. The number of columns of the matrix depends on the number of inputs and on the order of the polynomial used. For each parameter combination the voltage degradation of a single stack is computed by the Petri net model over a simulation time of 2000 h. The minimization of the square error between the estimated voltage degradation $\hat{y}$ and the voltage degradation y that is given by the Petri net simulation, leads to Eq. (6) [16]:

$$b = (X'X)^{-1}X'y. \tag{6}$$

5.3. Executing the example

The above-mentioned 96 combinations of values are cycled 2 times; 1 and then 50 simulations per combination are done. A linear model is chosen because the Petri net is well described with it. According to Pareto analysis, b-values are multiplied with the size of the parameter interval (Table 2), so that the contribution of the assigned parameter to the voltage degradation is shown (Fig. 3).

5.4. Example's results and discussion

The normalized b-values show the contribution of the according parameters (Tables 2 and 3) to the voltage degradation. The natural ageing, which happens at every time step independent of operation mode, is the most important factor (50%), followed by SBZ (26.5%), fuel starvation (7%) and idle operation (6.5%). It can be seen from the difference of estimated voltage degradation $\hat{y}$ and the voltage degradation y given by the Petri net simulation against the parameter combination number in Fig. 4, that the estimated voltage degradation of the linear model matches the voltage degradation of the Petri net simulation very well; the difference is smaller than 3 μV h^{-1} cell^{-1}.

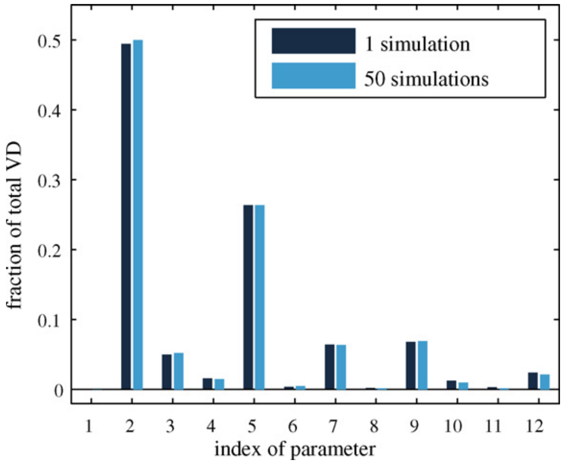

Fig. 3. Parameters and their contribution to the cell voltage degradation (VD).

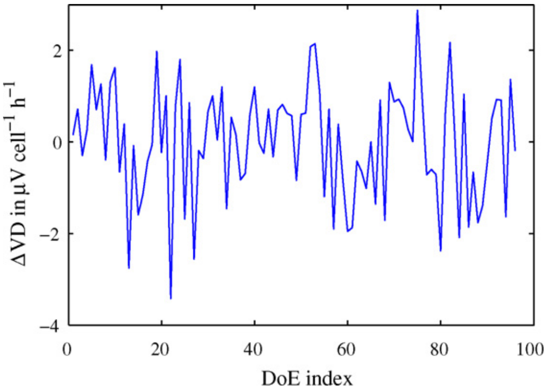

Fig. 4. Difference of the estimated voltage degradation $\hat{y}$ and the voltage degradation y given by the Petri net simulation.

For this example, experimentally determined but isolated data are linked with a Petri net and analyzed incorporating different operation modes. The obtained result is described with a simple linear model. When additional parameters have to be incorporated, a new Petri net has to be created, resulting in a new model describing it.

Although the data used is per se not comparable, all values have a realistic size. When changing the values in the intervals given (Tables 2 and 3) no remarkable changes in results are observed, meaning that the natural ageing and SBZs are of the investigated modes the ones most severely affecting the cell voltage.

6. Discussion

The introduced model is designed with respect to a fast and easy adaptation to new situations. If there are degradation mechanisms which do not fit in the model, a new transition with the required features can simply be added. The introduction of reversible events is important for the estimation of availability and service cycles, also, if they do not contribute to permanent voltage degradation.

On the other hand, there is a lot of simplification done to get this first model. For example, spontaneous events occur independently of the stack state and degradation is steady, instead of increasing at certain times such as summer or winter.

The most important improvement would be done if there were a model, which maps the operating time of the stack realistically. If this is achieved, an availability analysis will be possible.

The example simulation of the influence of different input parameters on voltage degradation shows that the natural ageing and the SBZs are the factors most strongly degrading the cell voltage. The presented reliability model based on a Petri net can help fuel cell producers identify design-related factors that influence degradation the most, in order to improve their products. Moreover fuel cell vehicle manufacturers may use it to set appropriate maintenance intervals in order to save their customers from unpleasant breakdowns.

References

[1] D. Schiraldi, J. Macromol. Sci. (Part C: Polym. Rev.) 46 (2006) 315–327.
[2] X. Huang, R. Solasi, Y. Zou, M. Feshler, K. Reifsnider, D. Condit, S. Burlatsky, T. Madden, J. Polym. Sci. (Part B: Polym. Phys.) 44 (2006) 2346–2357.
[3] J. Larminie, A. Dicks, Fuel Cell Systems Explained, John Wiley & Sons, Ltd., Chichester, 2000.
[4] G.S. Fishman, Monte Carlo-Concepts, Algorithms and Applications, Springer Verlag, New York, Inc., 1996.

[5] J. Desel, Petrinetze, lineare Algebra und lineare Programmierung, Teubner-Texte zur Informatik, Bd. 26, Stuttgart, Leipzig, 1998.
[6] W. Pedrycz, F. Gomide, IEEE Trans. Fuzzy Syst. 2 (4) (1994) 295–301.
[7] J. Okano, Y. Matsushita, K. Okajima, Study of PEFC stack performance and effect of cooling failure, 214th Meeting of ECS—The Electrochemical Society, Poster 196, 2008.
[8] M. Fowler, R. Mann, J. Amphlett, B. Peppley, P. Roberge, J. Power Sources 106 (2002) 274–283.
[9] J. Stumper, C. Stone, J. Power Sources 176 (2008) 468–476.
[10] B. Wahdame, D. Candusso, X. François, F. Harel, M. Péra, D. Hissel, J. Kauffmann, Int. J. Hydrogen Energy 32 (2007) 4523.
[11] J. Yu, T. Matsuura, Y. Yoshikawa, M.N. Islam, M. Hori, Phys. Chem. Chem. Phys. 7 (2005) 373–378.
[12] A.S. Arico, A. Stassi, E. Modica, R. Ornelas, I. Gatto, E. Passalacqua, V. Antonucci, J. Power Sources 178 (2008) 525–536.
[13] H. Yu, J. Hou, S. Zang, S. Sun, H. Wang, B. Yi, P. Ming, J. Power Sources 162 (2006) 513–520.
[14] R. Mohtadi, W. Lee, J.W. van Zee, J. Power Sources 138 (2004) 216–225.
[15] S. Kundu, M. Fowler, L.C. Simon, R. Abouatallah, J. Power Sources 182 (2008) 254–258.
[16] H. Pruscha, Statistisches Methodenbuch, Springer, Heidelberg, 2006, p. 108.