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Effects of temperature uncertainty on the performance of a degrading PEM fuel cell model

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ABSTRACT

The performance of a fuel cell is subject to uncertainties on its operational and material parameters. Among operational parameters, temperature is one of the most influential factors. This work focuses on this parameter. A statistical analysis is developed on the output voltage of proton exchange membrane fuel cell models. The first model does not include any degradation, whereas the second one introduces a degradation rate on the cell active area. To complete the simulation work, a full factorial design is carried out and a statistical sensitivity analysis (ANOVA) is used to compute the effects and contributions of important parameters of the model on the output voltage.

1. Introduction

Proton exchange membrane fuel cells are considered to be reliable for transportation applications due to their low operating temperature and pressure resulting in a possible quick start-up [1,2]. The cell performance can be determined by its output voltage [3,4]. It is mainly controlled by the issues of water and thermal management [5,6]. Thus, studies on PEM modelling for improved water and thermal management were done by Bernadi and Verbrugge [7,8], Springer et al. [9,10], Baschuk and Li [11] and also Rowe and Li [12].

Then, works on parametric analysis for model based design were done by Mishra et al. [13], Mawardi et al. [14] and Min et al. [15]. Those authors considered the different parameters deterministic. Subramanyan et al. [16] were aware of the fact that operating parameters such as temperature are subject to uncertainties. Recently, design of experiment method was used for parametric analysis by Yu et al. [17] and Wu et al. [18].

A mathematical framework that incorporates all the main parameters of a cell and with most terms and coefficients derived from theory and also with empirical parameters for the changing performance is necessary for physics-based simulation and robust design. To achieve this objective, a model developed by Fowler et al. [19] will be used. For the stochastic analysis, the uncertainty on a parameter is at first quantified and then propagated through a deterministic model to build the output distribution. This latter is finally analysed for robust design objectives.

In this present work, the operating parameters with uncertainty are represented as Gaussian and uniform probability distributions. Gaussian distributions are quantified in terms of the mean and variance values and uniform distributions are quantified in terms of lower and upper bounds. A Gaussian distribution is a quasi-realistic approach whereas a uniform distribution is a severe approach. More information about these two distributions can be found in ref. [31].

Parameters are randomly generated with their respective distributions and a semi-empirical model is used for the cell operation. The results of the simulations are used to construct the probability distribution of the output voltage delivered by the cell. Parametric analysis is performed on the output voltage distribution for several values of the input parameters.

The present work is organised as follows: an introduction to uncertainty in systems engineering is described in Section 2 then the semi-empirical PEM fuel cell used for the analysis without considering degradation is described in Section 3 with its stochastical analysis and results. It is followed by the description of a new model based on the first one completed with a degradation of the cell active area in Section 4 with its stochastical analysis and results. Finally, a full factorial design of experiment is made and an analysis of variance (ANOVA) is used to compute the effects and contributions of important parameters of the model to the output voltage in Section 5.

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2. Uncertainty in systems engineering

Uncertainty plays a major role in the analysis of many fields from engineering to economics. Its concepts and ideas have been associated with gambling and games for a long time. The ancient Greeks of the 4th century BC were the first civilization having considered uncertainty primarily in the context of epistemology. In fact, the word "epistemology" is derived from the Greek "episteme", meaning "knowledge", and logos which one meaning is "theory". Epistemology considers the possibilities and limits of human knowledge. Aristotle thought that people should make decisions on the basis of "desire and reasoning to some end" but suggested no guidance to the likelihood of a successful outcome. In spite of considering uncertainty, the Greeks turned to the oracles when they wanted to predict the future [20].

In systems engineering there are two definitions for uncertainty: a rigorous and theoretical one and a more relaxed and practical one [21–23]. The rigorous definition refers to "uncertainty" as "vagueness" or "ambiguity". "Vagueness" is considered as the difficulty of making sharp and precise distinctions in the world. "Ambiguity" refers to "situations in which the choice between two or more alternatives is left unspecified." For Klir and Folger [24], ambiguity is separated into nonspecificity of evidence, dissonance in evidence, and confusion in evidence.

The practical definition refers to "uncertainty" as a distribution of outcomes with various likelihoods of both occurrence and severity. It interferes with the definition of risk which is a measure of uncertainty of achieving an objective. Risk level is determined by the probability of occurrence and the consequences of occurrence. *INCOSE Systems Engineering Handbook* [25] classify risk into technical, cost, schedule and programmatic. The two distinct classifications are in Fig. 1.

In the present work, the practical definition of uncertainty will be used.

3. Nondegrading PEM fuel cell model

The model used for this study is a semi-empirical model of Fowler et al. [19] giving a unique equation that links the voltage delivered by a cell to the inputs parameters. It is useful for introducing for example, a degradation rate and studying its effects on the output voltage.

3.1. Model mathematical equation and its validation

Starting with the general expression for the voltage for a single cell:

$$V_{\text{cell}} = E_{\text{Nernst}} + \eta_{\text{activation}} + \eta_{\text{ohmic}} \tag{1}$$

The meanings of the different terms of Eq. (1) are presented in Table 1. All quantities in Eq. (1) are in units of volts and the overvoltage terms ($\eta_{\text{activation}}$, η_{ohmic}) are all negative (Tables 2 and 3).

For a more accurate model, the concentration overvoltage term $\eta_{\text{concentration}}$ is added to Eq. (1) [26,27] but this term is not taken into account in this model because the current density i will be supposed to be inferior to 1 A cm^{-2} in order to prevent concentration losses.

$$E_{\text{Nernst}} = E_T^0 + \left(\frac{RT}{2F}\right) \times [\ln(P_{H_2} \times P_{O_2}^{1/2})] \tag{2}$$

Numerically, $E_T^0 = 1.229 - 0.85 \times 10^{-3}(T - 298.15)$ and replacing constants by their values, we will have the expression:

$$E_{\text{Nernst}} = 1.229 - 0.85 \times 10^{-3}(T - 298.15) + 4.31 \times 10^{-5} \times T \times [\ln(P_{H_2} \times P_{O_2}^{1/2})] \tag{2'}$$

Table 1
Nomenclature [19].

A	cell active area (cm^2)
$C^*_{H^+}$	proton concentration at the cathode membrane/gas interface (mol cm^{-3})
$C^*_{H_2}$	liquid phase concentration of hydrogen at anode/gas interface (mol cm^{-3})
$C^*_{H_2O}$	water concentration of the cathode membrane/gas interface (mol cm^{-3})
$C^*_{O_2}$	oxygen concentration of the cathode membrane/gas interface (mol cm^{-3})
E_{Nernst}	thermodynamic potential (V)
E_T^0	standard electrode potential
F	Faraday's constant (96487 C eq.$^{-1}$)
i	current density (A cm^{-2})
I	current (A)
k_a^o, k_c^o	rate constants for the anode and cathode reactions, respectively (cm s^{-1})
k_{cell}	empirical term accounting for the apparent rate constants for the anode and cathode reactions
P_{H_2}	partial pressure of hydrogen at anode/gas interface (atm)
P_{O_2}	partial pressure of oxygen at the cathode membrane/gas interface (atm)
l	thickness of the membrane layer (cm)
r_M	membrane specific resistivity for the flow of hydrated protons (Ω cm)
T	cell temperature (isothermal assumption in degrees K)
ΔG_e	standard state free energy of the cathode reaction (J mol^{-1})
ΔG_{ec}	standard state free energy of chemisorptions from the gas state (J mol^{-1})
n_c	number of cells
$R^{\text{electronic}}$	resistance to electron transfer in the graphite collector plates and graphite electrodes
R^{proton}	resistance to proton transfer in the solid polymer membrane
R^{internal}	internal resistance of the membrane
$k2$	empirical parameter representing the ageing of the polymeric membrane (h^{-1})
Greek letters	
α_c	chemical activity parameter for the cathode
ε	diffusivity correction factor
$\eta_{\text{activation}}$	the activation contribution to the cell activation overvoltage (V)
η_{ohmic}	ohmic contribution to cell overvoltage (V)
$\eta_{\text{ohmic}}^{\text{electronic}}$	electronic ohmic contribution to cell overvoltage (V)
$\eta_{\text{ohmic}}^{\text{proton}}$	protonic ohmic contribution to cell overvoltage (V)
$\eta_{\text{concentration}}$	concentration overvoltage (V)
$\xi_1, \xi_2, \xi_3, \xi_4$	empirical coefficients for calculation of activation overvoltage
λ	semi-empirical parameter representing the equilibrium water content of the membrane, H_2O/SO_3^-

$$\eta_{\text{activation}} = \xi_1 + \xi_2 T + \xi_3 T \left[\ln(c^*_{O_2})\right] + \xi_4 T[\ln(I)] \tag{3}$$

where

$$\xi_1 = -\left(\frac{\Delta G_{ec}}{2F}\right) - \left(\frac{\Delta G_e}{\alpha_c n_c F}\right) \tag{3a}$$

Table 2
Values of parameters used.

$P_{H_2} = 1.5$ atm
$P_{O_2} = 1.5$ atm
$\Delta G_e = 237,190$ J/mol
$\Delta G_{ec} = -664, 167.8$ J/mol
$n_c = 1$
$F = 96{,}487$
$k_{\text{cell}} = 0.00295$
$R = 8.3147$
$\alpha_c = 0.5$
$A = 50$ cm^2
$c_{H_2} = 0.85$ mol cm^{-3}
$c_{O_2} = 0.05$ mol cm^{-3}
$i = I/A$