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# A random-effects model for long-term degradation analysis of solid oxide fuel cells

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ABSTRACT

Solid oxide fuel cells (SOFCs) are electrochemical devices converting the chemical energy into electricity with high efficiency and low pollutant emissions. Tough very promising, this technology is still in a developing phase, and degradation at the cell/stack level with operating time is still an issue of major concern. Methods to directly observe degradation modes and to measure their evolution over time are difficult to implement, and indirect performance indicators are adopted, typically related to voltage measurements in long-term tests. In order to describe long-term degradation tests, three components of the voltage measurements should be modelled: the smooth decay of voltage over time for each single unit; the variability of voltage decay among units; and the high-frequency small fluctuations of voltage due to experimental noise and lack of fit. In this paper, we propose an empirical random-effects regression model of polynomial type enabling to evaluate separately these three types of variability. Point and interval estimates are also derived for some performance measures, such as the mean voltage, the prediction of cell voltage, the reliability function and the cell-to-cell variability in SOFC stacks. Finally, the proposed methodology is applied to two real case-studies of long-term degradation tests of SOFC stacks.



## 1. Introduction

A solid oxide fuel cell (SOFC) is an electrochemical device, which directly converts the chemical energy into electricity with high efficiency and low pollutant emissions. Thus, SOFCs are expected to play a significant role in helping to meet the demand of distributed and stationary power generation systems, provided that high reliability levels are demonstrated by this technology. Indeed, due to high operating temperatures, system components are subjected to significant thermo-mechanical stresses which negatively impact performance and lifetimes. Thus, in the last years a big effort was devoted by industrial companies, universities, and research institutions to improve understanding of degradation mechanisms, materials and processes in order to extend durability of SOFC systems (typically stacks of serially connected cells).

In particular, degradation at the cell/stack level is an issue of major concern. A number of features affecting cell/stack degradation have been identified which include: electrode contact loss and increased contact resistance, changes in material composition and structure, interdiffusion, phase changes, and deactivation of catalysts [1]. However, methods to directly observe degradation modes and to measure their evolution over time are difficult or even unfeasible to be implemented, and only indirect cell/stack performance indicators are available. Usually, an overall metric of cell/stack degradation is assumed to be the cell/stack output voltage [2], so that typical degradation studies are based on long-term tests where the cell/stack is operated under steady state conditions and the evolution of its voltage over time is measured. These measurements usually contain information about product reliability. In fact, by defining unit failure in terms of the crossing of a specified level of degradation, a time to failure distribution can in principle be derived from the degradation measurements [3].

Available long-term tests on SOFC stacks revealed that different shapes of the cell/stack voltage as a function of time can be observed, as a consequence of technological state of the art and/or operating conditions. In particular, these shapes can be divided into four different types: two shapes with a significant initial drop (wear-in period), followed either by a long-term linear decay during the remainder of operation or by only a short period of linear decay before the degradation becomes progressive in time (wear-out period); and two other shapes where the long-term behaviour is the same as for the previous ones, but the initial drop is absent [4]. Furthermore, when each single cell in a stack is monitored, a variability of the voltage degradation path is often observed across units, as a consequence of lack of uniformity in the manufacturing process and of different

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**Nomenclature**

*Acronym*

ACF autocorrelation function
AR($q$) autoregressive of order $q$
$CoV(x)$ coefficient of variation at time $x$
d.o.f. degrees of freedom
FGLS feasible generalized least squares
GLS generalized least squares
i.i.d. independent identically distributed
OLS ordinary least squares
SOFC solid oxide fuel cell

*Notation*

$n$; $i$ number of units; subscript denoting the $i$th unit
$m$; $j$ number of measurements; subscript denoting response and covariates levels for the $j$th measurement
$p$ number of parameters in the linear regression model
$\mathbf{x}_j$ $(p \times 1)$ vector of covariate (independent variable) level for the $j$th measurement, common across units
$\mathbf{X} = \begin{bmatrix} \mathbf{x}_1^T \\ \vdots \\ \mathbf{x}_m^T \end{bmatrix}$ $(m \times p)$ matrix of covariate values at which the $m$ observations are taken
$\mathbf{B}$ $(p \times 1)$ vector of r.v.'s, i.e. the coefficients of the linear regression model
$\boldsymbol{\mu}_\mathbf{B}; \hat{\boldsymbol{\mu}}_\mathbf{B} = \sum_{1=1}^{n} \hat{\mathbf{B}}_i / n$ $(p \times 1)$ vector of expected value of $\mathbf{B}$; least squares estimator
$\boldsymbol{\Sigma}_\mathbf{B}$ $(p \times p)$ covariance matrix of $\mathbf{B}$
$MVN(\boldsymbol{\mu}_\mathbf{B}, \boldsymbol{\Sigma}_\mathbf{B})$ multivariate normal distribution
$\mathbf{B}_i$; $\hat{\mathbf{B}}_i$ $(p \times 1)$ vector of r.v.'s containing sampling realization of $\mathbf{B}$ for unit $i$, $\mathbf{B}_i \sim MVN(\boldsymbol{\mu}_\mathbf{B}, \boldsymbol{\Sigma}_\mathbf{B})$; least squares estimator
$\varepsilon_{ij}$ random error on the true response for $i$th unit at time $x_j$
$\sigma^2 = \text{var}[\varepsilon_{ij}]$ unexplained variance in the regression model, common across units
$\boldsymbol{\varepsilon}_i$ $(m \times 1)$ noise vector for the $i$th unit, $\boldsymbol{\varepsilon}_i \sim MVN(\mathbf{0}, \boldsymbol{\Omega})$
$\boldsymbol{\Omega}$ $(m \times m)$ covariance matrix of $\boldsymbol{\varepsilon}_i$, common across units, $\boldsymbol{\Omega}_i \equiv \boldsymbol{\Omega} = \sigma^2 \mathbf{V}$
$\mathbf{V}$ $(m \times m)$ autocorrelation matrix with $V_{jj} = 1$, $V_{jj}$ being the $(j, j)$ entry of the matrix $\mathbf{V}$
$Y_{ij} = \mathbf{B}_i^T \mathbf{x}_j + \varepsilon_{ij}$ response (dependent variable) level for $i$th unit at time $x_j$
$\hat{Y}_{ij} = \hat{\mathbf{B}}_i^T \mathbf{x}_j$ least squares estimator of the expected response at time $x_j$ for $i$th unit
$\hat{Y}_j = \hat{\boldsymbol{\mu}}_\mathbf{B}^T \mathbf{x}_j$ least squares estimator of the mean regression line at time $x_j$ over the population of items;
$\boldsymbol{\Sigma}_{\hat{\mathbf{B}}|\mathbf{B}}$ $(p \times p)$ covariance matrix of $\hat{\mathbf{B}}_i$, given $\mathbf{B}_i = \mathbf{B}$
$\boldsymbol{\Sigma}_{\hat{\mathbf{B}}} = \boldsymbol{\Sigma}_\mathbf{B} + E_\mathbf{B}\left[\boldsymbol{\Sigma}_{\hat{\mathbf{B}}|\mathbf{B}}\right]$ $(p \times p)$ unconditional covariance matrix of $\hat{\mathbf{B}}_i$

operating conditions across units in the stack [5,6]. This phenomenon appears to be a relevant aspect to be analysed because, in systems comprising groups of stacks, variance in stack characteristics may cause an uneven distribution of load among the stacks which, in turn, may have a negative impact on system performances and durability [7]. Thus, an index able to measure the lack of uniformity and then this quality component of the manufacturing and the assembly process is identified. Moreover, voltage measures are affected by experimental noise, whose primary sources are measurement errors and temperature, pressure and reactant concentration fluctuations during the tests.

### 1.1. Problem statement and related works

The purpose of this paper is modelling the degradation phenomenon of SOFC cells in long runs by analysing voltage measurements, in order to estimate some SOFC performance measures, such as the mean voltage, the future degradation growth (measured by predicting cell voltage), the reliability function, and the cell-to-cell variability related to both the manufacturing process and inhomogeneous operating conditions across the stack.

To this aim, three components of the voltage measurements have to be modelled: (a) the smooth decay of voltage over time for each single unit; (b) the variability of voltage decay among units; and (c) the small fluctuations of voltage superimposed on the smooth decay due to experimental noise. It is worth noting that noise characterization can be useful *per se*. For instance, a change in the noise pattern during operating time may be a signature of a specific degradation phenomenon.

Some attempts have been made to evaluate the long-term decay of cell voltage on a physical or electrochemical basis [8,9], which however fail to satisfactorily reproduce the observed voltage decay over the entire cell life. Degradation phenomena are often analysed by using empirical random-coefficients regression models [3,10–15] or stochastic processes, e.g. Gamma or Extended Gamma processes [16], in absence of mechanistic models. Indeed, in the field of energy systems, a simple empirical model based on a (linear) polynomial regression approach was introduced in [13] to model battery degradation data to the aim of the online estimation of the state of health of the batteries. However, more sophisticated degradation models can be fruitfully selected on the basis of some physical or chemical models describing the dynamics of the system under analysis, when available. In [14], a (nonlinear) random-effects bi-exponential model was introduced to predict the degradation rate of membrane electrode assemblies in direct methanol fuel cells, accounting for two heterogeneous degradation characteristics related to the typical chemical reactions and the kinetics of current density in the system. Estimation procedures are performed on some response time series affected by independent identically distributed (henceforth i.i.d.) random errors. A model combining polynomial and exponential functions has been also proposed in [15], focusing on the residual performance of lithium-ion batteries, whose parameters are adjusted online by a particle filter on measurements corrupted by an i.i.d. noise sequence.

### 1.2. The case studies and the rationale behind the modelling approach

The data sets under analysis are part of a larger data set provided by the Swiss company HEXIS AG to the Consortium of the GENIUS project, a European Community-funded research project, on the diagnosis of SOFC systems. Data refer to two different SOFC systems: an early generation system (henceforth *case study A*) and a subsequent evolution (henceforth *case study B*). Because of industrial reserve reasons, the original voltage and time values have been rescaled in the present paper. Rescaled voltage time series are reported in Fig. 1, together with the corresponding estimated empirical models. Case study A shows some initial drop, while in the case study B the wear-in period is practically absent; in both cases, a long-term almost linear decay is present in most