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Statistical analysis of the effect of temperature and inlet humidities on the parameters of a semiempirical model of the internal resistance of a polymer electrolyte membrane fuel cell

J.J. Giner-Sanz, E.M. Ortega, V. Pérez-Herranz*

IEC Group, Depto. Ingeniería Química y Nuclear, Universitat Politècnica de València, Camino de Vera S/N, 46022 Valencia, Spain

HIGHLIGHTS

- Internal resistance of an individual fuel cell was experimentally measured.
- A semiempirical model was proposed for the internal resistance.
- Experimental data for different operation conditions was fitted to the model.
- The effect of operation conditions was studied using ANOVA.
- Response surface method was applied in order to obtain a regression model.

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ABSTRACT

The internal resistance of a PEM fuel cell depends on the operation conditions and on the current delivered by the cell. This work's goal is to obtain a semiempirical model able to reproduce the effect of the operation current on the internal resistance of an individual cell of a commercial PEM fuel cell stack; and to perform a statistical analysis in order to study the effect of the operation temperature and the inlet humidities on the parameters of the model. First, the internal resistance of the individual fuel cell operating in different operation conditions was experimentally measured for different DC currents, using the high frequency intercept of the impedance spectra. Then, a semiempirical model based on Springer and co-workers' model was proposed. This model is able to successfully reproduce the experimental trends. Subsequently, the curves of resistance versus DC current obtained for different operation conditions were fitted to the semiempirical model, and an analysis of variance (ANOVA) was performed in order to determine which factors have a statistically significant effect on each model parameter. Finally, a response surface method was applied in order to obtain a regression model.

1. Introduction

The need of a clean, efficient and reliable energy vector has led to the development of fuel cell technology [1]. Fuel cells (FCs) are electrochemical devices that transform the chemical energy contained in a fuel, directly into electricity. PEM fuel cells (PEMFCs) are a particular type of FC in which a proton exchange membrane (PEM) is used as electrolyte. In recent years, this type of FC has been considered a very promising alternative for power generation devices for automotive, portable and distributed applications [2]. The main advantages of PEMFCs are their compactness [3], their high power density [4], their light weight and low cost [5], their low environmental load [6,7], and their high efficiency [8,9]. However, there are still issues that have to be tackled in order to make them economically competitive. For this reason, great research efforts have been made in recent years in order to increase the performance [10–13] and the reliability [14–19] of such FCs, and to decrease their cost [20–23].

The internal resistance is a key parameter to characterize the performance of a PEMFC [24], since it determines the ohmic losses within the PEMFC. According to Ohm's law:

$$\eta_{Ohmic} = I \cdot R_{int} \quad (1)$$

Where η_{Ohmic} denotes the ohmic overvoltage; I stands for the current delivered by the PEMFC; and R_{int} corresponds with the internal resistance of the PEMFC. This parameter encompasses 3 major contributions: the electronic resistance (R_{int}^{ele}), the ionic resistance (R_{int}^{ion}), and the contact resistance (R_{cont}). On the one hand, R_{int}^{ele} arises from the

* Corresponding author.
E-mail address: vperez@iqn.upv.es (V. Pérez-Herranz).

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resistance to the electron flow in the electronic conductors of the PEMFC (e.g. graphite electrodes and current collectors). On the other hand, R_{int}^{ion} arises from the resistance to protonic flow in the ionic conductors of the PEMFC (e.g. PEM membrane). Finally, R_{cont} corresponds with the contact resistance between the different conductors of the PEMFC. The internal resistance of a PEMFC depends mainly on the operation conditions and on the polarization current at which the fuel cell is operated [25].

A large variety of PEM resistance models can be found in literature [26]. These models can be classified in two main types: microscopic and macroscopic models. On the one hand, microscopic models [27–34] try to explain the trends in PEM resistance starting from the ion/solvent/polymer interactions in the molecular level (v.g. Grotthus mechanism). On the other hand, macroscopic models relate PEM resistance to macroscopic variables, such as the water content of the membrane, the current delivered by the PEMFC or the temperature. In this type of PEMFC internal resistance models, several groups can be identified. The simplest one is the constant resistance model [35], in which the resistance of the membrane is considered as a constant. Some authors [36] modify the constant resistance model considering an Arrhenius-like-expression for modelling the effect of the temperature on the PEMFC internal resistance. Another group of macroscopic internal resistance models [37–41] is formed by the models that are based on the empirical model proposed by Amphlett and co-workers [42]. This model consists in a quadratic regression model with two independent factors: temperature and delivered current. In many cases, the quadratic (T^2 and I^2) and the interaction ($T\cdot I$) terms are neglected [39]. This assumption reduces the model to a simple linear regression model [43]. The parameters of the empirical model can only be obtained by fitting the model to experimental data. Other macroscopic internal resistance models that have extensively been used in literature are the diffusive flow type models [44–46], and the hydraulic flow type models [47–49]. The diffusion models are based on the empirical expression proposed by Springer and co-workers [44], or on one of its variants. These empirical expressions relate the membrane resistivity with its water content. Some works [50] consider the water content parameter as an adjustable parameter; while others [51–53] calculate it using the expression relating the water content parameter with the water vapour activity, presented in Ref. [54]. Meanwhile, the hydraulic models are based on the model developed by Bernardi and Verbrugge [47]. Apart from these main types of macroscopic models, other less common models can be found in literature, such as models that use the chemical potential as the driving force [55–57], or two-phase models [58] that include the simultaneous presence of liquid water and vapour in the PEM.

The goal of this work is to obtain a semiempirical model able to simulate the effect of the operation current on the internal resistance of a single cell of a 300 W commercial PEMFC stack; and to study the effect of the operation conditions (temperature and inlet humidities) on the parameters of the proposed semiempirical model. The present study is based on the diffusive flow type model developed by Springer et al. [44]. This work's objective is to build a simple semiempirical model able to predict the internal resistance of a PEMFC, and to validate it using experimental data. In order to fulfil this goal, the internal resistance of a single cell of a commercial PEMFC stack was measured experimentally by electrochemical impedance spectroscopy (EIS) at different operation currents, and at different operation conditions (temperature and inlet humidities). A semiempirical model was proposed in order to reproduce the effect of the operation current on the internal resistance. The proposed semiempirical model was fit to the R_{int} vs I experimental curves obtained for different operation conditions. In this way, the value of the model parameters was obtained for different temperatures and inlet humidities. Finally, a statistical analysis was performed on the obtained results, in order to determine the effect of the operation conditions on the parameters of the semiempirical model. Firstly, an analysis of variance (ANOVA) analysis was performed in order to determine which operation conditions have a statistically significant effect on each model parameter. Then, a surface response method was applied in order to obtain a black box model relating each model parameter to the operation factors that have a significant effect on it.

2. Experimental design

A full 2^3 replicated factorial design with centerpoint was used in this work. This kind of experimental design consists in an experimental design where 3 factors are studied at 2 levels: level -1 and level $+1$. On the one hand, full factorial designs involve running in each replicate, all the 2^3 combinations of 3 factors at 2 levels. On the other hand, replication consists in the repetition of the whole set of treatments defined in the factorial design. Finally, a centerpoint consists in a treatment in which all factors are at level 0, defined as the arithmetic mean of levels -1 and $+1$. One of the main reasons for including centerpoints in an experimental design is that they allow to identify curvatures in the output variables. This experimental design is much more efficient than the traditional sequential experimental design, since it requires fewer experiments to analyse a given number of input factors, and it allows to study the interaction between the considered factors [59].

The three factors that were considered in this work were the operation temperature, the humidity of the hydrogen inlet, and the humidity of the air inlet. Table 1 sums up the 3 levels considered for each one of these factors. On the one side, the temperature levels were selected according to the nominal temperature operation range of the commercial PEMFC. On the other side, as it will be explained in section 3, the experimental setup allows to control the humidification temperatures, and not directly the inlet gas humidities. Preliminary experimentation was performed in order to obtain the relation between the gas humidity and the humidification temperature. Level $+1$ of the humidity factors were selected considering a humidification temperature of $70°C$, the maximum humidification temperature allowed by the humidification system. While level -1 of the humidity factors were selected considering a humidification temperature of $30°C$. In this work, all the humidities are expressed as absolute humidities, in units of $g_{H_2O}\cdot g_{dry\ gas}^{-1}$.

In this work, experiments were identified with a sign triplet, in which each sign denotes the level of the corresponding experimental factor. For instance, experiment (-;-; +) denotes the experiment in which the operation temperature is in level -1 (30 °C), the hydrogen humidification temperature is in level -1 (30 °C), and the air humidification temperature is in level $+1$ (70 °C).

3. Methodology and experimental procedure

First, for each one of the 18 treatments (set of operation conditions) considered in this work's experimental design, the internal resistance of an individual cell of a commercial PEMFC stack was experimentally measured for different operation currents. In order to achieve this, the electrochemical impedance spectrum of the individual cell was measured at different polarization currents, for each one of the experiments considered in the experimental design. The EIS measurements were done using the experimental setup shown in Fig. 3 of reference [60].

The main element of the experimental setup is a 300 W commercial

Table 1
Quantitative values of the encoded factor levels.

Factor	Level -1	Level 0	Level $+1$
Temperature ($°C$)	30	50	70
Hydrogen humidity ($g_{H_2O}\cdot g_{dry\ H_2}^{-1}$)	0.28	1.26	2.25
Air humidity ($mg_{H_2O}\cdot g_{dry\ air}^{-1}$)	3.5	9.8	16.0