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Generalized scaling-up approach based on Buckingham theorem for Polymer Electrolyte Membrane Fuel Cells impedance simulation

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Abstract

The present paper describes a generalized scaling-up methodology applied to Polymer Electrolyte Membrane Fuel Cells. The use of proper scaling-up algorithms can reduce testing costs within fuel cell manufacturing process by evaluating full stack performance (i.e., impedance behavior) from a single cell/short stack measurement. The algorithm here described relies on a former approach developed by the authors and consists in a generalized methodology combining information measured on single cell and simple physical models (e.g., charge transfer resistance expressed through Tafel equation). A robust technique for the identification of cell reference operational state, such as membrane hydration, from non-scaled data is also introduced. Connection between charge transfer resistance and limiting current is established through diffusion losses modelling. Single cell internal states are estimated by means of inverse models function of numerical intercepts of measured cell spectrum. Stack impedance estimation is then performed through stack internal states assumptions. To prove the consistency and robustness of the proposed methodology, literature data used to design and test the former algorithm version are here considered for algorithm testing and verification.

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1. Introduction

The manufacturing process of Proton Exchange Membrane Fuel Cell (PEMFC) stacks generally entails the following consecutive steps: i) single cells production, ii) stack assembly and iii) stack testing and conditioning [1].

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Each step has a specific cost, which depends on consumed materials as well as basic manufacturing procedures scheduling and time. According to a cost analysis carried out in 2016 by the Battelle Institute for the U.S. Dept. of Energy [1], testing and conditioning costs related to a 60 kW stack for stationary applications (i.e., backup or Combined Heat and Power – CHP – uses) may go from 4% (100 produced units) to 1.6% (50000 produced units) of the overall stack cost. Stack testing required proper devices capable of performing correctly stack conditioning and performance assessment, so as to determine the quality of the stack and if it can be installed into the system. It is clear that the choice of device type, amount of reactants to be provided and time required for the testing process depend on the stack size, which then influences the overall test and conditioning procedure cost.

The scaling-up approach introduced in a previous authors' work [2] offers an innovative methodology to reduce stack testing costs since it allows stack performance estimation by scaling in size the performance related to a single cell or a shorter stack from the same technology. This advantage implies that a direct testing of full stack is not necessary and, consequently, a smaller testing device type and less reactants are required. Nevertheless, the limitation of the proposed approach resides in the use of non-general models that must be formerly identified over the tested technologies before scaling-up application. This requires a wide amount of experimental data that may be difficult to retrieve or, in the case of new technologies, not yet available. Moreover, the internal state (i.e., humidification, reactants distribution, etc.) of the single cell to be scaled is assumed known according to hypothetical reasoning, without a specific estimation, thus incurring in less robust performance assessment.

To overcome these issues, an improved approach is here presented, in which two main features have been introduced: i) a more generalized modelling framework is taken into account in order to reduce methodology dependence over experimental data, and ii) single cell internal states are specifically retrieved from the available experimental data used for the scaling-up approach. These improvements are illustrated in the following, after a brief overview of the scaling-up methodology, and the performance assessment of the new approach is tested on the same data used for the design and verification of the former approach, so as to check algorithm consistency.

2. Scaling-up approach description

The proposed scaling-up approach is based on the Buckingham's π Theorem, through which it is possible to describe the link between the physical variables involved in the problem and their fundamental dimensions. This link is represented by non-dimensional parameters that allow the scaling of such variables by means of proper physical assumptions. For a given problem with a dependent variable y function of n-1 independent variables x_1 through x_{n-1}:

$$y = f\left(x_1, ..., x_{n-1}\right) \tag{1}$$

and being v the number of the involved fundamental dimensions, the number of the non-dimensional parameters that can be defined is:

$$p = n - k \tag{2}$$

where $k \leq v$ represents a complete and dimensionally independent subset of the n variables describing the problem.

The non-dimensional parameters π are then evaluated as the ratio between each remaining variable not included in the k subset and the product of the k variables raised to exponents α that bring to zero the dimension of the parameter:

$$\pi_0 = \frac{y}{\prod_{j=1}^{k} x_j^{\alpha_j}}; \quad \pi_i = \frac{x_i}{\prod_{j=1}^{k} x_j^{\alpha_j}} \tag{3}$$

where π_0 represents the non-dimensional parameter related to the dependent variable y and can be also expressed as function of all the other parameters:

$$\pi_0 = f\left(\pi_1, ..., \pi_{p-1}\right) \tag{4}$$

The problem accounted in this work, and extensively discussed in [2], involves the representation of a PEMFC impedance by means of electrochemical and physical variables. The achieved non-dimensional parameters are illustrated in the following.

2.1. Problem formulation and non-dimensional groups estimation

The complex impedance Z of a PEMFC is here expressed as function of equivalent cell resistance R_{eq} and capacitance C, current I and frequency ω at which the impedance measurement has been carried out and the fuel cell surface area A_{fc} of the cell ($n = 6$):

$$Z = f\left(R_{eq}, C, \omega, I, A_{fc}\right) \tag{5}$$

The involved fundamental dimensions are mass [M], length [L], current [I] and time [T] ($v = 4$), and a possible subset of variables can include R_{eq}, ω, I and A_{fc} ($k = 4$). Therefore, the number of non-dimensional parameter is $p = n - k = 6 - 4 = 2$. According to the procedure illustrated in [2], the non-dimensional parameters are:

$$\pi_0 = \frac{Z}{R_{eq}}; \quad \pi_1 = CR_{eq}\omega \tag{6}$$

As can be argued from equation (6), the evaluation of the non-dimensional parameters requires information from the performed measurements, in terms of impedance Z and frequency ω, and specific electrochemical parameters, i.e., the equivalent resistance R_{eq} and capacitance C.

2.2. Parameters modelling

Focusing on the impedance reconstruction, the non-dimensional parameter π_0 only requires the definition of the equivalent resistance R_{eq} that can be modelled as summation of the membrane resistance R_m and the charge transfer resistance R_{ct}:

$$R_{eq} = R_m + R_{ct} \tag{7}$$

The membrane resistance is modelled following the model proposed by Springer et al. [3]:

$$R_m = \frac{t_m}{\sigma_m}\frac{1}{A_{fc}} \tag{8}$$

with t_m and σ_m being the membrane thickness and water conductivity, respectively. This latter parameter can be modelled as function of water content λ_m and fuel cell operating temperature T_{fc} as follows [3]:

$$\sigma_m = \left(0.005139\lambda_m - 0.00326\right)\exp\left[1268\left(\frac{1}{303}-\frac{1}{T_{fc}}\right)\right] \tag{9}$$

The first improvement with respect to the approach presented in [2] consists in the generalized modelling of the charge transfer resistance, achieved as the derivative in current of activation and diffusion losses expressed as [4]:

$$\begin{aligned} V_A &= \frac{\bar{R}T_{fc}}{2\alpha F}\log\left(\frac{I}{I_0}\right) \\ V_D &= \frac{\bar{R}T_{fc}}{2F}\log\left(\frac{I_L}{I_L - I}\right) \end{aligned} \tag{10}$$

Thus, the final model is:

$$R_{ct} = \frac{d}{dI}\left(V_A + V_D\right) = \frac{\bar{R}T_{fc}}{2F}\left(\frac{1}{\alpha I}+\frac{1}{I_L - I}\right) \tag{11}$$

Considering known current I and temperature T_{fc} from the measurements, the only unknown parameters are the membrane water content λ_m and the limiting current density I_L. The second innovation introduced in this work consists in the identification of such variables from the measured impedance.

Being R_{HF} and R_{LF} the measured impedance values with zero imaginary part at high and low frequency, respectively, the membrane water content λ_m and the limiting current density I_L are estimated as:

$$\lambda_m = 194.59\frac{t_m}{R_{HF}A_{fc}}\exp\left[-1268\left(\frac{1}{303}-\frac{1}{T_{fc}}\right)\right] + 0.634 \tag{12}$$

$$I_L = I + \frac{\bar{R}T_{fc}\alpha I}{2\alpha F I\left(R_{LF} - R_{HF}\right) - \bar{R}T_{fc}} \tag{13}$$

and the equivalent resistance R_{eq} can be then computed. It is worth noting that the terms R_{HF} and R_{LF} can be directly used to estimate fuel cell membrane and equivalent resistance R_m and R_{eq}. Nevertheless, the evaluation of λ_m and I_L is fundamental for the scaling up process, since they give specific information on the internal state of the single cell. From their values, the impedance scaling is achieved through reasoned assumptions of water content and limiting current distribution from cell to stack, as illustrated in the following section.

2.3. Impedance scaling-up process

The impedance reconstruction of a full stack is achieved from the non-dimensional parameter π_0 evaluated through equation (6), the R_{eq} model of equation (7) and the water content and limiting current values obtained through equations (12) and (13), respectively. Assuming that for the first and last cells λ_m and I_L values are:

$$\lambda_m^{C_1} = \lambda_m\left(1-\Delta\lambda_m^{low}\right);\quad \lambda_m^{C_N} = \lambda_m\left(1+\Delta\lambda_m^{up}\right);\quad I_L^{C_1} = I_L\left(1-\Delta I_L^{low}\right);\quad I_L^{C_N} = I_L\left(1+\Delta I_L^{up}\right) \tag{14}$$

and introducing a linear distribution within the stack, the i-th cell shows the following internal properties:

$$\lambda_m^{C_i} = \frac{\lambda_m^{C_N} - \lambda_m^{C_1}}{N-1}(i-1) + \lambda_m^{C_1}$$
$$I_L^{C_i} = \frac{I_L^{C_N} - I_L^{C_1}}{N-1}(i-1) + I_L^{C_1} \quad (15)$$

From these values, the i-th conductivity can be evaluated introducing $\lambda_m{}^{Ci}$ in equation (9) and then the related membrane and charge transfer resistances, and in turn the equivalent resistance, can be computed through equations (8), (11) and (7), respectively. The overall equivalent stack resistance is then:

$$R_{eq}^S = \sum_{i=1}^{N} R_{eq}^{C_i} \quad (16)$$

and the scaled-up impedance is evaluated as:

$$Z^S = \pi_0 R_{eq}^S \quad (17)$$

3. Scaling-up methodology verification

The verification of the algorithm has been performed on the same experimental data of Westerlain et al. [5], already used for the testing of the former algorithm version [2]. The reference physical and operational parameters are illustrated in Table 1.

Table 1. Physical and operational parameters related to the experimental activity of Wasterlain et al. [5].

Parameter	Value
Operating temperature T_{fc}	80°C
Operating current I	50 A
Cells number N	20
Fuel cell area A_{fc}	100 cm^2

The single cell impedance spectrum represented on a Nyquist plot, from which the non-dimensional parameter has been calculated, is shown in Fig. 1-a with red line and circle markers. In the same figure, the R_{HF} and R_{LF} significant points are also highlighted. From these points, the following internal properties are obtained: $\lambda_m = 13.4$ and $I_L = 51.6$ A. According to the stack configuration illustrated in [5], the single cell impedance reported in Fig. 1-a refers to the cell located at air inlet/H_2 outlet side. This means that this cell may experience hydrogen diffusion problems due to some water accumulation and a hydrogen flow reduction with respect to the cells located at the H_2 inlet. Nevertheless, since most of the produced water accumulates at the cathode side, the overall humidification of this cell could be also lower than that of the other cells (although more water may be present at anode side).

According to these observations (also supported by the comments given in [5]), it is assumed that the membrane humidification and limiting current experienced by the single cell are the lowest of the stack, meaning that $\Delta\lambda_m{}^{down} = \Delta I_L{}^{down} = 0$. Then, it is also considered that the cell at the opposite edge has an optimal humidification level (i.e., $\lambda_m = 14$), which is about 5% higher than the reference cell, implying $\Delta\lambda_m{}^{up} = 0.05$. With respect to limiting current, the opposite cell shows as well a higher limiting current, since more hydrogen is provided, and an increase of about 8% (i.e., $\Delta I_L{}^{up} = 0.08$) is assumed. Then, according to the values reported in Table 1, the scaling-up process is applied and the related results are illustrated in Fig. 1-b. It can be observed that the scaled stack impedance Z^S computed through equation (12) has a good similarity with the experimental stack impedance from [5], in line with the results obtained with the former approach described in [2]. A comparison with the single cell spectrum multiplied with the cells number N is also shown, to further highlight the robustness of the approach. Overall, it can concluded that the

introduced simplifying assumption on the linear distribution of key internal state variables, such as water content [6] and limiting current, is suitable for the targeted scaling-up deployment of proposed Buckingham-based generalized modeling and reconstruction of PEM EIS spectra. Furthermore, upon extension of spectra reconstruction to faulty cells/stacks [7], it is envisaged that the reduced complexity achieved via non-dimensional analysis will significantly help develop advanced online applicable diagnostic algorithms [8][9]. Moreover, the use of detailed modelling of degradation mechanisms affecting voltage behavior, such as those illustrated in [10], may also allow the application of the proposed approach in conjunction with model-based prognostic algorithms.

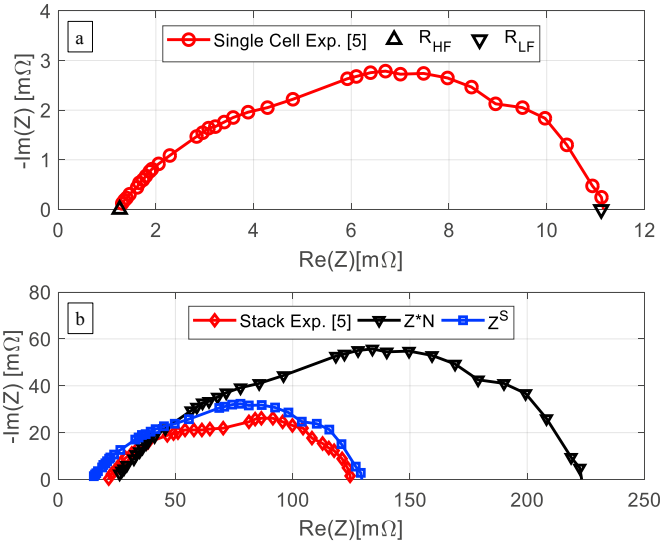

Fig. 1. Identification of significant points R_{HF} and R_{LF} on single cell impedance Z (a) and reconstruction of stack impedance Z^S (b), with comparison to the cell impedance times the cells number N. Experimental data taken from Wasterlain et al. [5].

4. Conclusions

In this paper, an improved approach for fuel cell impedance scaling-up has been presented. The procedure shows two main innovations: i) a generalized modelling for the computation of the non-dimensional parameters is introduced, so as to avoid the need for further experimental data for modelling characterization; ii) the evaluation of cell internal states through parameters extraction from reference cell impedance measurement. Concerning the first point, a detailed connection between charge transfer resistance and limiting current has been introduced through diffusion losses modelling and derivative. The estimation of cell internal states is then performed upon inverse modelling of water content and limiting current density as function of high and low frequency intercepts of the measured cell spectrum. Afterwards, scaling-up stack impedance estimation was performed through water content and reactants internal distribution assumption. The improved algorithm has been tested on the same experimental data used for the former version design and validation, proving its performance and robustness.

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