



Mechanistic equivalent circuit modelling of a commercial polymer electrolyte membrane fuel cell



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HIGHLIGHTS

- 12 different EECs were proposed for an individual cell of a commercial PEMFC.
- The EECs were fitted to experimental EIS spectra.
- A preselection was done based on goodness-of-fitting parameters.
- The selection was refined using mechanistic arguments.
- The selected EEC fits perfectly the spectra, and has physical meaning.

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ABSTRACT

Electrochemical impedance spectroscopy (EIS) has been widely used in the fuel cell field since it allows deconvolving the different physic-chemical processes that affect the fuel cell performance. Typically, EIS spectra are modelled using electric equivalent circuits. In this work, EIS spectra of an individual cell of a commercial PEM fuel cell stack were obtained experimentally. The goal was to obtain a mechanistic electric equivalent circuit in order to model the experimental EIS spectra. A mechanistic electric equivalent circuit is a semi-empirical modelling technique which is based on obtaining an equivalent circuit that does not only correctly fit the experimental spectra, but which elements have a mechanistic physical meaning. In order to obtain the aforementioned electric equivalent circuit, 12 different models with defined physical meanings were proposed. These equivalent circuits were fitted to the obtained EIS spectra. A 2 step selection process was performed. In the first step, a group of 4 circuits were preselected out of the initial list of 12, based on general fitting indicators as the determination coefficient and the fitted parameter uncertainty. In the second step, one of the 4 preselected circuits was selected on account of the consistency of the fitted parameter values with the physical meaning of each parameter.

1. Introduction

Fuel Cells (FCs) are electrochemical devices that are able to directly transform the chemical energy of the fuel oxidation reaction into electricity [1]. In the last decades, Proton Exchange Membrane FC (PEMFC) have raised as promising alternatives for power generation devices for automotive, portable and distributed applications [2], on account of their high power density, compactness and light weight [3,4]. In recent years, a great amount of research has been focused on increasing the performance [5] and the durability of PEMFC [6], and on decreasing their cost [7]. Numerous studies have focused on the different elements of a FC: membranes [8,9], gas diffusion layers [10–14], catalyst layers [15–18], and flow fields [19].

The main characteristic of a FC is its polarization curve, which corresponds with the steady state measurement of the cell voltage versus the delivered current intensity [20]. However, this steady state measurement does not allow the distinction of single processes. If single loss factors have to be distinguished, dynamic measurements are needed [21]. Nowadays, Electrochemical Impedance Spectroscopy (EIS) has gained significant relevance in the FC field, since this dynamic electrochemical measurement technique allows to obtain information on the fuel cell internal state and on its electrochemical behavior [22,23]. This technique provides meaningful information for both, the development and the operation of FCs. On the one hand, from the operator's point of view, EIS allows to determine the humidification level of the membrane and if the gas diffusion layers are flooded. On the

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other hand, from the developer's point of view, EIS is useful in order to quantify the charge transfer, the contact, and the mass transport resistances; assessing in this manner, any of the designed elements [24]. The wide range of applications of EIS within the FC field is due to the fact that this electrochemical method is able to deconvolve the different physico-chemical phenomena that take place in the system at different timescales [25]; allowing to obtain a large number of electrochemical properties of the system such as electrolyte properties (i.e. ohmic resistance and proton conductivity), electrode properties (i.e. double layer capacitance and charge transfer resistance), and mass transport properties (i.e. diffusion coefficients and effective concentrations) [26].

EIS is a frequency domain method that consists in the application of a monofrequency sinusoidal perturbation signal (voltage or current) to a given system; and the measurement of the generated output signal (current or voltage) [27,28]. From the ratio of the amplitudes of both signals, and from the phase difference between them, the complex impedance of the system at the excited frequency is determined [29]. A frequency sweep is performed: the process is repeated for different perturbation frequencies [30]. With this procedure, the EIS spectrum of the system, consisting in the complex impedance of the system at the different excited frequencies, is obtained [31].

One possible way to interpret an EIS spectrum is in terms of models. There are two types of models for interpreting EIS data [32]: analogs and physical models. On the one hand, analogs, generally in the form of electrical equivalent circuits (EEC), follow an empirical modelling methodology: they just seek to reproduce the experimental behavior of the impedance, without considering the physico-electrochemical properties of the system. This modelling strategy has been used in a great number of works in literature [33–45]. The great advantage of this type of models is that they do not require nearly any knowledge of the system: an EEC can be proposed just by pattern recognition, without identifying any of the real processes that take place in system [29]. In return, this type of model does not provide any insight of the mechanisms of the phenomena that take place.

On the other hand, physical models try to reproduce the impedance behavior of the system by taking into account the physical mechanism of the different electrochemical processes. De Levie was the pioneer of this approach [46]: he determined the analytical solution for the impedance model of a porous electrode subject to a potential gradient, considering linear kinetics and no concentration differences [47]. Lasia extended this model in order to consider Butler-Volmer kinetics [48], and to consider concentration gradients [49]. The aforementioned porous electrode model with concentration gradient is the foundation of now-a-days impedance models [46]. Springer and co-workers developed one of the first PEMFC impedance models [50], which consisted in a 1D macro-homogeneous model of the gas diffusion layer and the catalyst layer of a PEMFC. Guo and White extended Springer's model, considering a flooded agglomerate model for the catalyst layer [51]. Kulikovski developed an analytical impedance model for catalyst layers of PEMFCs [52–55]. All the works mentioned above focus mainly on charge and mass transport. Other works have focused on the low-frequency behavior of PEMFCs (i.e. low-frequency inductive semi-circle). Some of them have attributed the low-frequency features to water transport phenomena [56–60]; others have attributed them to ORR intermediated buildup [61–63]; and finally, others have attributed them to PtO formation [62,64]. Extensive reviews on the state-of-the-art PEMFC impedance modelling can be found in literature [36,65,66]. The advantage of this type of models is that it allows unveiling and studying the different electrochemical processes taking place in the system. However, real physical models can be hard to obtain, especially for complex electrochemical processes [30].

In this work, a semiempirical modelling methodology was selected. This hybrid between the analog and the physical model combines the advantages of both methodologies. The semiempirical model considered in this case was a mechanistic EEC: an EEC which elements have clearly defined mechanistic physical meanings. This work's aim is to

obtain a mechanistic EEC for an individual cell of a commercial PEMFC stack. In order to fulfil this goal, the experimental EIS spectrum of the considered system was measured. Then, different mechanistic EECs were proposed and fitted to the experimental spectrum. The EEC that resulted in a better fitting and whose fitted parameters had physically consistent values was selected.

2. Experimental work

Fig. 1 shows the experimental setup used in this work. Its main element is a 300 W commercial PEMFC stack, provided by Heliocentris[®], composed by 20 individual cells, with an effective area of 58 cm². The air supply is provided by a compressor and the hydrogen comes from a 200 bar high-pressure storage tank. The humidification of the gas inlets is assured by a humidification system and the fuel cell stack operating temperature is controlled by a refrigeration system. The humidification system consists in two independent bubbling humidification systems, with humidification temperature control. And the refrigeration system consists in a heat exchanger equipped with a continuous pump and a temperature controller. The reactant gases flow rates are controlled using mass flow controllers. The reactant inlet pressures are monitored by pressure gauges and are regulated using manual valves. All the relevant system temperatures are monitored by thermocouples. The overall control was done using a control computer with a Labview[®] application. All the experiments were carried out in open end anode mode, with constant inlet reactant flow rates: 5 NL·min⁻¹ for the hydrogen stream and 35 NL·min⁻¹ for the air stream. All the experiments were performed in the same operation conditions: an operation temperature of 30°C; and the same humidification temperature for both gases, 30°C.

The individual cell galvanostatic impedance spectra were obtained using an Autolab[®] 302 N potentiostat/galvanostat with FRA module and 20A booster, controlled using NOVA[®] software. The selected frequency range extended from 5 kHz to 10 mHz, with 50 frequencies logarithmically spaced. The spectra were measured for 3 different polarization currents: 1 A ($\approx 17 \text{ mA}\cdot\text{cm}^{-2}$), 4 A ($\approx 69 \text{ mA}\cdot\text{cm}^{-2}$) and 8 A ($\approx 138 \text{ mA}\cdot\text{cm}^{-2}$); and with the optimum perturbation amplitude determined in a previous work [67]. Table 1 lists the measurement parameters used to perform the EIS measurements in this work; they correspond with the optimum measurement parameters obtained in a previous work [68].

The I-V polarization curve was obtained by galvanodynamic sweep. The intensity sweep was done in increasing sense, starting at 0.0 A; with a sweep speed of 3.0 mA·s⁻¹, since it was observed in preliminary studies that this sweep speed was slow enough to reach the quasi steady state for each applied current. The DC resistance for each considered operation current was obtained from the slope of the polarization curve at the corresponding operation point [69].

The I-V polarization curve and the EIS spectra at the 3 considered operation currents were obtained in triplicate in order to control the reproducibility of the obtained results. Replicates of each measurement were not performed sequentially; instead, the order of the experiments was randomized. The randomization strategy allows to orthogonalize the studied factors and the time factor: therefore, it allows identifying any possible time drifts.

A 15 min preconditioning was performed before each measurement in order to assure that the state of the system was the same in all the experiments. The preconditioning was done at the DC current associated to the experiment that was going to be performed; and at 1.0 A, in the case of the polarization curves.

3. Results and discussion

3.1. Experimental EIS spectra

Fig. 2 shows the experimental EIS spectra of the studied single

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