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A hybrid method combining genetic and Nelder-Mead algorithms for the interpretation of electrochemical impedance data - application to Proton Exchange Membrane Fuel Cells

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Abstract - Electrochemical Impedance

Spectroscopy (EIS) is a technique commonly used for characterizing electrochemical systems such as fuel cells, supercapacitors or batteries [1]–[3]. Modeling of the experimental results is mostly done under the form of equivalent electrical circuits (EEC) aiming to represent the charge and mass transport phenomena and electrochemical reactions occurring at the material scale inside the individual components of the electrical components, such as resistors, capacitances, etc.

It is necessary to use a numerical solver to estimate the values of the model parameters starting from experimental data. Traditional methods use deterministic algorithms, which makes the results highly dependent on the initial values chosen as starting points. Obtaining reliable and consistent results even requires sometimes to analyze separately the low, intermediate and high frequencies regions of the impedance spectra [4], [5]. In this work, we propose to use a hybrid method combining a genetic algorithm (GA) with a deterministic Nelder-Mead (NM) algorithm. The GA is used for a first estimate because of the main advantages it offers as a global optimization method: it does not require initial values for parameter estimation and is also robust and well adapted for problems with -possibly- multiple solutions. However, GA are well known to require many iterations and are therefore rather slow when

some of the optimization parameters are -even partially- correlated [6]. This is the reason why the GA was combined with a NM algorithm to accelerate convergence. Both types of algorithms were taken from MATLAB standard libraries.

This hybrid GA-NM method is used mainly to interpret the data measured on Proton Exchange Membrane Fuel Cells (PEMFC), which are generally modeled with Randles-type circuits or Transmission Line Models [7], depending on the shape of the spectra at high frequencies. Such EEC include at least 5 and sometimes up to 12 parameters.

The results show that the combined GA-NM method converges toward satisfying solutions in most of the cases, with low least-square residuals, including when the range of parameter values is unknown and/or when the sensitivity of some of them is low.

Keywords—electrochemical impedance spectroscopy, equivalent electrical circuit modeling, proton exchange membrane fuel cells, genetic algorithm, Nelder-Mead algorithm, least-square fitting.

I. INTRODUCTION

EIS is based on the application of small amplitude sinusoidal variations of the electrical current (potentiostatic mode) or voltage (galvanostatic mode) around a given operation point. The response, assumed

linear, is used to determine a transfer function, i.e. the impedance. The impedance depends on the frequency at which the perturbation is applied, as well as on the system operating point. It is a complex number, often represented in a Nyquist plot (negative of the imaginary part vs. real part), allowing to analyze the phenomena occurring in the system in the frequency domain according to the shape, or other typical characteristics (inflexion points, radii, etc.) of the spectra.

Modeling of the experimental results, i.e. of the impedance spectra, is mostly done under the form of equivalent electrical circuits (EEC) aiming to represent the charge and mass transport phenomena as well as the electrochemical reactions occurring in the components of the system using -more or less- simple electrical components, such as resistors, capacitances, etc. The most used EEC with PEMFC are the Randles circuit and the Transmission Line Model (TLM) suitable for thin and thick electrodes, respectively. The TLM is a generalization of the Randles circuit [7], taking into account the electrical potential variation through the electrode thickness. Then, mass transport limitations at low frequencies, are usually accounted for by adding a finite **Warburg** element in the EEC. The Warburg impedance is based on the hypothesis of Fickian diffusion, surface reaction and constant gas concentration at the interface with the gas channel [8]. This element can be placed in series with the charge transfer resistance (in the case of the Randles circuit) or in series with the **Cathode Catalyst Layer** (CCL) circuit, depending on which is the most limiting layer for gas diffusion: the CCL or the **Gas Diffusion Layer** (GDL) [7].

The identification of EEC parameters requires the use of **Least-Square** (LS) fitting algorithms, minimizing the global difference between the experimental data and the EEC impedance. One of the most common LS fitting algorithms is the **Nelder-Mead algorithm** using the concept of simplexes [9]: a determinist and local method, which always converges to the same, and nearest minimum, starting from input (initial) values. On the other hand, **Genetic Algorithms** are global stochastic algorithms inspired by the theory of natural evolution of Charles Darwin. A group of individuals is generated randomly at the beginning of each execution, each one being associated with a fitness value calculated using the function defined by the user. At each iteration, only a part of individuals, including those with higher fitness value (lower error function) are authorized to reproduce, following a certain way of crossover and mutation. Hence, the population evolves to improve their fitness score from one generation to the other. GA allow thus to explore the entire space of solutions to identify possible multiple local minima, but are therefore much slower

than deterministic algorithms. Another difference between GA and NM is that GA only require a range of variables¹ instead of starting points (NM algorithm can be adapted to look for a minimum over a given variable range but their performances are not very good in these conditions). Both kinds of algorithm can be executed directly by calling the MATLAB functions “ga” and “fminsearch”.

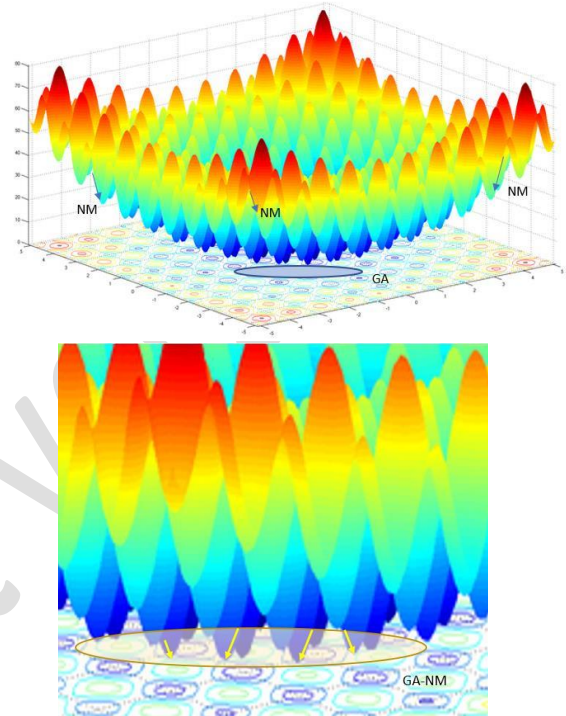


Figure 1: Top: Comparison of GA and NM algorithm, example for a 2-dimension function, bottom: concept of the GA-NM algorithm[10].

Taking figure 1 as an example, NM algorithms will converge rapidly towards the nearest “bottom” of the function, while GA can analyze the entire area and converge to one of the lowest “bottoms” (deep blue ones) [10]. In such a case, if the GA is repeated many times, more than one solution, i.e. some of the best solutions illustrated by the blue circle may be found.

In our work, we mainly focused on the validation of GA-NM algorithm: a combination of these two algorithms, applied to different PEMFC **Membrane-Electrode Assemblies** (AME) and cells, which will be explained in details in the following paragraphs.

II. METHODOLOGY

Both NM and GA algorithms have their advantages and weaknesses. The NM algorithm is rapid and stable in convergence but is very sensitive to the starting point: a tiny change in one parameter initial value could lead to a

¹ The EEC model parameters sent to the algorithms are considered as “variables” of the error function.

completely different result. On the other hand, GA are powerful tools to identify a global minimum and do not require starting point but a search range for each parameter. However, they are much slower and less stable in convergence. These weaknesses are more evident when the problem dimension (number of parameters to fit) is high. To combine the advantages of both and limit their weaknesses, we considered the possibility of a hybrid GA-NM algorithm: in a first step, the GA is used to search in given ranges of the parameters and returns an intermediary result x_1 , which is then used as a second step through a loop of successive executions of `fminsearchbnd` to accelerate the convergence to the final result. The “`fminsearchbnd`”² function is repeated until the results between 2 successive calls are close enough to each other (variation of the residuals below 1%). The entire method is illustrated in figure 2.

The idea of combining a global stochastic algorithm and a local deterministic algorithm has already been tested in different domains. Zhou Jian [12] used a hybrid GA algorithm to simultaneously identify the geometric parameters, joint compliance values, and the transition joint torques for industrial robots. Li Wang [13] tested a hybrid method of GA coupled with Levenberg-Marquardt method for the interpretation of EIS data applied on a

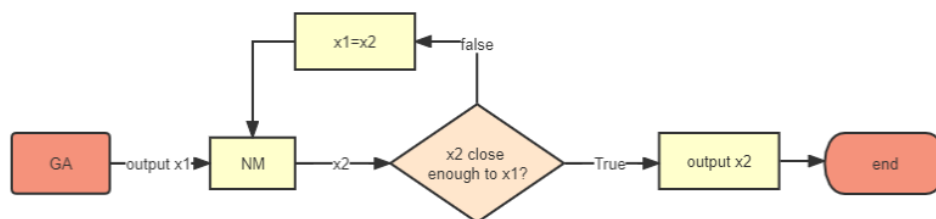


Figure 2: Procedure of GA-NM algorithm.

III. EXPERIMENTAL SETUP

The experimental data we studied cover a wide range of different electrochemical systems (mainly PEMFC single cells and to a lower extend supercapacitors) who differ mainly by the type of electrolyte membrane and cell geometry. We present here the most representative cases: the results and tendency obtained on these various systems are similar.

Cell A: The MEA used were manufactured in the laboratory using 25.6 cm² (64 × 40 mm²) Nafion XL100 membranes and 7.22 cm² (19 × 38 mm²) commercial Gas Diffusion Electrodes (GDE) with 0.5 mg_{Pt}.cm⁻² catalytic layers and 235µm thick gas diffusion layers (5% PTFE and 80% porosity) coated with Sigracet 29BC **Micro-Porous Layers** (MPL). This PEMFC is evaluated under

² The default `fminsearch` function of MATLAB does not admit to set bound constraints to variables of the error function. We thus used a slightly modified version “`fminsearchbnd`” which also uses the Nelder-Mead

biological cell suspension model interpretation. G.Cai applied GA combined with COMSOL to optimize the structure of their PEMFC [14]. Researches being little developed on electrochemical systems, our work will be focused on the application of this concept to solve the least-square problem of EIS parameter estimation in PEMFC modeling, with the final objective to extend later this method to other electrochemical systems such as supercapacitors and batteries.

As mentioned previously, the GA is a stochastic algorithm. So, when the problem is complex (often because of large number of parameters, correlations between them, or minor influence of some of them, i.e. some parameters influence the error function much more/less than the others), it is possible to obtain more than one result for different calls (figure 1). These results represent different local minima of the error function and could stand for different physical hypotheses. On the other hand, when the parameter search interval is too narrow, the function may miss a better local minimum i.e. a result that minimizes better the error function. Therefore, the parameter interval sometimes needs to be reduced for a more stable convergence, or extended to make sure to explore more physically consistent possibilities.

air supply, the other operating conditions are exactly the same as for “cell B” mentioned in [7].

Cell B is fed with pure oxygen and hydrogen. The MEA performance was tested in a single cell made of two identical gold-coated stainless-steel plates on the anode and cathode sides, with single serpentine channel (19 passes) of 0.7 mm in depth and 1 mm in width. The cell was operated at atmospheric pressure and fed in counter-flow with 80% Relative Humidity (RH) hydrogen and oxygen. The gas stoichiometries were set to 1.5 on both sides. The flow field plate temperature was controlled thanks to a water circulation loop and set to 70°C. To avoid any damage to the MEA during the start-up procedure, the temperature was slowly increased from 40°C to 70°C -with 600 seconds steps of 10°C- while

algorithm but with bounds applied to the variables [11]. For short, “`fminsearch`” always stand for “`fminsearchbnd`” in this paper.

both the anode and cathode compartments were flushed with 10 SLPH (standard liters per hour) of nitrogen.

IV. RESULTS

For a PEMFC supplied with air, mass transfer limitations are much more significant than with pure oxygen. Therefore, the mass transport loop in the EI spectra (at low frequencies) of the PEMFC fed with oxygen is much less pronounced or even sometimes negligible compared to a FC supplied with air (figure 4 - PEMFC fed with air, figure 5- PEMFC fed with oxygen), especially at low current densities (i.e. below 1 A/cm²). Therefore, numerical methods (GA and NM) may not be able to clearly identify the mass transport impedance parameters, resulting in many solutions at the output.

After several tests and comparisons, it was not possible to satisfyingly fit the high frequency part of the spectra of cell B using either a TLM EEC alone to represent the CCL, or by adding an anode EEC. This difficulty corresponds more likely to the influence of inductive phenomena [15], which are pronounced mostly at high current densities (1.5 to 2 A/cm²). So, in this case, it was necessary to add an inductive component to the EEC to enhance the fitting quality, although this parameter adds some uncertainty to the parameter estimation without bringing any physical information regarding the MEA.

The EEC used for analyzing cell A and B are shown in figure 3. The EEC used for cell A (figure 3 – left side)

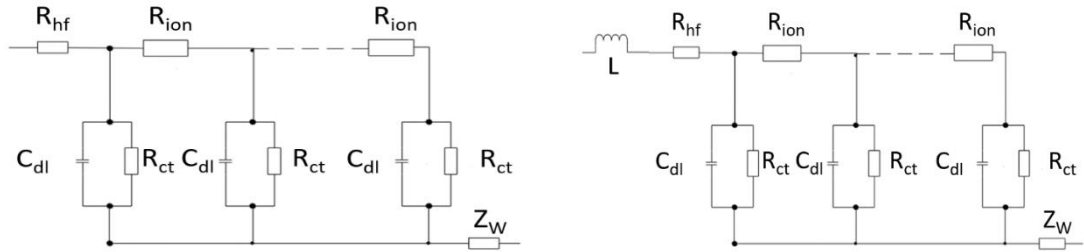


Figure 3: EEC of the two PEMFC. Left: Modified TLM + Warburg in series (tW) used for cell A. Right: Modified TLM + Warburg in series + inductance (tWL) used for cell B.

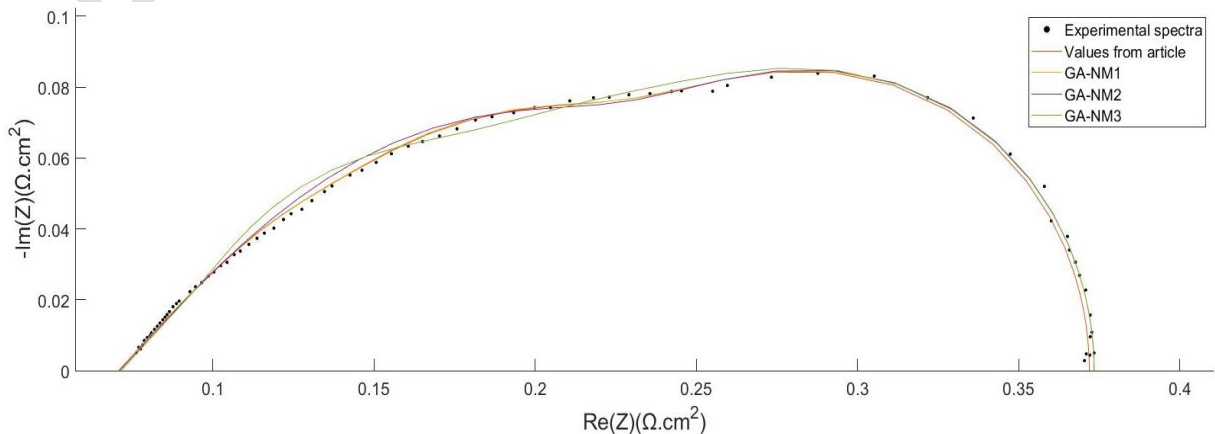


Figure 4: Comparison of different fitting results of cell A, $I = 0.5 \text{ A/cm}^2$, $T = 70^\circ\text{C}$, $\text{RH} = 80\%$.

is composed of a modified TLM EEC and a Warburg element in series (tW), supposing the GDL responsible for mass transport [7]. The only difference with the EEC used for cell B (figure 3 – right side) is the inductance element in series (tWL). The associated impedance expressions are hence (with or without $Z_L(\omega)$):

$$Z_{\text{Cell}}(\omega) = R_{\text{hf}} + Z_{\text{TLM}} + Z_{\text{W}}(\omega)(+Z_L(\omega)) \quad (1)$$

with,

$$Z_{\text{TLM}} = \frac{\sqrt{R_{\text{ion}}}}{\sqrt{i\omega C_{\text{dl}} + \left(\frac{1}{R_{\text{ct}}}\right)}} \coth\left(\sqrt{i\omega R_{\text{ion}} C_{\text{dl}} + \left(\frac{R_{\text{ion}}}{R_{\text{ct}}}\right)}\right),$$

$$Z_{\text{W}}(\omega) = \frac{R_{\text{d}}}{\sqrt{i\omega\tau}} \tanh\sqrt{i\omega\tau} \quad \text{and} \quad Z_L(\omega) = i\omega L, \quad \text{and} \quad \omega = 2\pi f \text{ the angular frequency.}$$

The model parameters to fit are:

- R_{hf} : high frequency resistance, representing the resistance phenomena at high frequencies.
- R_{ct} : charge transfer resistance, characterizing the rate of the electrochemical reaction of the FC
- C_{dl} : double layer capacity, an indicator of the electrode ability to separate the positive and negative charges.
- R_{d} : diffusion resistance.
- τ : characteristic diffusion time.
- R_{ion} : ion conduction resistance.

Cell A

100 repetitions of GA-NM algorithm result in 3 solutions, corresponding to 3 numerically different local minima (marked as GA-NM 1, 2 and 3 in table 1), with the result

GA-NM1 being the most frequent (66 occurrences) and the most coherent with the values obtained in the former work of Touhami et al. [7]. In this previous work, the results were obtained using a NM algorithm alone with carefully chosen initial parameters

TABLE 1: Comparison of estimated parameters of the three different local minima. Parameter bounds: 0 to 1 for all.

Data	$R_{hf} (\Omega.cm^2)$	$R_{ct} (\Omega.cm^2)$	$C_{dl} (F.cm^2)$	$R_{ion} (\Omega.cm^2)$	$R_{ds} (\Omega.cm^2)$	$\tau_s (s)$	Residuals	Occurrence
Article of Touhami et al. [7]	0.0710	0.0740	0.0570	0.191	0.172	0.0730	0.124	
GA-NM1	0.0707	0.0754	0.0550	0.188	0.173	0.0739	0.117	66
GA-NM2	0.0711	0.0164	0.316	1	0.174	0.0733	0.159	31
GA-NM3	0.0716	0.131	0.234	0.389	0.0610	0.0035	0.209	3

It is difficult to conclude on the best solution only by looking at the shape of spectra (figure 4), but we can see from the value of the residuals that the GA-NM1 fits best to the experimental spectrum (table 1). The tiny differences between that solution and the results previously published in the article confirms the advantage of GA-NM because the residuals are slightly lower. This also confirms the sensitivity of the NM algorithms to the starting points.

sometimes values without any physical meaning. This could be because of correlations between some parameters and/or of the poorly developed mass transport loop at low frequencies.

Cell B

Due to the complexity of the problem, multiple local minima are often observed if we repeat the GA-NM algorithm using the same variable bounds as cell A: the parameter values obtained vary drastically, giving

To solve this problem of instability, we reduced the bounds for the most influent parameters: R_{hf} and R_{ct} which stand for the intercept of the spectrum with the real axis at the highest frequencies and the diameter of cathode loop at intermediate frequencies, respectively. In fact, the approximative value of these 2 parameters can be evaluated graphically from the experimental spectrum, all values out of these magnitudes are physically meaningless. After the modification of bound limits, the combined algorithm resulted in one unique solution out of 100 repetitions for each tested EEC:

TABLE 1: Impedance parameters estimated for different EEC. Modified parameter bounds: $0.06 < R_{hf} < 0.1 \Omega.cm^2$, $0.04 < R_{ct} < 0.06 \Omega.cm^2$, and 0 to 0.1 for others.

Model	$R_{hf} (\Omega.cm^2)$	$R_{ct} (\Omega.cm^2)$	$C_{dl} (F.cm^2)$	$R_{ion} (\Omega.cm^2)$	$R_{ds} (\Omega.cm^2)$	$\tau_s (s)$	$L (H.cm^2)$	Residual
tW	$7,77*10^{-02}$	$5,47*10^{-02}$	$1,98*10^{-02}$	$1,27*10^{-09}$	$7,43*10^{-03}$	$1,71*10^{-01}$		$5,23*10^{-02}$
tWL	$6,19*10^{-02}$	$5,34*10^{-02}$	$2,08*10^{-02}$	$5,55*10^{-02}$	$7,34*10^{-03}$	$1,76*10^{-01}$	$9,04*10^{-07}$	$2,58*10^{-02}$

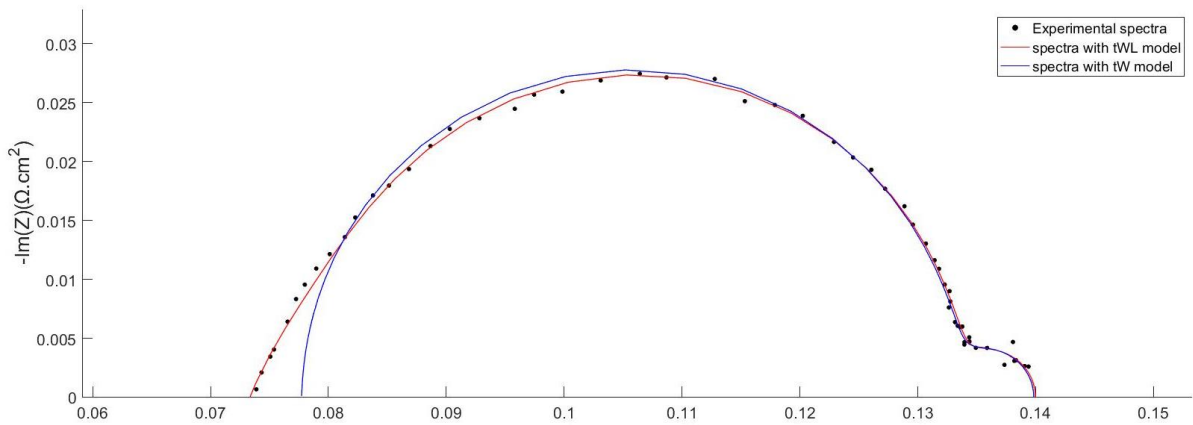


Figure 5: Comparison of the fitting curves obtained with different EEC models for cell B.

From figure 5, we can see that the addition of an inductive element improves significantly the fitting quality although the inductance value is relatively small. The residual value of the tWL model is less than half of that of the tW model. The common parameters are also close to each other except for R_{ion} , which means the algorithm ignored the influence of electrode thickness without the inductance element which is known to influence the EI spectrum at high frequencies [7]. It is worth mentioning that even if the high frequency slope typical of TLM behavior is only poorly developed for cell B, the use of TLM EEC clearly improved the fit quality compared to a Randles type circuit.

V. CONCLUSION

The results shown in the previous paragraphs are only a part of the work we carried out and are the most representative ones. We tested a lot of cases of PEMFC and SC impedance spectra with different MEA/electrode materials or dimensions, under different operating conditions (current/voltage), the tendencies of the different cases are similar.

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According to our results, the main conclusions are:

- Generally, our hybrid GA-NM algorithm can successfully converge to the right solution and explore more possible local minima and this without the need of a starting point.
- When the problem is complex, physical analysis will be necessary to evaluate the physical consistency of the results or limit parameter bounds for a more stable convergence.

Good performance is proven for different systems confirming the convenience and advantage of combined GA-NM algorithm. This method can be applied for further modeling of new configurations and systems in the future.

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