Identification of impedance parameters of electrochemical systems using differential evolution

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Abstract

Impedance data obtained by Electrochemical Impedance Spectroscopy (*EIS*) are fitted to a relevant electrical equivalent circuit in order to evaluate parameters directly related to the resistance and the durability of coated metal systems. An alternative method to non-linear regression algorithms for the analysis of measured data in terms of equivalent circuit parameters is provided by evolutionary algorithms, more especially the differential evolution (*DE*) algorithms (standard *DE* and a representative of the self-adaptive *DE* paradigm were used). Obtained results with *DE* algorithms were compared with commercial fitting software achieving a more accurate solution in all handled cases.

Keywords: Metal-coating systems, *EIS*, Modelling studies, Evolutionary Algorithms, Differential Evolution

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Electrochemical Impedance Spectroscopy (*EIS*) is an electrochemical analysis technique widely used in the field of corrosion. Due to the wide range of frequencies in which it is possible to work, it is a very useful technique for obtaining information related to interfacial electrochemical phenomena [1, 2, 3, 4, 5]. Thanks to the development of this technique, data acquisition is increasingly simplified. The recorded experimental data account for the physicochemical processes that take place in the system and their time constants, which allows the separation of processes that take place at different rates [6, 7, 8, 9, 10, 11, 12, 13]. The experimental data are usually fitted to an equivalent electric circuit that allows the determination of electrical parameters. This equivalent circuit is proposed from a qualitative analysis of the diagrams obtained and the electrochemical knowledge of the analysed system. The subsequent quantification of these parameters through the use of some specific software and its evolution in time allows qualitative and quantitative characterization of the studied system.

Even today, the analysis and interpretation of *EIS* data is an arduous task, though there are several commercial software available for the modelling of the experimental data, such as EQUIVCRT developed by Boukamp [14], ZSimpWin [15], as well as other included in the software of acquisition of experimental data such as Nova [16]. The adjustment procedures of the experimental data are always based on nonlinear regression algorithms such as the Gauss-Newton method (*GN*), its modified variant (*GNM*), and the Levenberg-Marquardt method (*LM*) [17, 18, 19]. The resulting fits can be very accurate, provided that a good initial estimation of the adjustment parameters was introduced. This feature is precisely their main disadvantage or limitation, for it is often hard for these algorithms to converge to the minimum [20]. In case of existence of various local minimums, the algorithm can stagnate in one of them. The usual procedure to avoid this situation, several executions taken from different initial points should be done as to find the so-called good initial estimate. Although those programs can make rather adequate initial estimates of the parameters, there are no guarantees of how to establish it to avoid the mentioned limitation, and it is a problem that has not been solved to full satisfaction.

A major development in computational optimization tools has occurred in recent years, leading to the availability of evolutionary algorithms [21, 22, 23], which are new methodologies that can be applied to the analysis and adjustment of impedance data [24]. These new procedures present advantages over the procedures commonly in use, that constitute a powerful search and optimization techniques with an easily parallelizable behaviour. This approach is inspired by the darwinian principle of natural selection and genetic reproduction. Among the paradigms encompassed in evolutionary algorithms, there are the genetic algorithms [25, 26, 27], genetic programming [28] and evolution strategies [29], as well as differential evolution [30]. These algorithms are global optimizers due to their population search [31, 32], and they can address the search for optimal single- and multi-objective solutions [33]. They have big advantages over traditional methods for problem optimization, because they can be applied simultaneously with integer, discontinuous or discrete variables. Furthermore, they have gained great importance for their potential as a technique for solving complex problems, and they are frequently applied in many engineering fields in general [34, 35, 36, 37], and in Process and Chemical Engineering in particular [38, 39, 40, 41, 42, 43, 44].

One of the paradigms of evolutionary algorithms is Differential Evolution (*DE*), an algorithm developed by Rainer Storn and Kenneth Price [45]. *DE* is inspired by processes from nature (bioinspired), and it has shown good performance and quality compared to other evolutionary algorithms in parameter adjustment problems involving real type variables analogous to the system considered in this work [46, 47, 48]. In recent decades, *DE* has been widely used to deal with a wide range of reference tests and real-world application problems [49, 50], in addition to being one of the most effective base paradigms in dealing with problems with continuous variables in different international competitions of Computational Intelligence. Yet, it was observed that the performance of the *DE* search process needed to be improved due to the increasing complexity of modern optimization problems [51]. Among the improvements proposed to the performance of *DE*, we highlight the recent proposal of algorithms where the values of the parameters and/or operators associated with the algorithm are self-adaptive during the evolution of the numerical search process. Several algorithms have been developed with these characteristics, namely *jDE* [52], Self-adaptive *DE* (*SaDE*) [53], Composite *DE*

(*CoDE*) algorithm [54], differential evolution with dynamic parameters selection (*DE-DPS*) [55], an ensemble of mutation strategies and control parameters with *DE* (*EPSDE*) algorithm [56], a modified differential evolution with *p*-best crossover (*MDE_pBX*) [57], and a differential evolution algorithm with self-adaptive strategy and control parameters (*SSCPDE*) [58].

A preliminary study to determine the impedance parameter setting of metal-organic coating systems modelled by equivalent electrical circuits was published by the authors in [59], where a standard *DE* is applied to a problem of real impedance data corresponding to a metal-paint system (single layer system composed of an 100 μm epoxy polyamine layer applied on carbon steel plate), immersed in a solution of NaCl. Results improve fitting given by commercial software. Kappel et al. [60] compare successfully the standard *DE* versus the Simplex method, proposing the use of experimental Direct Current values concerning the steady-state responses of an electrode as a regularization factor, besides considering *EIS* data. Recently, also Kappel et al. [61] uses *DE* and proposes a method for obtaining confidence regions to the estimated parameters of equivalent electrical circuits in *EIS* modelling with synthetic experimental data.

The main contributions of the present study are: first, to propose a fitting procedure using a more robust differential evolution algorithm approach, with a representative of the self-adaptation *DE* capabilities, both in terms of operators and parameters -particularly *SaDE* is used here in addition to the standard *DE*- and second, to apply the impedance parameter setting both in the case of tests based on data extracted from the literature and in the case of new experimental results considering the temporal evolution of the metal-coating system.

It will be shown that the fits obtained using differential evolution algorithms improve the robustness and precision of the proposed modelling solutions compared to commercial software. The structure of this contribution is as follows: a first section that describes the process of fitting the electrochemical impedance parameters, following by a section that describes aspects related to the *DE* algorithm and the self-adaptive algorithm (*SaDE*) employed. Next, results and their discussion are presented, and finally, the dissertation finishes with the conclusions section.

Adjustment of electrochemical impedance parameters

The equivalent circuit most widely employed for the modelling of a metal/organic coating system contains two time constants $R(C(R(CR))$ [62] (see Figure 1). It regards the polymeric coating as an non-sealing physical barrier separating the metal from the environment due to permeability of water and oxygen [63].

In this circuit, R_e accounts for the unbalanced resistance between the reference electrode and the working electrode, C_p is the capacity of the polymer coating and R_p is the pore resistance which is due to the formation of conductive ion paths through the coating, whereas R_t is the polarization resistance of the area at the metal-coating interface in which corrosion occurs, and C_d is the corresponding capacitance. For a satisfactory adjustment of the capacitive elements, a constant phase element (*CPE*) is usually introduced, that is defined as:

$$Z_{CPE} = \frac{1}{Q(j\omega)^n} \tag{1}$$

where Z_{CPE} is the impedance of the *CPE* element, j is the imaginary unit, ω is the angular frequency (expressed in rad s^{-1}), n is the phase constant angle of *CPE* (rad), and Q is the *CPE* amplitude ($\mathrm{s}^n\Omega^{-1}$). Adopting Q notation for the *CPE*, the equivalent circuit adopts the form $R(Q(R(QR))$, and its total impedance is given by:

$$Z = R_\mathrm{e} + \cfrac{1}{Q_\mathrm{p}(j\omega)^{n_\mathrm{p}} + \cfrac{1}{\cfrac{1}{Q_\mathrm{d}(j\omega)^{n_\mathrm{d}} + \cfrac{1}{R_\mathrm{t}}} + R_\mathrm{p}}} \tag{2}$$

Impedance fitting procedures aim to adjust the experimental data to this equivalent by minimizing the error between them and the data produced with the equivalent circuit. Mathematical quantification of the error is performed through the objective function (OF) shown in equation (3),

$$OF = \sum_{i=1}^{n-\text{freq}} [(\overline{Z_{\text{re}_i}} - Z_{\text{re}_i})^2 + (\overline{Z_{\text{im}_i}} - Z_{\text{im}_i})^2] \tag{3}$$

where $\overline{Z_{\text{re}_i}}$ and $\overline{Z_{\text{im}_i}}$ are the adjusted values for the real and imaginary component of the simulated circuit, respectively; Z_{re_i} and Z_{im_i} are the experimental values obtained for a given frequency; and the summation extends to all the frequencies under analysis (n-freq). A null value for OF would indicate a perfect fitting between them. In order to qualitatively visualize the quality of the fit, data are usually plotted as a Nyquist diagram, with the real component of impedance on axis X and the negative imaginary impedance component on axis Y. Figure 2 displays a typical sketch of the Nyquist diagram for the equivalent circuit of Figure 1.

Differential Evolution algorithms

Following, a description of Differential Evolution (DE) and Self adaptive Differential Evolution ($SaDE$) algorithms used in this work are presented. First, DE principles and algorithm are developed in sufficient detail. Later, in the second subsection, the relevant and distinct aspects of $SaDE$ are briefly exposed.

Standard Differential Evolution (DE)

DE belongs to the evolutionary algorithms (EAs) paradigm, being inspired in the natural Darwinian principle of survival of the fittest. The algorithm uses a population of NP individuals (being NP the population size), which allows to optimize functions in a n-dimensional continuous domain. Thus, each individual in the population is a n-dimensional vector representing a possible candidate solution to the handled optimization problem. The components of the aforementioned n-dimensional vector are each of the variables of the problem whose values we want to achieve (optimum solution). In the terminology of evolutionary algorithms, those vectors are called chromosomes, and the variables contained are called genes. Those chromosomes $\mathbf{x}_i$, as population members, are modified in a succession of iterations (or generations in EAs language), where evolutionary operators (mathematical/computational) of mutation, crossover and selection, are applied.

DE special feature is its characteristic mutation (operator which alters the genes of a chromosome). It is based on the idea of adding a scaled difference vector of two randomly chosen chromosomes to a third chromosome (which could be based on a random choice: *DE/rand*, based on the best chromosome found: *DE/best*, etc.), therefore creating a new candidate individual $\mathbf{v}_i$. The parameter defining the scale factor is called F hereafter. Figure 3 shows an example of the mutation operator in a three genes optimization problem. There are also versions of DE with addition of more than one difference vector in the mutation operator -usually one (*DE/—/1*) or two (*DE/—/2*) addition terms are the most used-. This mutation operator allows that variations associated to this process: a) diminish when the population is reaching the optimum solution as individuals converge to similar values; b) adapt in every dimension (every gene) considering the higher or lower proximity to the convergence; c) are correlated among variable dimensions which means an efficient search even in coupled problems.

$$DE/rand/1\text{: } \mathbf{v}_i = \mathbf{x}_{r1} + F(\mathbf{x}_{r2} - \mathbf{x}_{r3}) \tag{4}$$

$$DE/rand/2\text{: } \mathbf{v}_i = \mathbf{x}_{r1} + F(\mathbf{x}_{r2} - \mathbf{x}_{r3}) + F(\mathbf{x}_{r4} - \mathbf{x}_{r5}) \tag{5}$$

Crossover operator has the function of mixing the genetic information of two chromosomes to create a new solution $\mathbf{u}_i$; in DE, crossover mixes the genes of a particular chromosome $\mathbf{x}_i$ with a

mutation generated individual $\mathbf{v}_i$. Each gene is crossed (or not) depending on a probability variable called crossover rate (CR). Binary crossover is as follows:

$$u_{ij} = \begin{cases} v_{ij} \quad if \quad \text{random}(0,1) < CR \quad or \quad j = J_r \\ \\ x_{ij} \qquad\qquad otherwise \end{cases} \tag{6}$$

(index J_r varying from 1 to the number of genes guarantees that at least one component is always crossed).

Finally, the selection operator allows that the best fittest individuals (those with best values of the OF) have more survival probabilities and therefore propagate their genes to the following generations. OF values of the chromosome of reference and the generated after mutation and crossover $\mathbf{u}_i$ are compared, choosing the one with best OF to be passed to the next generation and discarding the other.

This process is repeated in successive generations, until reaching the stopping criterion, frequently governed by the maximum number of generations or OF evaluations, moment when the best solution obtained is considered as optimum solution.

In Figure 4, a diagram of the DE algorithm is depicted. It starts with the creation of an initial population composed of NP individuals $\mathbf{x}_i$. Each individual is formed by as many values as variables of the equivalent electric circuit used in the model and simulation of the electrochemical impedance data. Initially, randomly values are assigned to each variable, generating the initial population, which will be the parent population in the first generation. Then, each individual is corresponded with a mutation, that is, a mutant vector $\mathbf{v}_i$. Among the mutation alternatives, the most classical is called *DE/rand/1/bin* [45]. Parents and mutants are crossed over to generate the offspring $\mathbf{u}_i$, governed by the crossover rate parameter CR. After, offspring individuals $\mathbf{u}_i$ compete with their parents $\mathbf{x}_i$ based on their OF values (best fitted individuals) to decide which is transferred to the next population generation, while the looser is discarded. The parameters that govern the behaviour of the above described DE algorithm are: population size (NP), scale factor (F) and crossover rate (CR). DE convergence is sensitive to the appropriate election of those parameters depending on the particular problem handled. NP has a crucial role in the maintenance of equilibrium between exploration and exploitation when searching the optimum solution, as a population with a excessive number of individuals could lead to a very slow convergence, while a population with very few individuals could lead to a premature stagnation converging to a local suboptimum.

Self adaptive Differential Evolution ($SaDE$)

Due to its stochastic nature, to reach an appropriate performance in optimization by applying a standard DE to a given problem, it is frequent to tune the values of the corresponding parameters: CR, F and NP and the type of operator strategy, as different values and types may affect the outcome quality depending on the robustness of parameter and operators' variation in a particular given problem. Even some stages of the search could be benefited more from some values/operator strategies than from others.

A DE variant which is able to self-adapt both their parameter values and operator strategies "on the fly" according to the ongoing performance of the OF values of individuals, particularly $SaDE$ [53], has been implemented and tested in this paper for the modelling of the EIS problem.

The pool of operator strategies follows the suggestion given in [53] and their expressions are the following:

$$DE/rand/1\text{: } \mathbf{v}_i = \mathbf{x}_{r1} + F(\mathbf{x}_{r2} - \mathbf{x}_{r3}) \tag{7}$$

$$DE/rand/2\text{: } \mathbf{v}_i = \mathbf{x}_{r1} + F(\mathbf{x}_{r2} - \mathbf{x}_{r3}) + F(\mathbf{x}_{r4} - \mathbf{x}_{r5}) \tag{8}$$

$$DE/rand-to-best/2\text{: } \mathbf{v}_i = \mathbf{x}_i + F(\mathbf{x}_{best} - \mathbf{x}_i) + F(\mathbf{x}_{r1} - \mathbf{x}_{r2}) + F(\mathbf{x}_{r3} - \mathbf{x}_{r4}) \tag{9}$$

$$DE/current-to-rand/1\text{: } \mathbf{v}_i = \mathbf{x}_i + F_k(\mathbf{x}_{r1} - \mathbf{x}_i) + F(\mathbf{x}_{r2} - \mathbf{x}_{r3}) \quad (10)$$

The three first strategies are associated with a binary crossover strategy (as explained in previous subsection).

Each strategy has associated a probability depending on its capability to generate successful chromosomes after the crossover and selection procedure in previous generations. According to this probability, a stochastic universal sampling [64] is applied to assign the mutation strategy to each chromosome in the current generation. Memories are considered in order to store success and failure rates within a fixed number of previous generations (learning period *LP*).

Only *NP* is a user specified parameter in *SaDE*, being *CR* and *F* defined by normal distributions, whose initial values were kept from reference [53]. Mean value of *CR* depends on the strategy of mutation and crossover and its value is adapted through the search process based on the successful chromosomes generated.

For more details about *SaDE* algorithm, references [53, 65] can be consulted.

Being *EA*s stochastic methods which depend on an initial random population, as well as on probabilistic based operators (mutation, crossover), in order to compare behaviour of different parameter values, different operator types, or even different algorithms, it is necessary to compare not a single outcome of the algorithm, but a set of independent executions. Results of next section are based on a set of five independent runs for each algorithm.

Results and discussion

To validate the possibilities of the procedure, firstly synthetic impedance data from the literature were used in order to predict impedance parameters in a system composed of two time constants [66, 67]. Next, real impedance data corresponding to the temporal evolution of a metal-paint system, immersed in a solution of NaCl, were evaluated. It was a double layer system composed of an inner $100\,\mu$m epoxy polyamine layer and a $50\,\mu$m acrylic polyurethane finishing layer applied on carbon steel plate with Sa2 1/2 surface finish. Additional details on this system can be found in [68].

A population size (*NP*) of 200 individuals and stopping criterion of 5000 iterations has been used in the *DE* algorithms. Standard *DE* tested with three parameters combination: ($F = 0.5$; $CR = 0.5$), ($F = 0.9$; $CR = 0.1$) and ($F = 0.1$; $CR = 0.5$) are shown. Initial mean values of the Gaussian normal distribution in *SaDE* (mean, standard deviation) where: $CR = (0.5, 0.1)$, $F = (0.5, 0.3)$; and learning period (*LP*) was set to 30 generations.

Case 1. Validation of the procedure. TestB system taken from [66, 67]

The demonstration case labelled TestB in the *ZSimpWin* software [66], corresponding to the adjustment of synthetic impedance data generated from the equivalent circuit in Figure 1 to data extracted from a study performed by Esteban et al. (Figure 2-b in [67]), was considered first.

Table 1 shows the values of the parameters from the equivalent circuit obtained using *DE* and *SaDE* algorithms, together with those estimated using *ZSimpWin* [15] for reference. The values of the objective function *OF* obtained in each case are also listed. The corresponding Nyquist diagrams are depicted in Figure 5, allowing direct comparison of the experimental data with the simulated data delivered by the three fitting procedures under consideration. Additionally, Table 2 lists the final *OF* values obtained for each of the 5 executions employed for *DE* and *SaDE*, together with the average, best, worst, median and standard deviation found. The evolution of convergence using *DE* and *SaDE* algorithms on this system is given in Figure 6, whereas the horizontal line in the plots gives the corresponding *OF* values obtained using the parameter values produced using *ZSimpWin*. Figure 6-top depicts the average of best *OF* values (on axis *Y*) for each generation (on axis *X*). Analogously, Figure 6-bottom shows the best value among the individuals for each generation (i.e., the individual providing the best solution). Each execution involved 204 and 714 s computation costs

for *DE* and *SaDE*, respectively, on an Intel Core i7-2670QM-2.20GHz computer with 4Gb RAM and 64 bits operative system.

From the foregoing, the following observations regarding fit operation can be extracted:

1. As shown in Table 2, the obtained results with the standard *DE* depend on the values of F and CR parameters. E.g., the difference of the average between the best ($F = 0.5$; $CR = 0.5$) and worst ($F = 0.1$; $CR = 0.5$) tested parameter combination is greater than 400%. Therefore, the goodness of the performance of the values depends on the handled problem and is a priori unknown.

2. On the contrary, in the more robust *SaDE* algorithm there are no initial F and CR parameters to tune.

3. According to Tables 1 and 2, the best final solution produced by *DE* and *SaDE* algorithms is in the same order of magnitude (they only differ on the fourth significant figure). The convergence of *SaDE* is faster in the early stages of the evolution (cf. Figure 6).

4. There is a significant improvement of the best fitted plots using *DE* algorithms compared to that delivered by the commercial software taken as control. Thus, the objective function given by *ZSimpWin* amounted $OF = 1.8164 \cdot 10^3$, whereas smaller values (in the order of 50%) are obtained using either *DE* ($OF = 9.0955 \cdot 10^2$) or *SaDE* ($OF = 9.0982 \cdot 10^2$) algorithms. The divergence in the values of parameters of the equivalent circuit are generally below 14%, with the exception of Q_{p} that is almost 90%.

Case 2. Temporal evolution of a metal-paint system composed of two layers epoxy polyamine ($100\,\mu$m) + acrylic polyurethane ($50\,\mu$m) coating on carbon steel plate [68]

Simulations were also performed on a two-layer paint system applied on a carbon steel plate with Sa2 1/2 surface finish. In brief, the inner coating layer was a $100\,\mu$m thick epoxy-polyamine primer, and the topcoat consisted in $50\,\mu$m thick polyurethane. Impedance spectra were recorded at different times up to 890 hours during exposure in 3 wt.% NaCl aqueous solution, by applying a 10 mV amplitude sinusoidal voltage in the $10 \leq f \leq 50$ kHz frequency range, 14 points per decade [68]. A flat 3-electrode configuration was employed, with the coated metal placed at the bottom of the cell, facing upwards to the solution, with 5.56 cm^2 exposed area.

Since very similar outcomes were produced using *DE* and *SaDE* algorithms, only *SaDE* operation will be considered here due to the greater robustness of the procedure.

Figure 7 compares the experimental data, corresponding to measurements at various elapsed times (namely, 150, 215, 310, 385, 480, 550, 650, 720 and 890 hours), with the simulations obtained using *ZSimpWin* and *SaDE* fits. It must be noticed that no convergence was obtained using *ZSimpWin* for some of the exposures, whereas the experimental data could always be fitted using *SaDE*. The normalized *OF* values corresponding to the optimal solutions obtained for the 5 programmed executions of the *SaDE* algorithm to each impedance spectrum are depicted in Figure 8. Among them, the best fit trend (i.e., the circles joined by the black line) was employed to produce the simulated spectra in Figure 7. The total calculation time required to perform each of these independent runs was 465 seconds on an Intel Core i7-2670QM-2.20GHz computer with 4Gb RAM and 64-bit operating system.

From the foregoing, the following observations regarding fit operation can be extracted:

1. The use of the *SaDE* algorithm allowed fitting the chosen equivalent circuit to all the experimental impedance spectra, whereas *ZSimpWin* failed to find a consistent solution in some cases (i.e., for the *EIS* data recorded after 215, 385, 480, 720 and 890 hours exposure to the test solution).

2. Only small variations are found among the fits obtained in the 5 executions considered, a feature also observed in the system used for verification in Case 1 (System TestB included in the *ZSimpWin* software).

3. Though the Nyquist plots may significantly vary for measurements done at different elapsed times in the test solution, the *OF* values for the 5 executions exhibit similar variations for each impedance spectrum. Therefore, the *SaDE* algorithm is able to find a solution for the equivalent circuit in a robust and reliable way and, above all, continuously over the temporal evolution of the system.

Finally, the physicochemical characteristics of the metal-coating system can be analysed in terms of the temporal evolution of the components of the equivalent circuit for each impedance spectrum using the various executions as well as the corresponding best fit. These parameters are plotted as a function of the duration of exposure for the metal-coating system under investigation in Figure 9, allowing for the evolution of the process to be monitored. Firstly, it can be observed that R_{p}, R_{t} and Q_{d} values determined from the different executions closely match the results from the best fit, whereas there is a greater variability in the case of the remaining parameters Q_{p}, n_{d} and n_{p}. Therefore, they are more sensitive to the choice of the final solution requirement. Secondly, regarding the electrochemical behaviour of the system, the evolution of the equivalent circuit components is consistent with the typical expectations for a metal-coating system. The coating resistance R_{p} exhibits a steady decay with the elapse of time, amounting one order of magnitude for the duration of the experiment (i.e, a diminution from initial values close to $2.5 \cdot 10^7$ Ω cm^2 down to $2.5 \cdot 10^6$ Ω cm^2 after 890 hours). That is, increased ionic pathways are progressively developed through the coating allowing the underlying metal to be exposed to the environment. Next, the component R_{t}, related to the charge transfer resistance at the metal-coating interface, shows an almost 10-fold decrease (namely from $1.6 \cdot 10^7$ Ω cm^2 to $2.0 \cdot 10^6$ Ω cm^2), indicating that the corrosion rate of the metal increases simultaneously to the loss of barrier characteristics of the polymer coating.

Conclusions

This paper presents a novel computational strategy for the modelling of Electrochemical Impedance Spectroscopy (*EIS*) measurements using a self-adaptive differential evolution algorithm (*SaDE*).

The applicability of the new procedure has been tested for metal-coating systems exposed to aqueous electrolyte solutions that present two time constants in their impedance spectra, usually described by an equivalent circuit of the type $R(Q(R(QR))$.

The *SaDE* algorithm was implemented and tested both with a set of synthetic impedance data taken from the literature, and with a real metal-paint system composed of a 100 μm epoxy polyamine layer and a 50 μm acrylic polyurethane finishing layer applied on carbon steel plate. The results obtained in this work are very promising, because they significantly improve those delivered by the simulation and adjustment of the same systems using the commercial software most widely employed by scientists working on the characterization of metal-coating systems (namely *ZsimpWin*).

Work in progress focuses on the application of this analytical method to the physicochemical characterization of other electrochemical systems, as well as to improve the efficiency of the procedure in order to reduce the calculation time required to obtain the final solution.

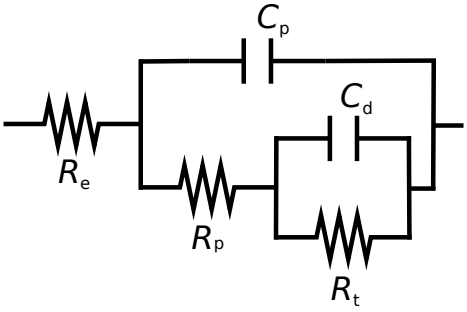


Figure 1: Equivalent circuit used for the simulation of metal-coating systems [2].

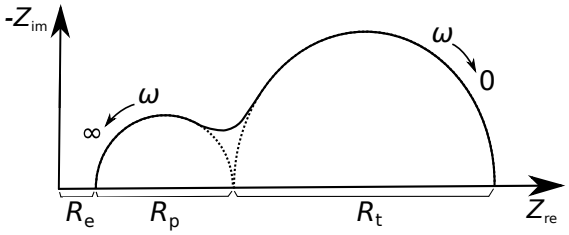


Figure 2: Typical Nyquist diagram of the metal-coating system.

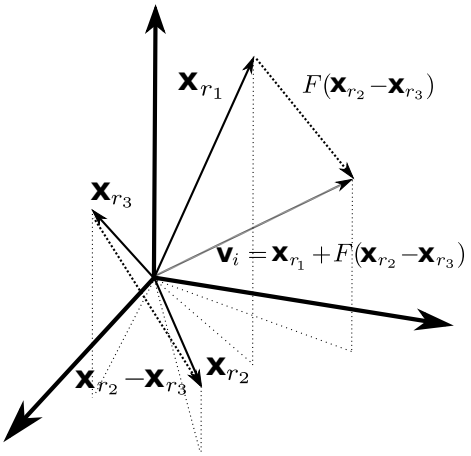


Figure 3: Differential evolution mutation (three dimensional optimization problem).

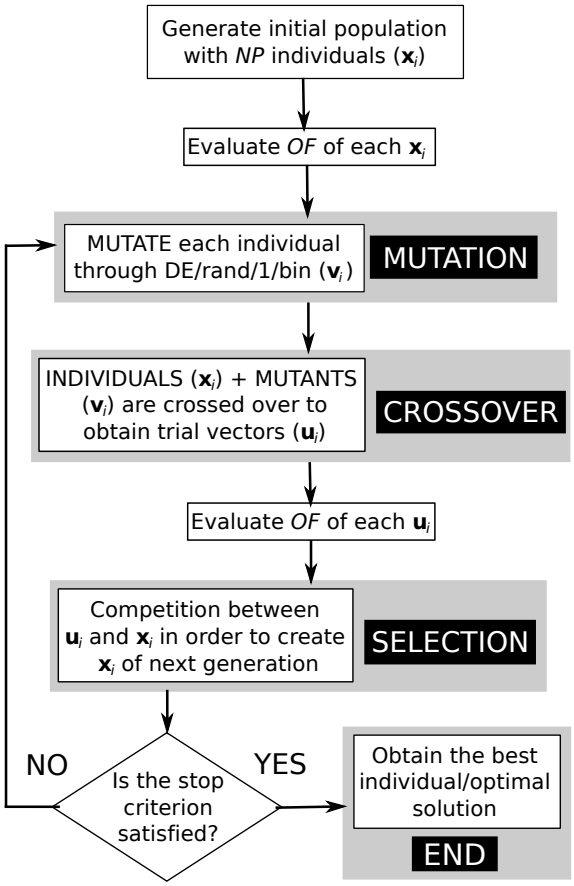


Figure 4: Block diagram of the differential evolution algorithm (*DE*).

	ZSimpWin	***DE***		***SaDE***	
R_e / Ω cm^2	9.92	8.66	(-12.70%)	8.60	(-13.31%)
R_p / Ω cm^2	111.42	120.70	(+8.33%)	120.95	(+8.55%)
R_t / Ω cm^2	190.70	180.88	(-5.15%)	180.66	(-5.26%)
Q_p / s^n Ω^{-1} cm^{-2}	$1.235 \cdot 10^{-5}$	$2.299 \cdot 10^{-5}$	(+86.15%)	$2.321 \cdot 10^{-5}$	(+87.94%)
n_p	0.9758	0.8872	(-9.08%)	0.8857	(-9.23%)
Q_d / s^n Ω^{-1} cm^{-2}	$2.867 \cdot 10^{-3}$	$2.988 \cdot 10^{-3}$	(+4.22%)	$2.992 \cdot 10^{-3}$	(+4.36%)
n_d	0.8474	0.9272	(+9.42%)	0.9281	(+9.52%)
OF	$1.8164 \cdot 10^3$	$9.0955 \cdot 10^2$	(-49.93%)	$9.0982 \cdot 10^2$	(-49.91%)

Table 1: Case 1. Validation of the procedure. TestB system taken from [66, 67]. Parameters of the equivalent circuit determined using *ZSimpWin* [15], and the best solutions with *DE* and *SaDE* algorithms.

	DE		***DE***		***DE***		
	F	CR	F	CR	F	CR	
	0.9	0.1	0.1	0.5	0.5	0.5	***SaDE***
Execution 1	1145.5034887		2614.7362320		909.5516225		909.8188502
Execution 2	1082.5334186		6051.9642576		909.5512448		911.4402325
Execution 3	971.1022822		2786.0926525		909.5521927		916.0706725
Execution 4	967.2706802		3360.1016781		909.5513893		927.2312285
Execution 5	997.6611296		5392.5337059		909.5511607		911.2602060
Average	1032.8141999		4041.0857052		909.5515220		915.1642379
Best	967.2706802		2614.7362320		909.5511607		909.8188502
Worst	1145.5034887		6051.9642576		909.5521927		927.2312285
Median	997.6611296		3360.1016781		909.5513893		911.4402325
Standard deviation	70.02		1410.20		$3.70 \cdot 10^{-4}$		6.39

Table 2: Case 1. Validation of the procedure. TestB system taken from [66, 67]. *DE* and *SaDE* algorithms independent execution statistics for the data in Figures 5 and 6.

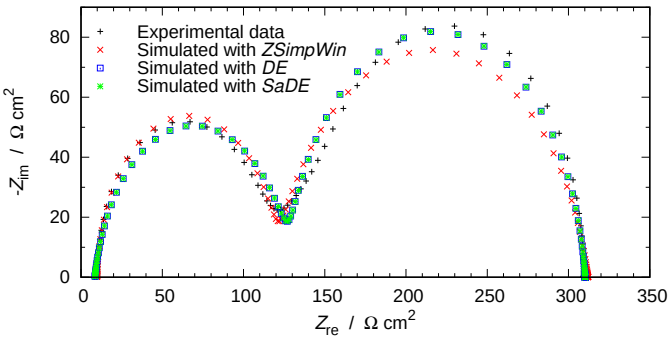


Figure 5: Case 1. Validation of the procedure. TestB system taken from [66, 67]. Nyquist diagrams of experimental data and simulations to equivalent circuits obtained from the best fit with *ZSimpWin* [15] and the algorithms *DE* ($F = 0.5$; $CR = 0.5$) and *SaDE* used.

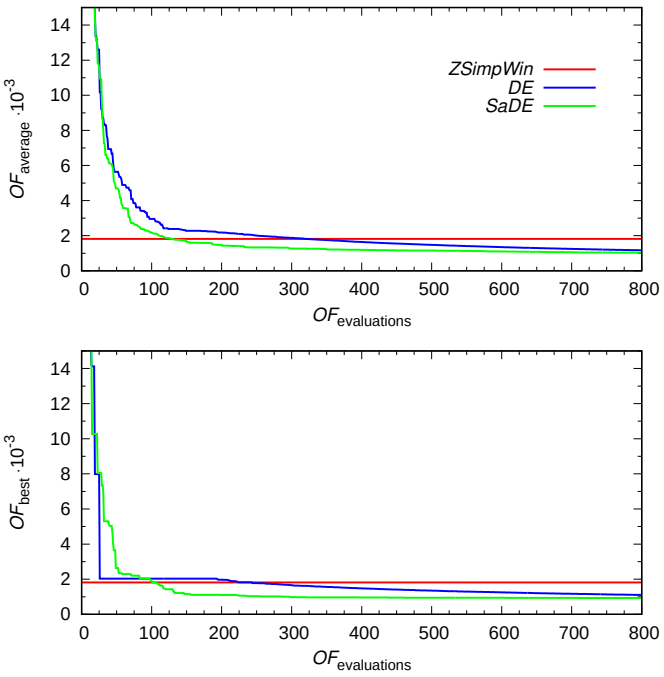


Figure 6: Case 1. Validation of the procedure. TestB system taken from [66, 67]. Evolution of the convergence of *DE* ($F = 0.5$; $CR = 0.5$) and *SaDE*. Average of best values of OF obtained in each generation (top). Best value of OF obtained in each generation (bottom). (In the interest of clarity only shows the evolution in the first 800 generations).

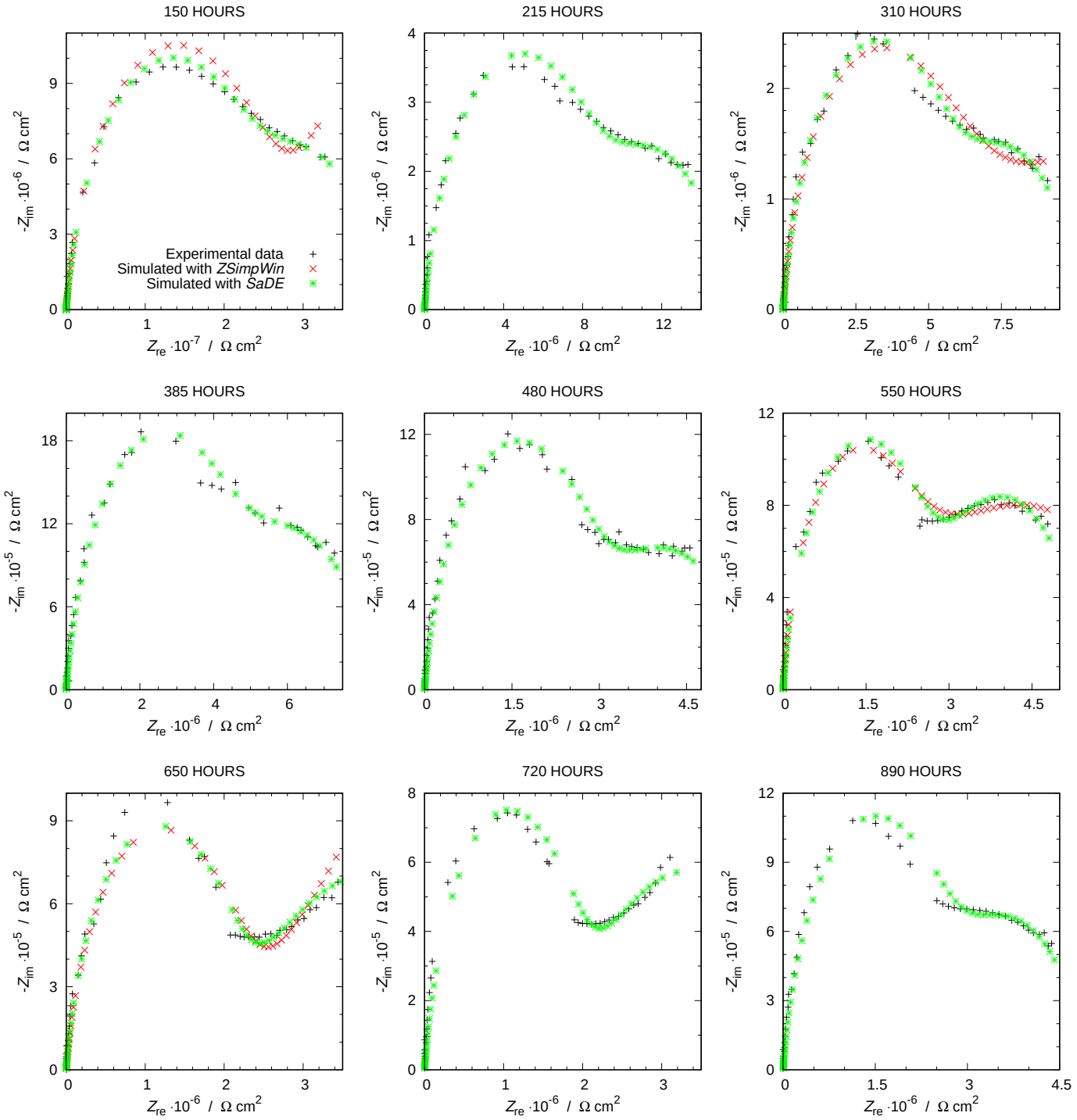


Figure 7: Case 2. Temporal evolution of a metal-paint system composed of two layers epoxy polyamine (100 μm) + acrylic polyurethane (50 μm) coating on carbon steel plate [68]. Evolution of the Nyquist diagram. Experimental data and response of equivalent circuits obtained using *ZSimpWin* [15] and *SaDE* algorithm.

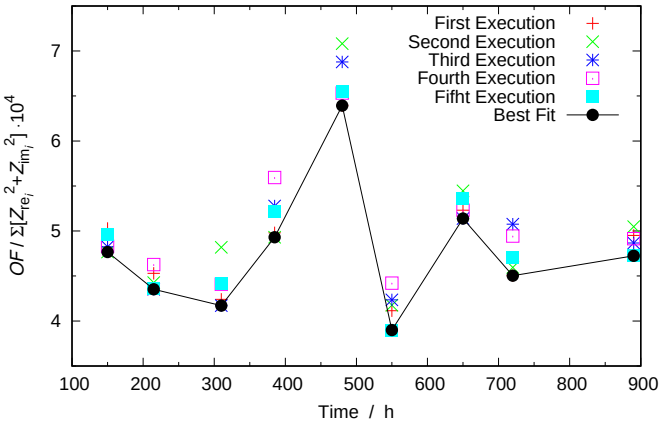


Figure 8: Case 2. Temporal evolution of a metal-paint system composed of two layers epoxy polyamine (100 μm) + acrylic polyurethane (50 μm) coating on carbon steel plate [68]. Normalized values of OF for the 5 executions carried out with the proposed *SaDE* algorithm.

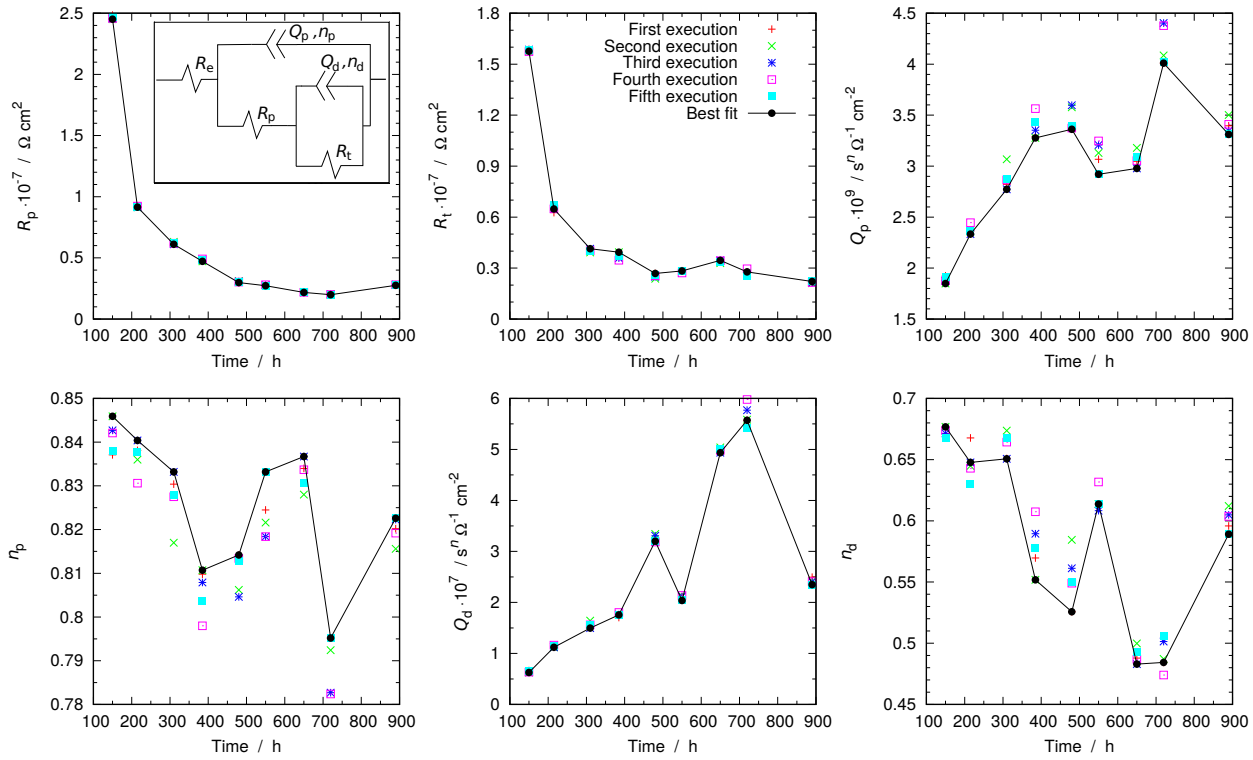


Figure 9: Case 2. Temporal evolution of a metal-paint system composed of two layers epoxy polyamine (100 μm) + acrylic polyurethane (50 μm) coating on carbon steel plate [68]. Evolution of the parameters of the equivalent circuit obtained from the *SaDE* setting.

References

[1] D. D. Macdonald and M. C. H. McKubre. Electrochemical Impedance Techniques in Corrosion Science. In *Electrochemical Corrosion Testing*, F. Mansfeld and U. Bertocci, editors, pages 110–150. ASTM International, Philadelphia, PA (1981).

[2] D. D. Macdonald. Application of electrochemical impedance spectroscopy in electrochemistry and corrosion science. In *Techniques for characterization of electrodes and electrochemical processes*, J. R. Selman and V. Ravi, editors, pages 515–579. Wiley, New York (1991).

[3] M. E. Orazem and B. Tribollet. *Electrochemical Impedance Spectroscopy*. John Wiley & Sons, Inc., Hoboken, NJ, USA (2008).

[4] F. Mansfeld. Electrochemical impedance spectroscopy. In *Analytical methods in corrosion science and engineering*, P. Marcus and F. Mansfeld, editors, pages 463–505. CRC Press, Boca Raton (2006).

[5] V. F. Lvovich. *Impedance epectroscopy: applications to electrochemical and dielectric phenomena*. John Wiley & Sons, Inc., Hoboken, NJ, USA (2012).

[6] D. D. Macdonald. Review of mechanistic analysis by electrochemical impedance spectroscopy. *Electrochimica Acta*, **35**(10), 1509 (1990).

[7] C. Gabrielli, M. Keddam, and H. Takenouti. New trends in the investigation of electrochemical systems by impedance techniques: multi-transfer function analysis. *Electrochimica Acta*, **35**(10), 1553 (1990).

[8] X. Wang, I.-M. Hsing, Y.-J. Leng, and P.-L. Yue. Model interpretation of electrochemical impedance spectroscopy and polarization behavior of H2/CO mixture oxidation in polymer electrolyte fuel cells. *Electrochimica Acta*, **46**(28), 4397 (2001).

[9] H. Wang, T. Löffler, and H. Baltruschat. Formation of intermediates during methanol oxidation: A quantitative dems study. *Journal of Applied Electrochemistry*, **31**(7), 759 (2001).

[10] I.-M. Hsing, X. Wang, and Y.-J. Leng. Electrochemical Impedance Studies of Methanol Electrooxidation on Pt/C Thin Film Electrode. *Journal of The Electrochemical Society*, **149**(5), A615 (2002).

[11] X. Wang and I.-M. Hsing. Kinetics investigation of H2/CO electro-oxidation on carbon supported Pt and its alloys using impedance based models. *Journal of Electroanalytical Chemistry*, **556**, 117 (2003).

[12] X. Wang, J.-M. Hu, and I.-M. Hsing. Electrochemical investigation of formic acid electrooxidation and its crossover through a Nafion® membrane. *Journal of Electroanalytical Chemistry*, **562**(1), 73 (2004).

[13] D. D. Macdonald. Reflections on the history of electrochemical impedance spectroscopy. *Electrochimica Acta*, **51**(8-9), 1376 (2006).

[14] B. A. Boukamp. A Nonlinear Least Squares Fit procedure for analysis of immittance data of electrochemical systems. *Solid State Ionics*, **20**(1), 31 (1986).

[15] B. Yeum. Electrochemical Impedance Spectroscopy: Data Analysis Software (2001).

[16] B. V. Metrohm Autolab. NOVA Impedance data analysis tools (2015).

[17] J. R. Macdonald and J. A. Garber. Analysis of Impedance and Admittance Data for Solids and Liquids. *Journal of The Electrochemical Society*, **124**(7), 1022 (1977).

[18] J. R. Macdonald, J. Schoonman, and A. P. Lehnen. Applicability and power of complex nonlinear least squares for the analysis of impedance and admittance data. *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry*, **131**, 77 (1982).

[19] J. R. Macdonald. Impedance spectroscopy: old problems and new developments. *Electrochimica Acta*, **35**(10), 1483 (1990).

[20] D. A. Ratkowsky. *Nonlinear Regression Modeling: A Unified Practical Approach*. Marcel Dekker, New York (1983).

[21] D. Simon. *Evolutionary Optimization Algorithms*. Wiley, New Jersey (2013).

[22] T. Bäck. *Evolutionary Algorithms in Theory and Practice: Evolution Strategies, Evolutionary Programming, Genetic Algorithms*. Oxford University Press, Oxford, UK (1996).

[23] D. Greiner, J. Periaux, J. M. Emperador, B. Galván, and G. Winter. Game Theory Based Evolutionary Algorithms: A Review with Nash Applications in Structural Engineering Optimization Problems. *Archives of Computational Methods in Engineering*, pages 1–48 (2016).

[24] H. Cao, J. Yu, and L. K. Kang. An evolutionary approach for modeling the equivalent circuit for electrochemical impedance spectroscopy. In *The 2003 Congress on Evolutionary Computation*, volume 3, pages 1819–1825. IEEE (2003).

[25] J. H. Holland. *Adaptation in Natural and Artificial Systems: An introductory analysis with applications to biology, control, and artificial intelligence*. Ann Arbor MI University of Michigan Press, Ann Arbor (1975).

[26] J. H. Holland. Genetic Algorithms. *Scientific American*, **267**(1), 66 (1992).

[27] D. E. Goldberg. *Genetic Algorithms in Search, Optimization and Machine Learning*. Addison-Wesley, Reading, MA (1989).

[28] J. R. Koza. *Genetic programming: on the programming of computers by natural selection. Complex Adaptive Systems Series*, volume 1. MIT Press (1993).

[29] H.-G. Beyer. *The Theory of Evolution Strategies*. Natural Computing Series. Springer Berlin Heidelberg, Berlin, Heidelberg (2001).

[30] K. V. Price, R. M. Storn, and J. A. Lampinen. *Differential Evolution: A Practical Approach to Global Optimization*. Springer Berlin Heidelberg (2005).

[31] K. Deb, S. Bandaru, D. Greiner, A. Gaspar-Cunha, and C. C. Tutum. An integrated approach to automated innovization for discovering useful design principles: Case studies from engineering. *Applied Soft Computing*, **15**, 42 (2014).

[32] G. Winter, B. Galván, S. Alonso, B. Gonzalez, J. I. Jimenez, and D. Greiner. A Flexible Evolutionary Agent: cooperation and competition among real-coded evolutionary operators. *Soft Computing*, **9**(4), 299 (2005).

[33] C. A. Coello Coello, G. B. Lamont, and D. A. Van Veldhuizen. *Evolutionary Algorithms for Solving Multi-Objective Problems*. Genetic and Evolutionary Computation Series. Springer US, Boston, MA (2007).

[34] G. Winter, J. Périaux, M. Galán, and P. Cuesta. *Genetic Algorithms in Engineering and Computer Science*. John Wiley & Sons, Inc., New York, NY, USA, 1st edition (1996).

[35] D. Quagliarella, J. Périaux, C. Poloni, and G. Winter. *Evolutionary Algorithms in Engineering and Computer Science: Recent Advances in Genetic Algorithms, Evolution Strategies, Evolutionary Programming, Genetic Programming and Industrial Applications*. John Wiley & Sons (1998).

[36] D. Greiner, B. Galván, J. Périaux, N. Gauger, K. Giannakoglou, and G. Winter, editors. *Advances in Evolutionary and Deterministic Methods for Design, Optimization and Control in Engineering and Sciences*, volume 36 of *Computational Methods in Applied Sciences*. Springer International Publishing (2015).

[37] J. Magalhães-Mendes and D. Greiner, editors. *Evolutionary Algorithms and Metaheuristics in Civil Engineering and Construction Management*, volume 39 of *Computational Methods in Applied Sciences*. Springer International Publishing (2015).

[38] C. B. Lucasius and G. Kateman. Understanding and using genetic algorithms Part 1. Concepts, properties and context. *Chemometrics and Intelligent Laboratory Systems*, **19**(1), 1 (1993).

[39] D. B. Hibbert. Genetic algorithms in chemistry. *Chemometrics and Intelligent Laboratory Systems*, **19**(3), 277 (1993).

[40] D. B. Hibbert. A hybrid genetic algorithm for the estimation of kinetic parameters. *Chemometrics and Intelligent Laboratory Systems*, **19**(3), 319 (1993).

[41] T. J. VanderNoot and I. Abrahams. The use of genetic algorithms in the non-linear regression of immittance data. *Journal of Electroanalytical Chemistry*, **448**(1), 17 (1998).

[42] J. Yu, H. Cao, Y. Chen, L. Kang, and H. Yang. A new approach to the estimation of electrocrystallization parameters. *Journal of Electroanalytical Chemistry*, **474**(1), 69 (1999).

[43] L. C. Wrobel and P. Miltiadou. Genetic algorithms for inverse cathodic protection problems. *Engineering Analysis with Boundary Elements*, **28**(3), 267 (2004).

[44] J. Valadi and P. Siarry, editors. *Applications of Metaheuristics in Process Engineering*. Springer International Publishing, Cham (2014).

[45] R. Storn and K. Price. Differential Evolution – A Simple and Efficient Heuristic for global Optimization over Continuous Spaces. *Journal of Global Optimization*, **11**(4), 341 (1997).

[46] E. C. Trejo-Zúñiga, I. L. López-Cruz, and A. Ruíz-García. Estimación de parámetros para un modelo de crecimiento de cultivos usando algoritmos evolutivos y bio-inspirados. *Agrociencia*, **47**, 671 (2013).

[47] B. Peng, B. Liu, F.-Y. Zhang, and L. Wang. Differential evolution algorithm-based parameter estimation for chaotic systems. *Chaos, Solitons & Fractals*, **39**(5), 2110 (2009).

[48] C. K. Chong, M. S. Mohamad, S. Deris, S. Shamsir, A. Abdullah, Y. W. Choon, L. E. Chai, and S. Omatu. Using an Improved Differential Evolution Algorithm for Parameter Estimation to Simulate Glycolysis Pathway. In *Distributed Computing and Artificial Intelligence. Advances in Intelligent and Soft Computing*, S. Omatu, J. De Paz Santana, S. González, J. Molina, A. Bernardos, and J. Rodríguez, editors, volume 151, pages 709–716. Springer, Berlin, Heidelberg (2012).

[49] F. Neri and V. Tirronen. Recent advances in differential evolution: a survey and experimental analysis. *Artificial Intelligence Review*, **33**(1-2), 61 (2010).

[50] S. Das and P. N. Suganthan. Differential Evolution: A Survey of the State-of-the-Art. *IEEE Transactions on Evolutionary Computation*, **15**(1), 4 (2011).

[51] Q. Fan and Y. Zhang. Self-adaptive differential evolution algorithm with crossover strategies adaptation and its application in parameter estimation. *Chemometrics and Intelligent Laboratory Systems*, **151**, 164 (2016).

[52] J. Brest, S. Greiner, B. Boskovic, M. Mernik, and V. Zumer. Self-Adapting Control Parameters in Differential Evolution: A Comparative Study on Numerical Benchmark Problems. *IEEE Transactions on Evolutionary Computation*, **10**(6), 646 (2006).

[53] A. K. Qin, V. L. Huang, and P. N. Suganthan. Differential Evolution Algorithm With Strategy Adaptation for Global Numerical Optimization. *IEEE Transactions on Evolutionary Computation*, **13**(2), 398 (2009).

[54] Y. Wang, Z. Cai, and Q. Zhang. Differential Evolution With Composite Trial Vector Generation Strategies and Control Parameters. *IEEE Transactions on Evolutionary Computation*, **15**(1), 55 (2011).

[55] S. M. Elsayed, R. A. Sarker, and D. L. Essam. A self-adaptive combined strategies algorithm for constrained optimization using differential evolution. *Applied Mathematics and Computation*, **241**, 267 (2014).

[56] R. Mallipeddi, P. N. Suganthan, Q. K. Pan, and M. F. Tasgetiren. Differential evolution algorithm with ensemble of parameters and mutation strategies. *Applied Soft Computing*, **11**(2), 1679 (2011).

[57] S. M. Islam, S. Das, S. Ghosh, S. Roy, and P. N. Suganthan. An Adaptive Differential Evolution Algorithm With Novel Mutation and Crossover Strategies for Global Numerical Optimization. *IEEE Transactions on Systems, Man, and Cybernetics, Part B (Cybernetics)*, **42**(2), 482 (2012).

[58] Q. Fan and X. Yan. Differential evolution algorithm with self-adaptive strategy and control parameters for P-xylene oxidation process optimization. *Soft Computing*, **19**(5), 1363 (2015).

[59] F. González, D. Greiner, J. J. Aznárez, V. Mena, R. M. Souto, and J. J. Santana. Chemical process simulation using evolutionary algorithms: application to the analysis of impedance parameters of electrochemical systems (in Spanish). *Afinidad*, **72**(572), 278 (2015).

[60] M. A. Kappel, R. Fabbri, R. P. Domingos, and I. N. Bastos. Novel electrochemical impedance simulation design via stochastic algorithms for fitting equivalent circuits. *Measurement*, **94**, 344 (2016).

[61] M. A. Abud Kappel, F. C. Peixoto, G. M. Platt, R. P. Domingos, and I. N. Bastos. A study of equivalent electrical circuit fitting to electrochemical impedance using a stochastic method. *Applied Soft Computing*, **50**, 183 (2017).

[62] J. E. O. Mayne. The mechanism of the protective action of paints. In *Corrosion*, L. L. Shreir and R. A. Jarman, editors, pages 15:24 – 15:37. Newnes, 2nd edition (1976).

[63] F. Mansfeld. Models for the impedance behavior of protective coatings and cases of localized corrosion. *Electrochimica Acta*, **38**(14), 1891 (1993).

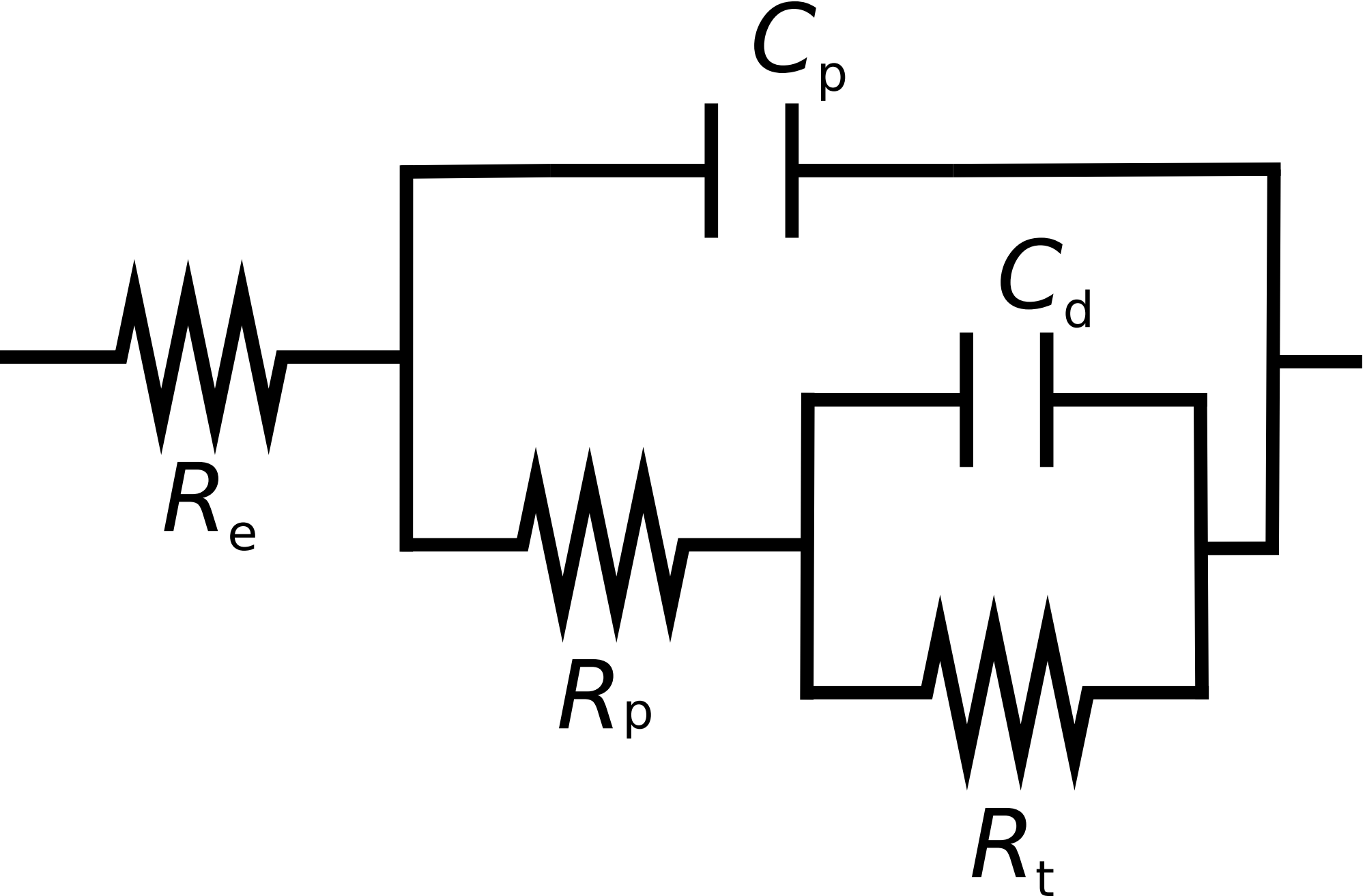
[64] J. E. Baker. Reducing Bias and Inefficiency in the Selection Algorithm. In *Proceedings of the Second International Conference on Genetic Algorithms on Genetic Algorithms and Their Application*, pages 14–21. L. Erlbaum Associates Inc., Hillsdale, NJ, USA (1987).

[65] A. K. Qin and P. N. Suganthan. Self-adaptive Differential Evolution Algorithm for Numerical Optimization. In *IEEE Congress on Evolutionary Computation*, volume 2, pages 1785–1791. IEEE (2005).

[66] B. Yeum. Technical Note 1: Extrapolation using Kramers-Kronig relations. *Technical report*, EChem Software, Ann Arbor, Michigan, USA (2002).

[67] J. M. Esteban and M. E. Orazem. On the Application of the Kramers-Kronig Relations to Evaluate the Consistency of Electrochemical Impedance Data. *Journal of The Electrochemical Society*, **138**(1), 67 (1991).

[68] J. J. Santana, J. E. González, J. Morales, S. González, and R. M. Souto. Evaluation of ecological organic paint coatings via electrochemical impedance spectroscopy. *International Journal of Electrochemical Science*, **7**(7), 6489 (2012).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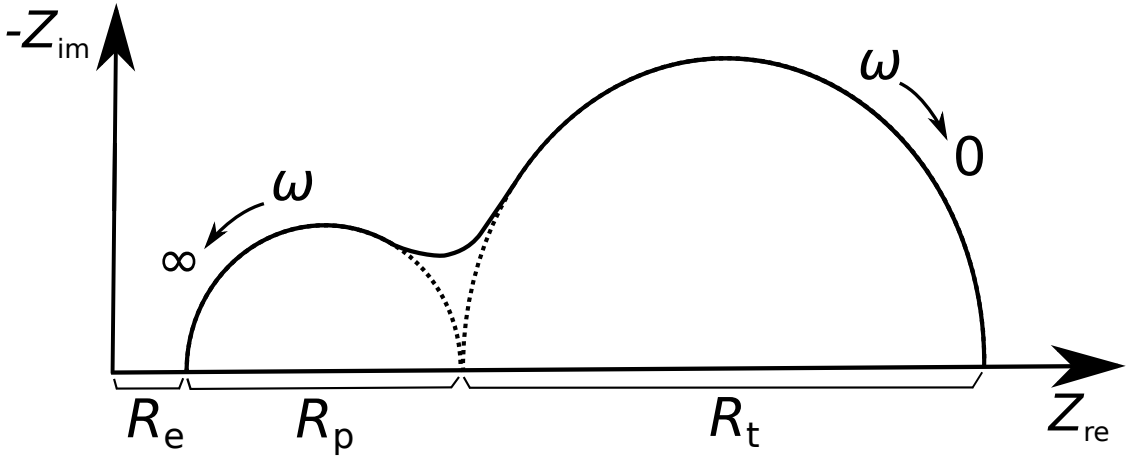
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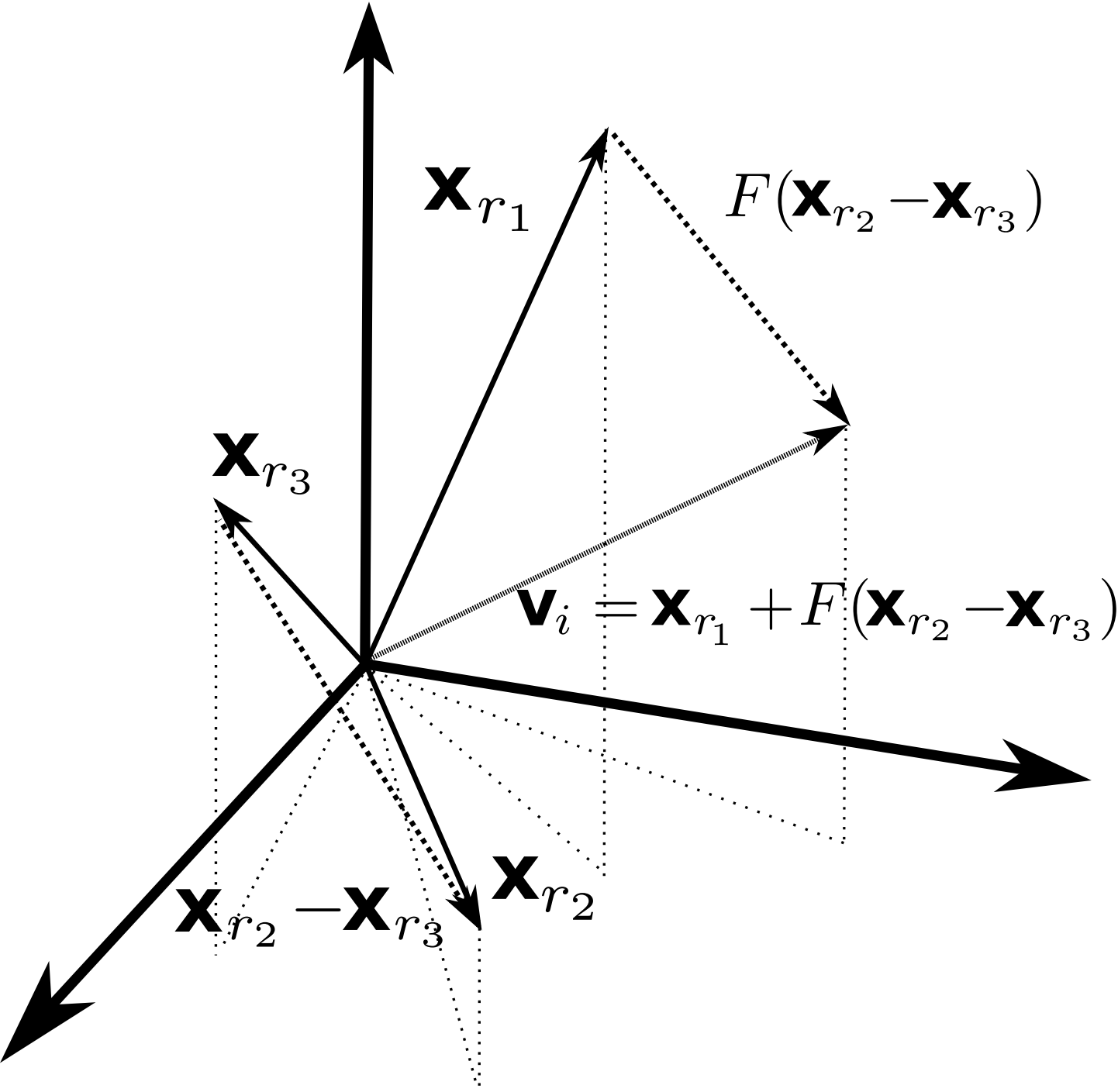
$\mathbf{x}_{r_1}$
$F(\mathbf{x}_{r_2} - \mathbf{x}_{r_3})$
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$\mathbf{v}_i = \mathbf{x}_{r_1} + F(\mathbf{x}_{r_2} - \mathbf{x}_{r_3})$
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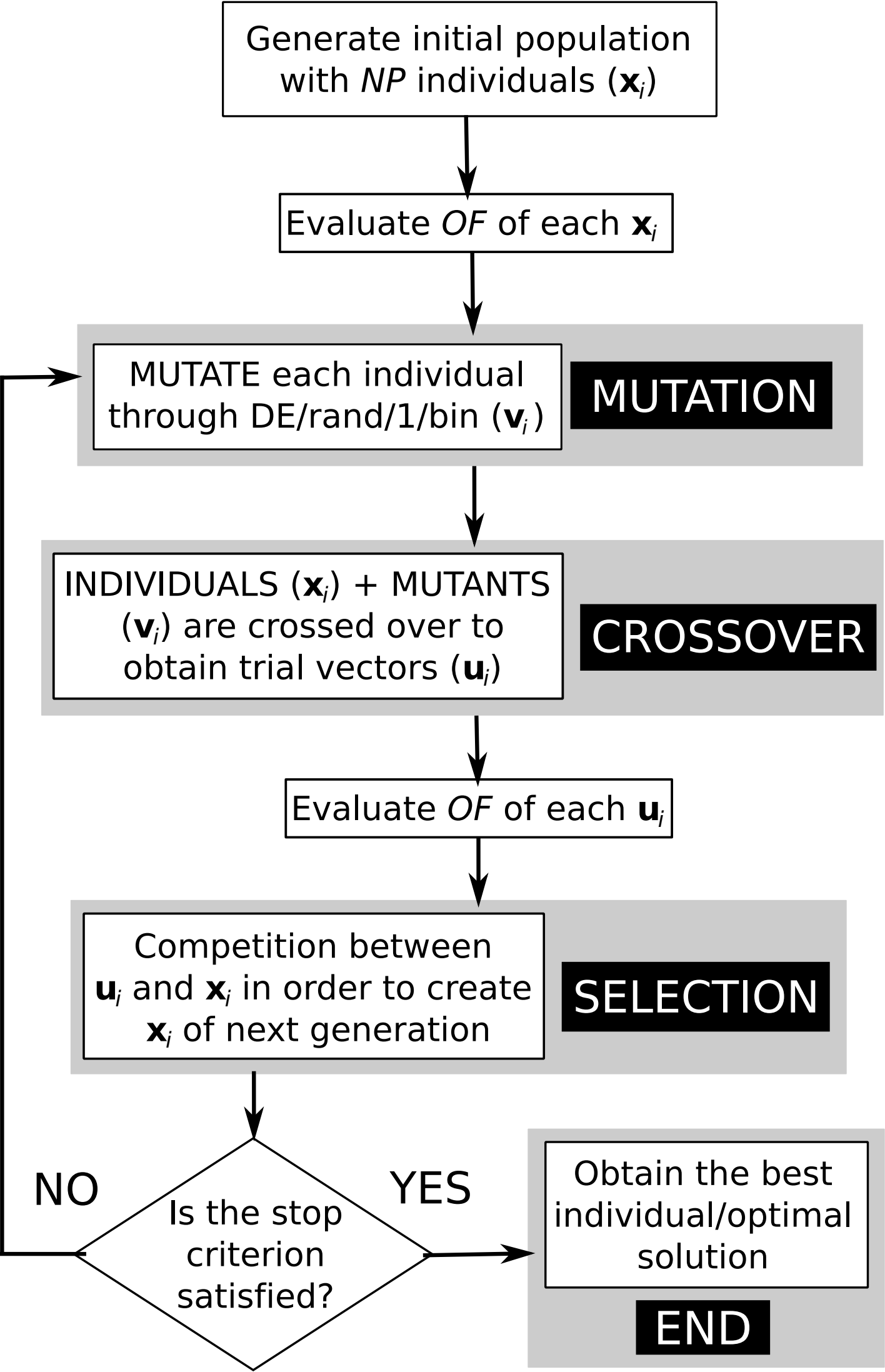
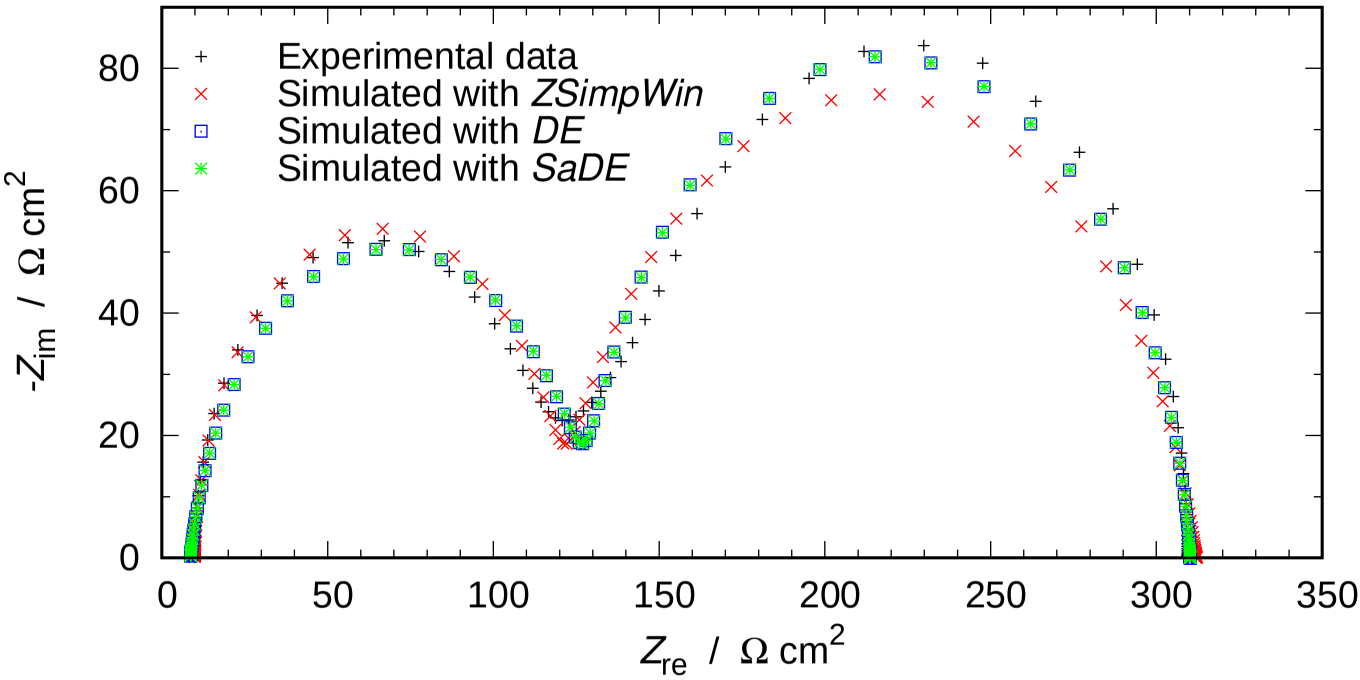

Generate initial population with NP individuals ($\mathbf{x}_i$)
Evaluate OF of each $\mathbf{x}_i$
MUTATE each individual through DE/rand/1/bin ($\mathbf{v}_i$)
MUTATION
INDIVIDUALS ($\mathbf{x}_i$) + MUTANTS ($\mathbf{v}_i$) are crossed over to obtain trial vectors ($\mathbf{u}_i$)
CROSSOVER
Evaluate OF of each $\mathbf{u}_i$
Competition between $\mathbf{u}_i$ and $\mathbf{x}_i$ in order to create $\mathbf{x}_i$ of next generation
SELECTION
Is the stop criterion satisfied?
NO
YES
Obtain the best individual/optimal solution
END


Experimental data
Simulated with ZSimpWin
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Simulated with SaDE
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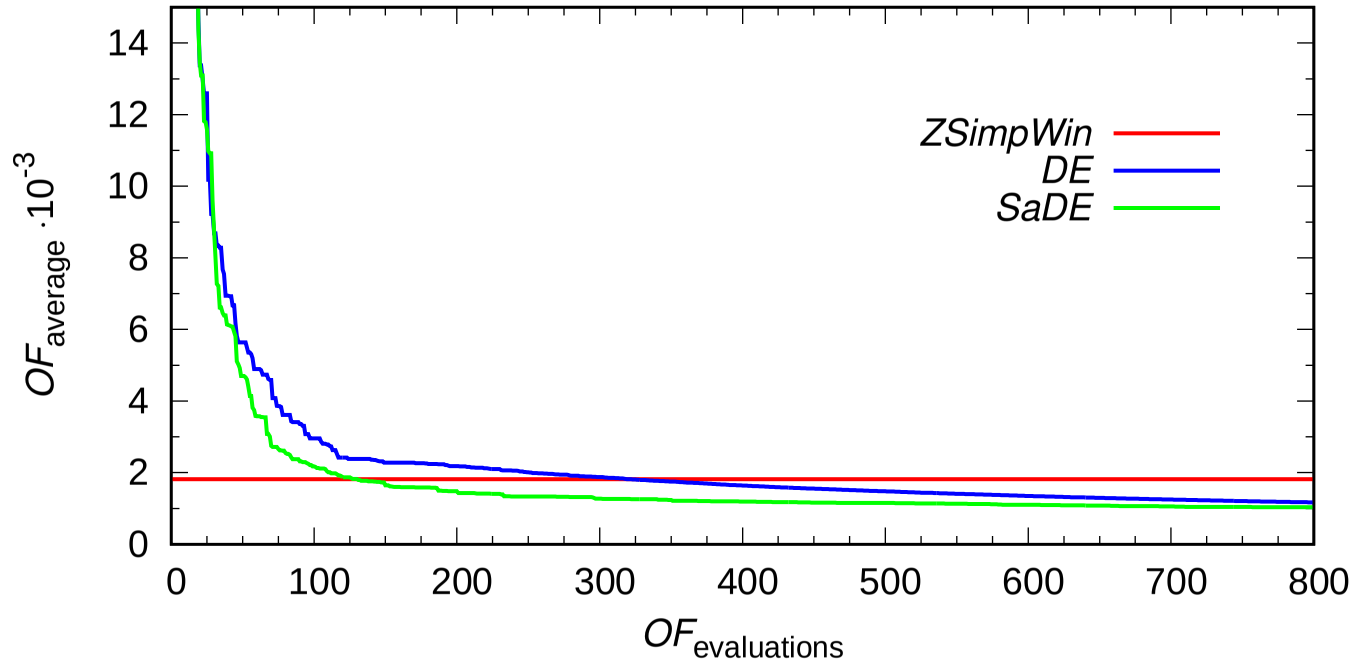
ZSimpWin
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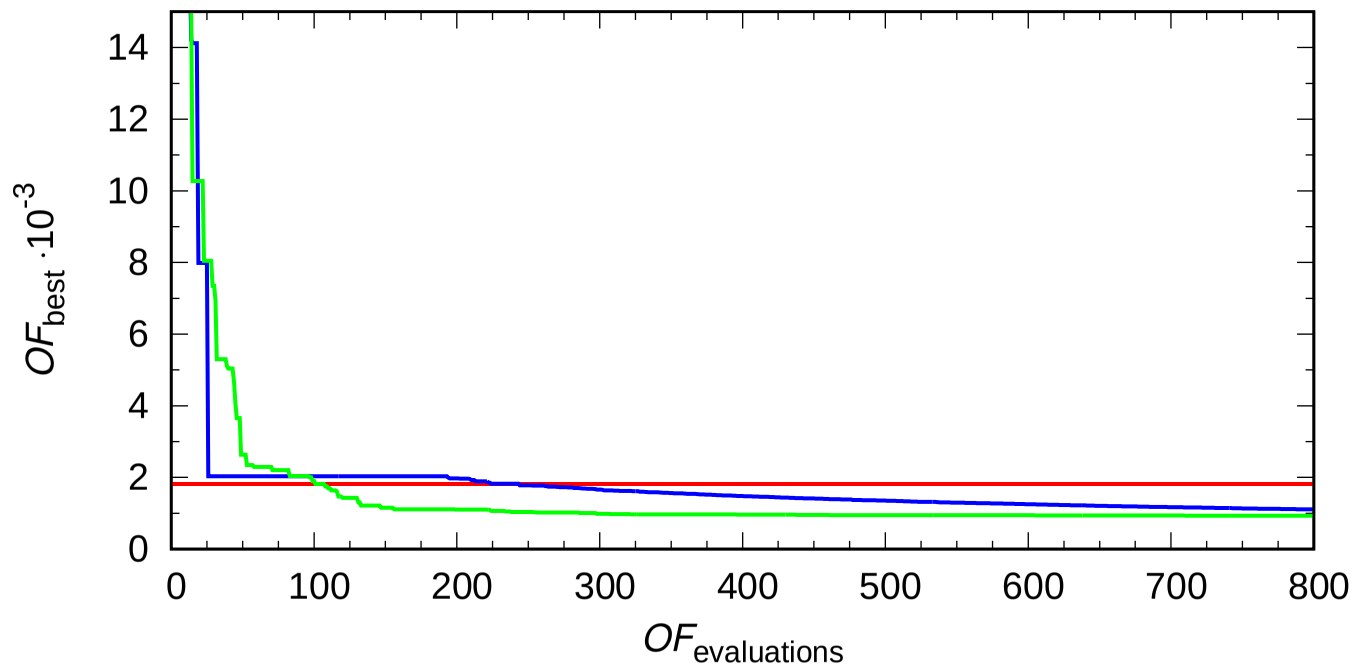
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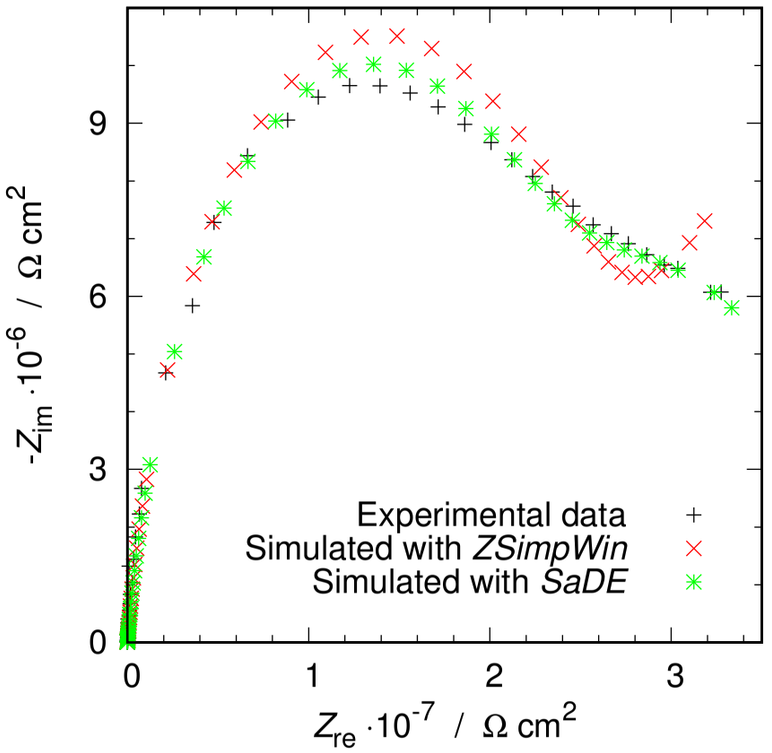
150 HOURS



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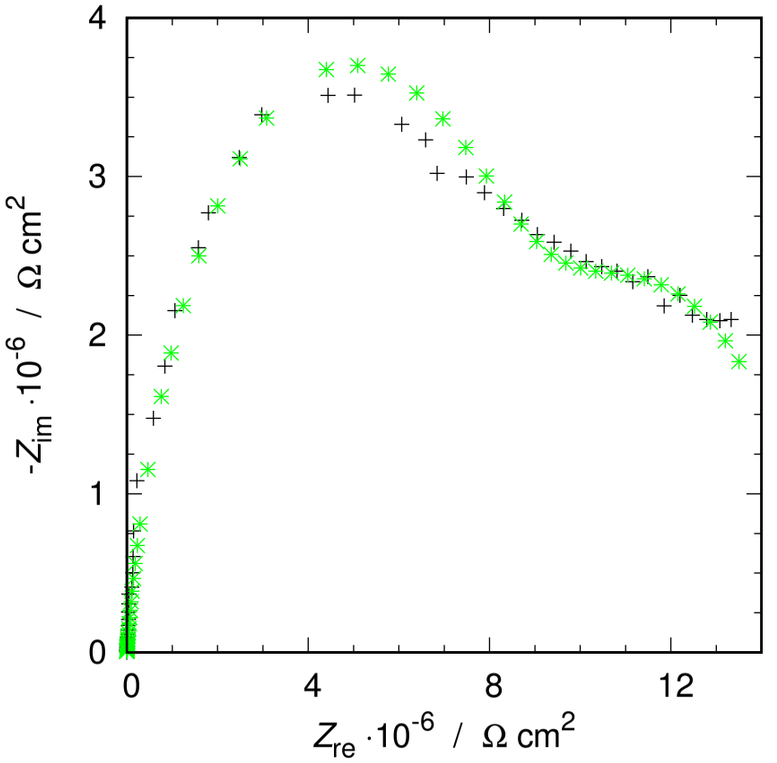

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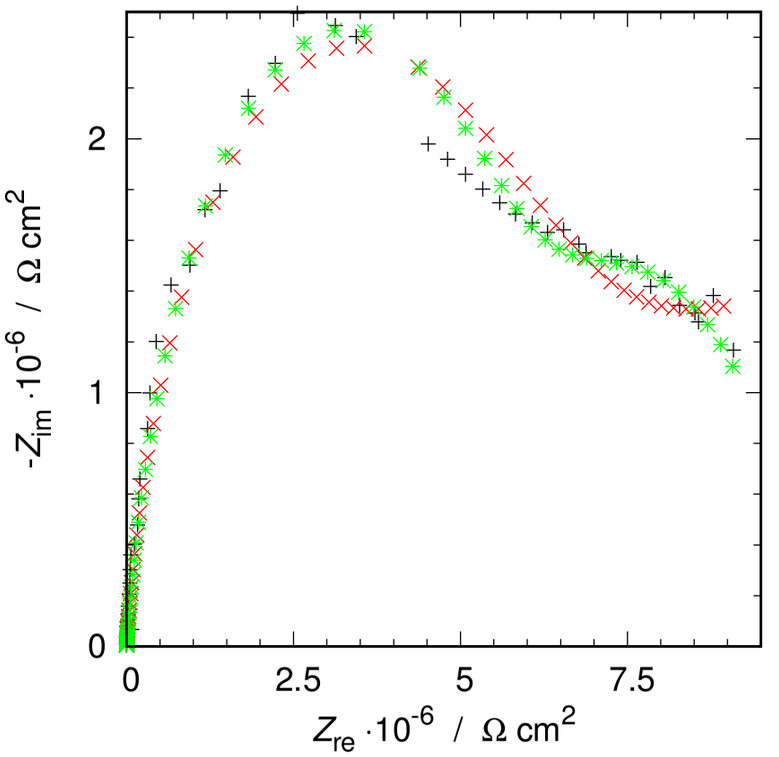

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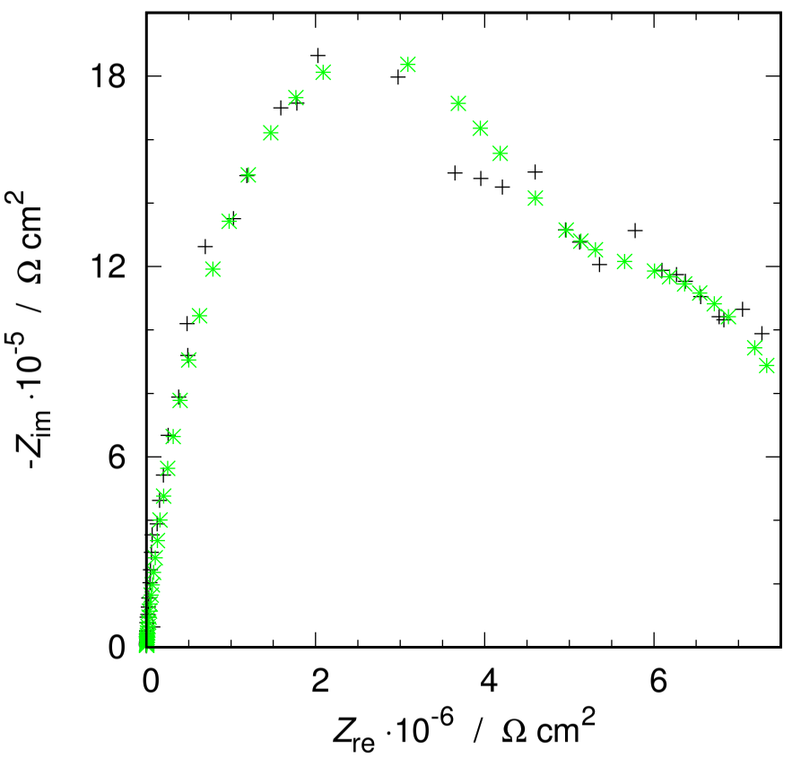

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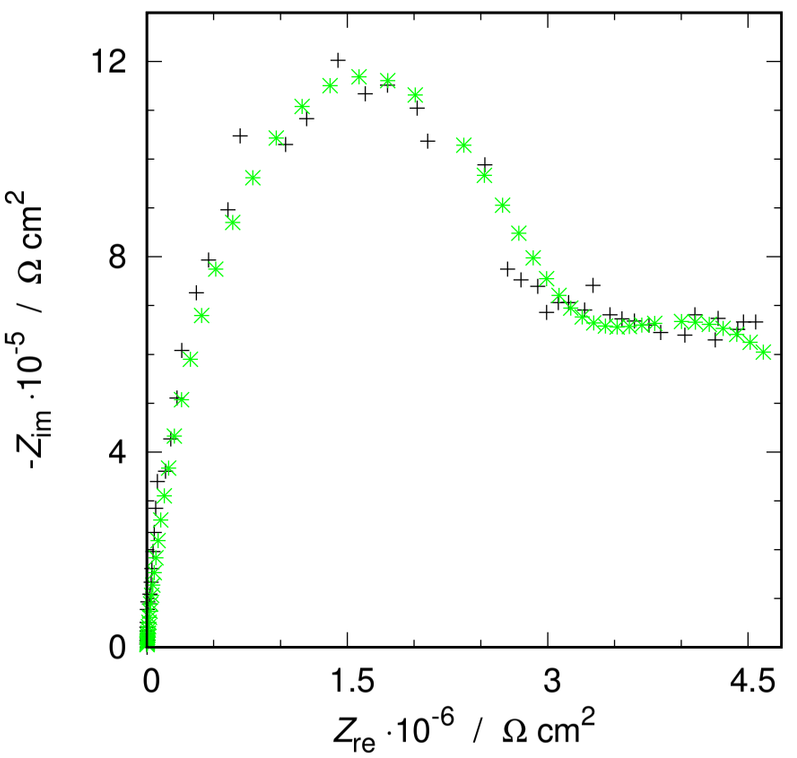

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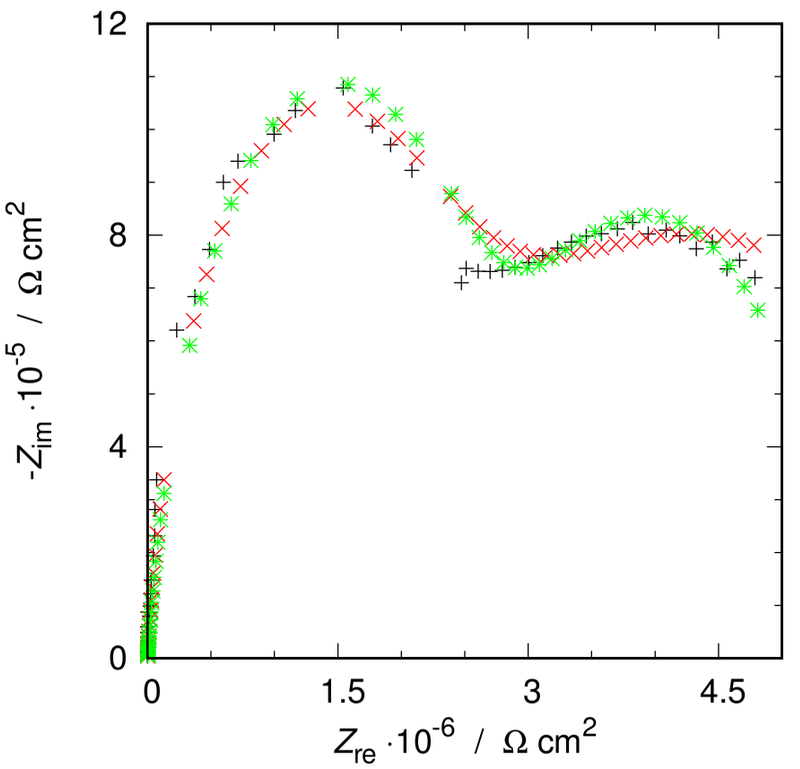

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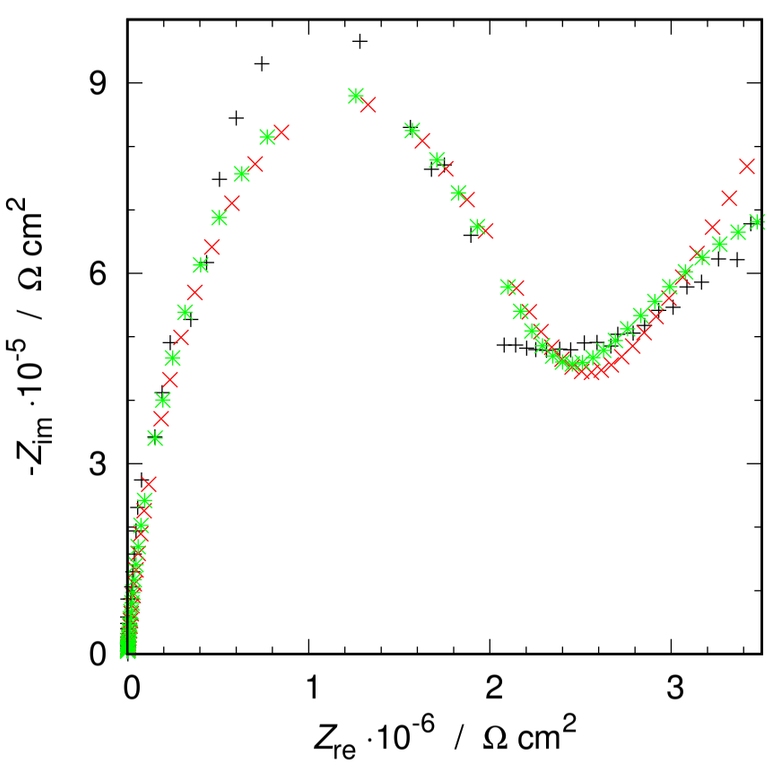

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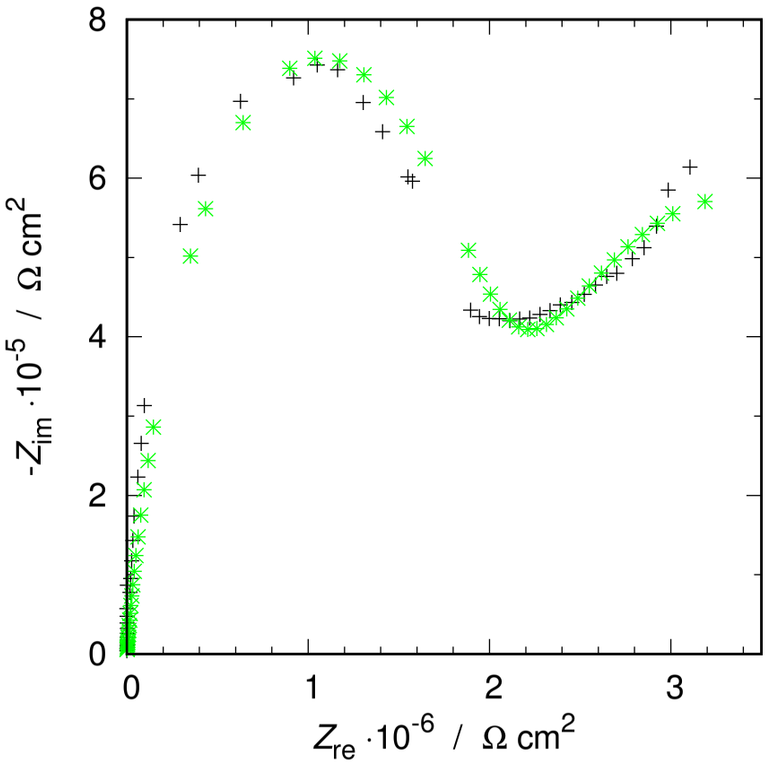

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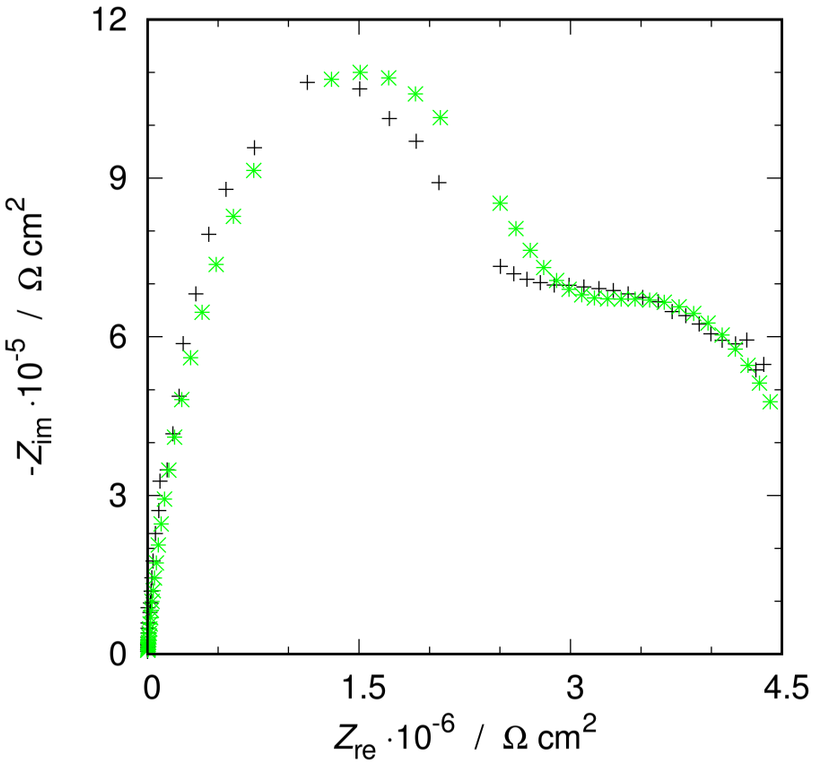
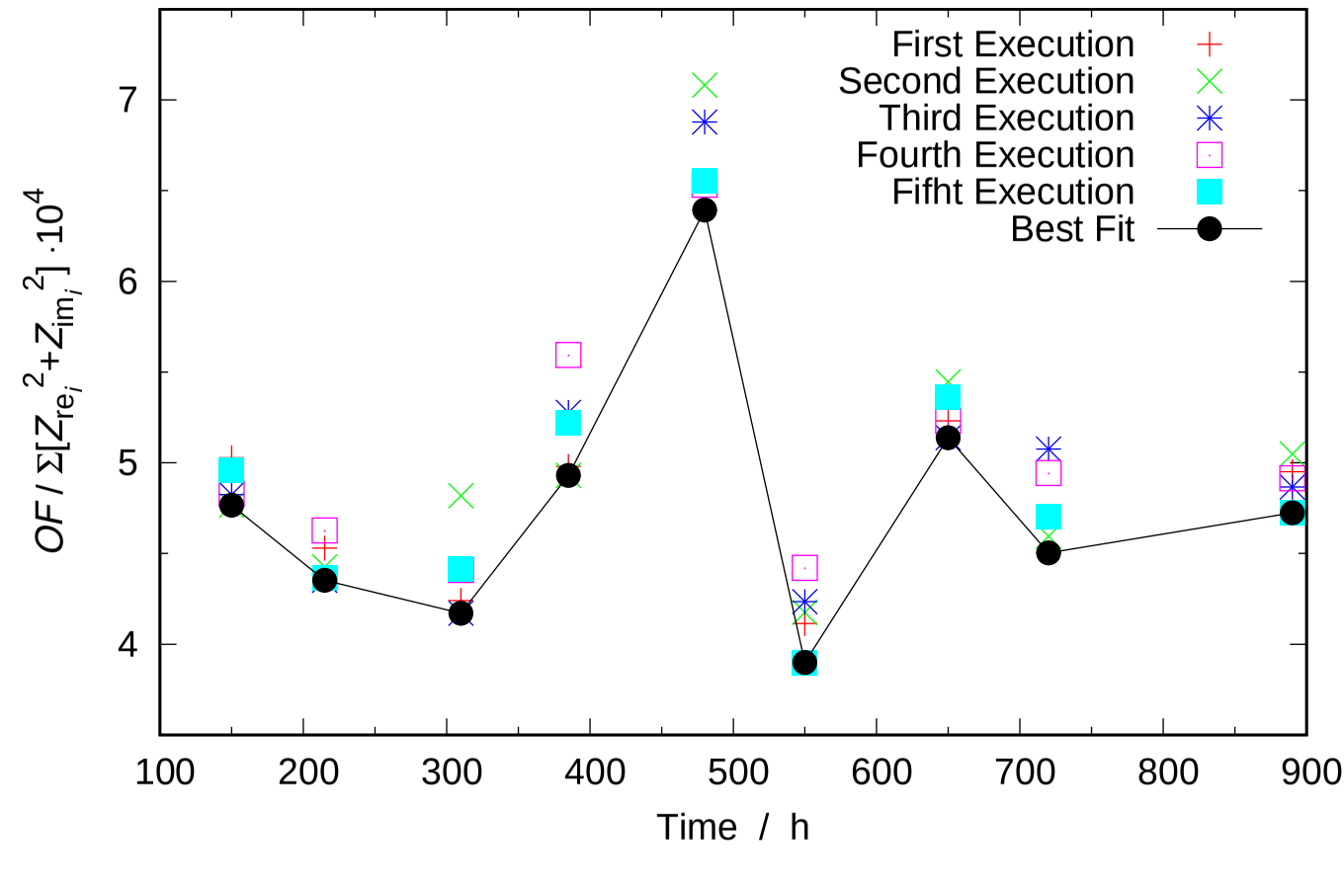
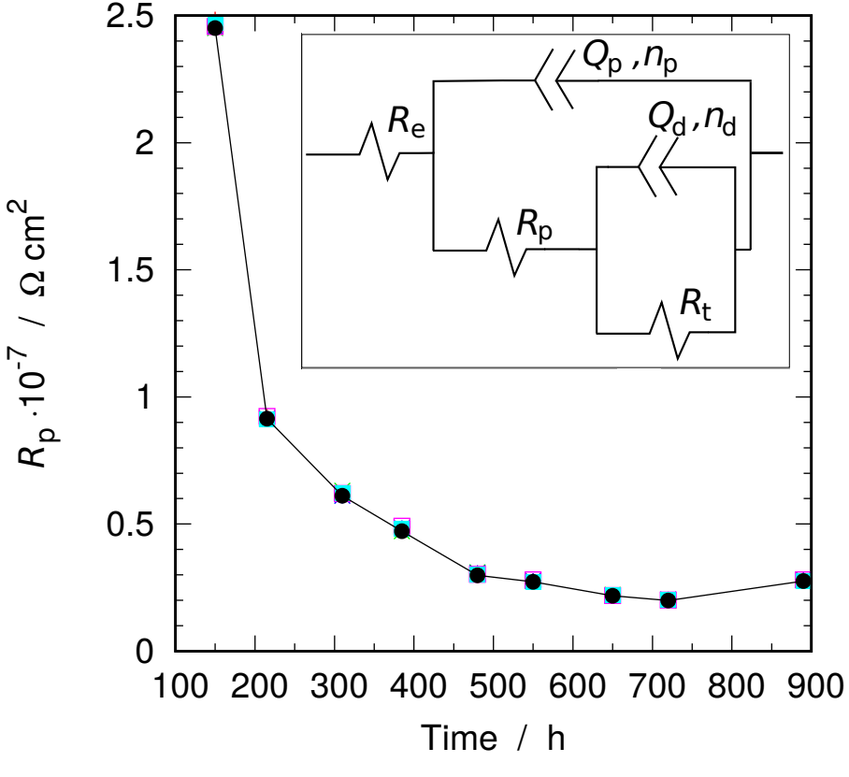
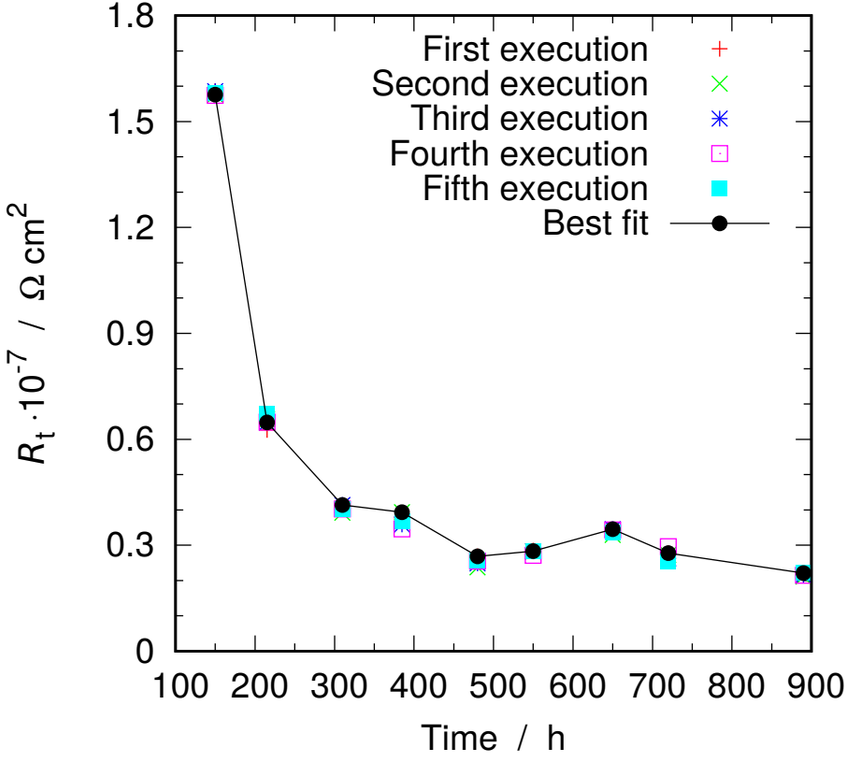
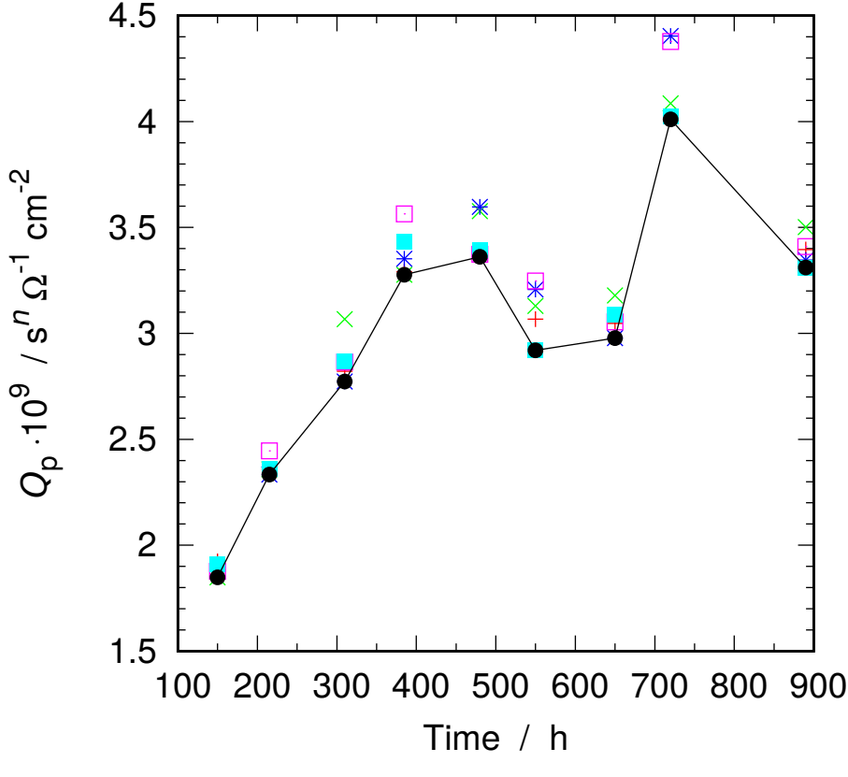
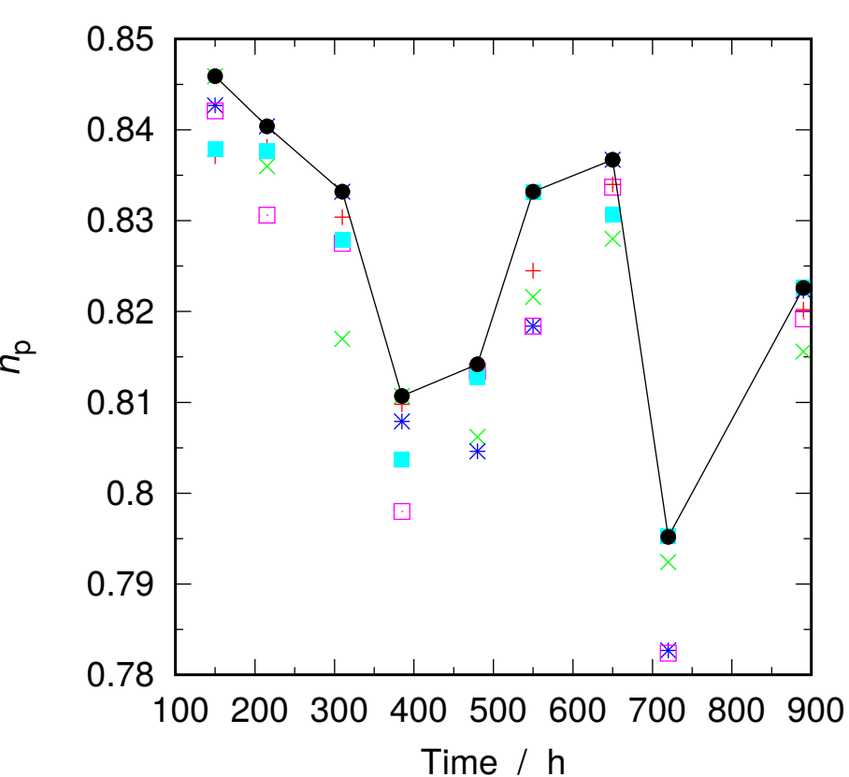


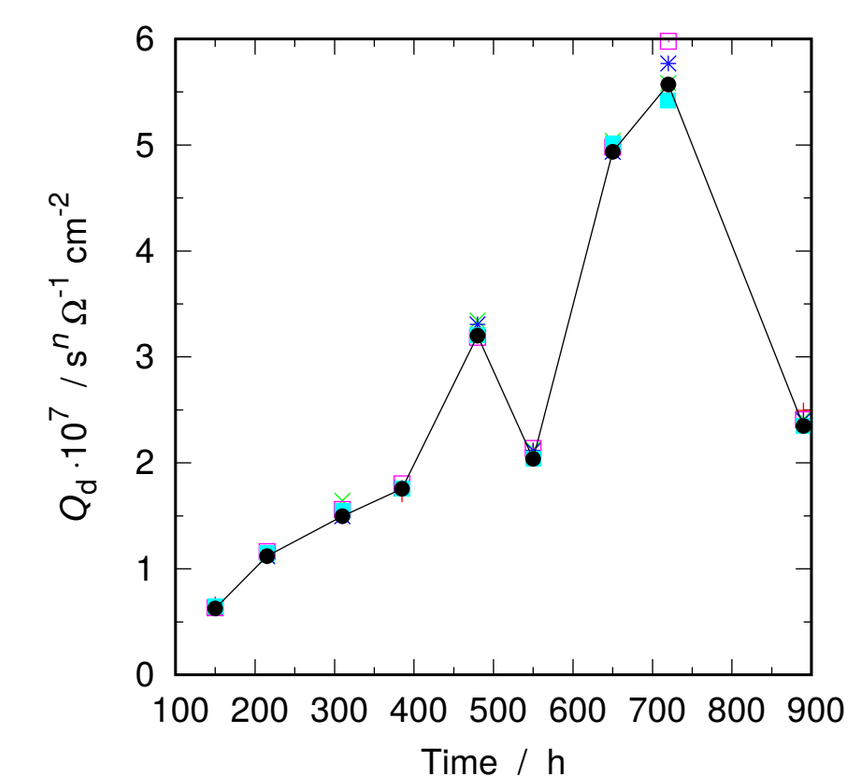

First Execution
Second Execution
Third Execution
Fourth Execution
Fifht Execution
Best Fit
OF / Σ[Z_re_i^2+Z_im_i^2] ·10^4
Time / h
7
6
5
4
100
200
300
400
500
600
700
800
900

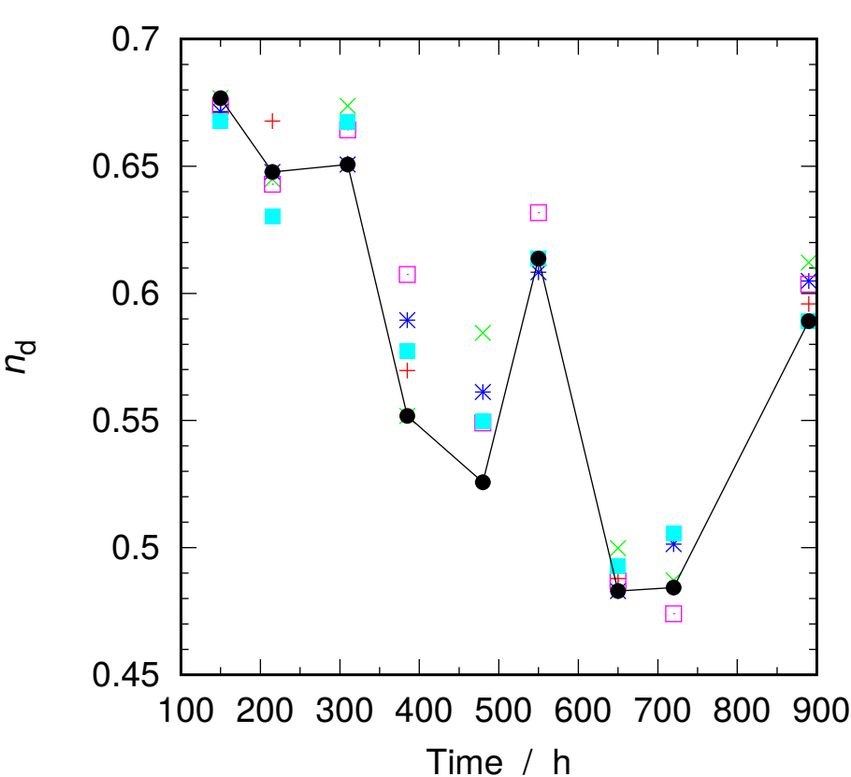

$R_p \cdot 10^{-7}$ / Ω cm^2
Time / h
Q_p , n_p
R_e
Q_d , n_d
R_p
R_t


$R_t \cdot 10^{-7}$ / Ω cm^2
Time / h
First execution
Second execution
Third execution
Fourth execution
Fifth execution
Best fit


$Q_p \cdot 10^9$ / s^n Ω^{-1} cm^{-2}
Time / h


n_p
Time / h


$Q_d \cdot 10^7$ / s^n Ω^{-1} cm^{-2}
Time / h


n_d
Time / h