# Experimental quantification of the effect of nonlinearities on the EIS spectra of the cathodic electrode of an alkaline electrolyser

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Abstract

Electrochemical Impedance Spectroscopy (EIS) is a very powerful tool to study the behaviour of electrochemical systems. According to Ohm's generalized law, the impedance concept is only valid if the linearity condition is met. In the case that the linearity condition is not achieved, the obtained impedance spectra will present distortions that may lead to biased or even erroneous results and conclusions. In this work, an experimental quantification of the effect of nonlinearities on EIS spectra was performed in order to determine the order of magnitude of the effect of the nonlinearity of the system on the obtained spectra of the cathodic electrode of an alkaline electrolyser.

1. Introduction

In current days, electrochemical impedance spectroscopy (EIS) has gained significant relevance in the electrochemistry research field, since this electrochemical measurement technique allows obtaining information on the internal state and on the electrochemical behaviour of a large number of electrochemical systems [1]. This electrochemical testing technique has been widely used in the fuel cell field: for fuel cell characterization [2-4]; for the study of polymer membrane fuel cells [5-7], solid oxide fuel cells [8-13] and high temperature fuel cells [14-16]; for fuel cell diagnosis [17-19]; for corrosion tests [20]; and for fuel cell control [21].

The impedance at angular frequency $\omega$, $Z(\omega)$, of a given system is defined by generalized Ohm's law. The complex Ohm's law, and thus the impedance concept, are only valid if the hypothesis of causality, linearity and stability are met [22]. If any of these conditions is not fulfilled the obtained spectra may be misleading and conclusions extracted from them may be biased or erroneous [23-24].

A lot of work has been done in literature in order to validate EIS spectra and verify that the 3 fundamental hypotheses are met. It has been shown that Kramers-Kronig (KK) transforms are a powerful tool for EIS validation [25-27]. The KK relations are integral equations that relate the real part and the imaginary part of complex quantities that meet the four fundamental conditions [28]. To date, three main methods for performing KK tests have been developed [29]: direct integration of the KK relations; experimental verification and regression to equivalent circuits.

The direct integration method consists in the prediction of one of the impedance components (real or imaginary) using the other component. The typical way found in literature to use this method is to use the KK relations for calculating the imaginary part using the experimental real part. The calculated imaginary part is then compared with the experimental imaginary part [30]. The major drawback of this method is that the integration of KK relations requires data in the frequency range $[0; +\infty[$; whereas, the measured frequency range is a finite interval. The integration of the KK relations over a narrow frequency range can lead to false negatives (i.e. reject the consistency with KK relations, when the data are consistent with them) [29]. One methodology available in literature to avoid this problem consists in the extrapolation of the measured data in the measured finite frequency range to the whole $[0; +\infty[$ range. Several extrapolation methods can be found in bibliography. The most important ones being the Kendig method [31], the Macdonald method [32] and the Haili method [33]. There is an alternative direct integration method that avoids the problem of having a finite range of measured frequencies without extrapolating: instead of predicting one of the components from the other component; both KK equations are used simultaneously in

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order to determine the complex impedance below the lowest experimentally measured frequency [27]. All these direct integration methods have a major drawback: they cannot be used if the measured frequency range is too narrow or if the maximum imaginary part point has not been obtained experimentally [29].

The experimental verification method consists in verifying experimentally and separately that the conditions of causality, linearity and stability are met [29].

Finally, the regression method is based in the following theorem: if a system can be fitted to an equivalent circuit model that satisfies the KK relations (e.g. The Voigt's circuit) then the system also satisfies these relations [34]. The regression method was initially introduced by Boukamp [35-36]. This methodology has the great advantage that it does not require the evaluation of integrals over an infinite frequency range. The measurement model tool for assessing the consistency of impedance data is mainly based in this kind of regression method for KK validation. The measurement model validation tool has been mainly developed by Orazem's group [27, 37-40]. In previous works, a Montecarlo based quantitative Kramers-Kronig test was presented [41-42]: this test is a regression method since it is an hybrid between Orazem's measurement model and Voigt's method.

A linear system is a system where the superposition principle holds: the response to the sum of individual perturbations is the sum of the individual responses to each of these perturbations [43]. However, the electrochemical systems are in general highly nonlinear systems since they are governed by Buttler-Volmer's equation [44]. Thus, in order to ensure compliance with the linearity condition in this kind of systems, the applied perturbation amplitude has to be small enough [45].

It has been shown in literature, that while KK relations are very sensitive to the non-compliance with the causality and the stability conditions, they are not sensitive to the violation of the linearity condition [26]. Hirschorn and Orazem observed that electrochemical systems only exhibit nonlinear behaviour for frequencies under a threshold frequency [38]. For frequencies higher than the threshold frequency the system behaves linearly even if very large perturbations are applied. The measurement model validation method was able to detect the violation of the linearity condition if data were acquired in a frequency range wide enough to contain the threshold frequency [25].

Today, some EIS softwares (e.g. NOVA®) include tools for linearity assessment, such as Lissajous plots and resolution plots [1], that can be displayed during data acquisition. These plots allow identifying nonlinear behaviour by monitoring the time domain raw signal. Even an hybrid EIS is available: this technique continually changes the

perturbation amplitude in order to fulfil the linearity condition during the whole measurement [46].

The nonlinearity of a system leads to the generation of harmonics, which distort the obtained EIS spectra [47]. There are a great number of theoretical works that demonstrate the generation of non-fundamental harmonics due to the nonlinearity of the system during electrochemical impedance measurements; such as the works of Darowicki [45], Diard and coworkers [48], Van Gheem and coworkers [49] and Victoria and Ramanathan [47].

Popkirov and co-workers presented a linearity assessment method based on the comparison of the input spectrum (input signal in the frequency domain) and the output spectrum (output signal in the frequency domain) [23, 50]: this method is based on the theoretical result according to which non-fundamental harmonics are generated due to nonlinearity. The works of Pintelon and co-workers are also based in this result [51-52].

As reviewed above, a lot of works can be found in literature on nonlinearity identification and spectra validation. This work does not aim to propose a method for nonlinearity identification. The aim of this work is to experimentally quantify the effect of nonlinearity on the EIS spectra of a given electrochemical system: the cathodic electrode of an alkaline electrolyser. In this work, authors intend to quantify experimentally the errors in the EIS spectra caused by the violation of the linearity condition; and determine if these errors are significant or not. An experimental approach has been selected for this work since there are already a great number of theoretical works in bibliography that deal with this issue, as the theoretical works cited in the previous literature review.  On the contrary, to our knowledge, there are few works that determine quantitatively the effect of nonlinearity on EIS spectra using an experimental approach, one of such works being the work of Diard and co-workers [53].

## 2. Methodology and experimental procedure

A highly nonlinear electrochemical system was selected for this work: the cathodic electrode of an alkaline electrolyser. The system was described in detail by Herraiz-Cardona [54-56]. Due to its high nonlinearity, the selected system allows to obtain a wide range of nonlinearities, simply by varying the amplitude of the imposed disturbance. Therefore, the experimental work consisted in the measurement of the EIS spectra of the selected system for different perturbation amplitudes.

The experimental set up is shown in figure 1: it consists in a three-electrode electrochemical cell patented by the Dpto. Ingeniería Química y Nuclear of the Universitat Politècnica de València [57]. This setup was described in detail by Herraiz-Cardona [54].

On the one hand, one of the electrodes developed by Herraiz-Cardona and co-workers was used as the working electrode. It consisted in a nickel electrode produced at very high current densities using the procedure described in [55]. This procedure yields rough porous electrodes with very high active areas. It had a geometric area of 0.5 cm$^2$. On the other hand, a nickel foam with very high surface area (Incofoam® 0.17 cm thick and 50 pores per linear inch) was used as counter-electrode. The mentioned counter-electrode was 1 cm wide, and its submerged length was of 5 cm. Finally, a commercial Ag/AgCl (3M KCl) electrode was used as the reference electrode. The employed electrolyte was an oxygen free 30 wt.% KOH solution. All experiments were performed at 30℃; in galvanostatic mode, for a DC current of $-10\ mA$ (the working electrode corresponds with the cathodic electrode), since in previous works it was determined that it corresponded to the most nonlinear operation point of the system. A different perturbation amplitude was used in each experiment. 12 perturbation amplitudes were considered: $0.1\ mA$, $0.5\ mA$, $1\ mA$, $2\ mA$, …. , $10\ mA$. The maximum considered perturbation amplitude was $10\ mA$, since it corresponds with the maximum amplitude that can be used for a DC current of $-10\ mA$ that guarantees that the working electrode works as cathode during the whole experiment.

The measurements were performed using an Autolab® 302N potentiostat/galvanostat with FRA module, controlled using NOVA® software. The selected frequency range was 10 kHz – 5 mHz, with 10 frequencies per decade. The used measurement parameters are listed in table 1. These parameters were selected using the methodology presented in [58], where the meaning of each measurement parameter was widely explained.

Measurements were obtained in triplicate in order to control the reproducibility of the obtained results. Replicates of each measurement were not performed sequentially; instead, the experiments were done in three different blocks as shown in table 2, which

gives the temporary order in which the experiments were performed. As it can be seen in the table mentioned above, the order of the experiments inside each block was randomized; instead of performing the experiments in order of increasing or decreasing amplitude. The pseudo-random order strategy was selected since randomization makes the factors of time and amplitude orthogonal: this means that it allows to distinguish the effects of the perturbation amplitude from the effects of possible time drifts. On the contrary, if an increasing amplitude strategy is used, it is not possible to know if the observed trends are due to a time drift of the system or to the effect of the perturbation amplitude.

Before each experiment, a pre-treatment was applied to the working electrode in order to ensure similar surface conditions in all experiments. The applied pre-treatment consisted in applying a $-1.6V$ (vs. Ag/AgCl) potential during 30 minutes. This treatment was done to reduce any oxide film that could exist on the surface of the porous electrode [54], in order to guarantee that the surface of the electrode was in similar conditions in all the experiments. This pre-treatment is critical in order to ensure the reproducibility of the results.

## 3. Results and discussion

### 3.1. Impedance spectra

The impedance spectra obtained for each perturbation amplitude can be seen in figure 2. It can be observed that all the spectra present a depressed capacitive semicircle. Actually, this semicircle is formed by two overlapping semi-circles, one for high frequencies and the other one for intermediate frequencies [54]. The high frequency semi-circle is related to the diffusion of $H_2$ through the porous network of the electrode; whereas, the intermediate frequency semi-circle is related to the Hydrogen Evolution Reaction (HER) kinetics [54]. Moreover, the semi-circles are displaced away from the origin. This displacement is due to the electrolyte resistance. Although the general shape of the spectrum is the same for the different perturbation amplitudes (except for extreme amplitudes, for which even the general shape varies), a significant variation of the spectra with the perturbation amplitude can be observed. Small inductive effects are observed at high frequencies. These inductive effects are due to cable connections, and not to the system itself [59-60]. Because of this, these small inductive effects were not taken into account in this work.

The results obtained in the three replicates of each experiment are nearly identical: the results have a very high reproducibility. For clarity purposes, since they are nearly identical, only the results of one of the replicate blocks are presented in figure 2. Since a random order strategy was used, the fact that the results are highly reproducible implies that no significant time drift took place during the experiments. Consequently, the observed variation of the experimental spectra is only due to the perturbation amplitude and not to a time drift or a non-stationarity of the system.

As it can be observed in figure 2.a, the spectra obtained for low amplitudes (from 1 mA to 3 mA) are almost identical, and discrepancies can only be observed in the low frequency zone. This variation of the spectra for low frequencies is not due to the effect of the perturbation amplitude; it is due to the measurement variability at low frequencies, which is significantly higher than the measurement variability for high and intermediate frequencies [29]. For the spectra obtained for very low amplitudes (0.1 mA and 0.5 mA) the variability of the measurement for low frequencies is much higher than in the case of amplitudes in the range 1 mA to 3 mA. This is due to the fact that for such low amplitudes the signal-to-noise ratio is very low, and this results in a very high variability in the measurement at low frequencies. This causes the noisy pattern in the low frequency zone in the spectra obtained with very low perturbation amplitudes. Furthermore, the 50 Hz point presents a high variability from one spectrum to another. This is due to the coupling of the measurement with the electric supply grid.

In order to verify the above hypothesis, the signal-to-noise ratio was determined experimentally. The following expression was used to calculate the signal-to-noise ratio (SNR) in decibels (dB) [61]:

$$SNR\ (dB) = 20 \cdot log_{10} \left( \frac{I_{signal}}{I_{noise}} \right) \qquad (1)$$

Where $I_{signal}$ stands for the input signal amplitude and $I_{noise}$ represents the signal noise amplitude. $log_{10}$ corresponds with the decimal logarithm. The values of $I_{signal}$ and $I_{noise}$ can be obtained from the Fourier transform of the applied perturbation signal. On the one hand, $I_{signal}$ corresponds with the amplitude of the fundamental component of the perturbation signal. Naturally, the value of $I_{signal}$ obtained in this manner has to be very similar to the perturbation amplitude selected for performing the EIS measurement. On the other hand, $I_{noise}$ corresponds with the amplitude of the most important non fundamental harmonic of the perturbation signal. In this work, the perturbation applied for each frequency was stored (in the time domain) during the EIS measurement. Then, a Fast Fourier Algorithm (FFT) was applied to each one of the stored signals, in order to obtain the signals in the frequency domain. In this way, the values of $I_{signal}$ and $I_{noise}$, and therefore the value of $SNR$, were obtained for each frequency and for each perturbation amplitude. Figure 3 shows the input signal-to-noise curves for the different perturbation amplitudes. The SNR curves correspond with the representation of the signal-to-noise ratio in dBs versus the excited frequency. As it can be observed in figure 3.a, for low amplitudes an increase of the perturbation amplitude causes a displacement of the SNR curve towards higher SNR values: an increase in the perturbation amplitude improves the signal-to-noise ratio. The most significant increase is observed comparing the 0.1 mA and the 0.5 mA experiments: the SNR improves in nearly 15 dB for all frequencies. As it can be observed in figure 3.b, for high perturbation amplitudes no clear trend can be observed for the SNR curves with the perturbation amplitude. This means that after a threshold amplitude, further increases in the perturbation amplitude do not improve significantly the signal-to-noise ratio. These observations confirm the hypothesis that the signal-to-noise ratio for low perturbation amplitudes (0.1 mA and 0.5 mA) is significantly lower than the signal-to-noise ratio for the rest of the experiments.

As it can be observed in figure 2.b, the spectra obtained with high perturbation amplitudes (greater than 3 mA) are significantly affected by the amplitude in the intermediate and low frequency zones. The observed variability is much greater than the measurement variability observed for low amplitudes. In addition, no noisy pattern is observed; instead, a systematic distortion is observed: an increase of the perturbation amplitude, for amplitudes greater than 3 mA, causes a significant expansion of the

intermediate frequency capacitive semicircle. In the extreme case of a perturbation amplitude of 10 mA, a variation of the overall shape of the spectrum compared to the spectra obtained for lower amplitudes is observed. From this systematic distortion of the spectrum, it can be deduced that the observed variations of the spectra are due to the perturbation amplitude and not only to the variability inherent to the measurement, as in the low amplitude case. The expansion of the low frequency zone of the EIS spectrum of an electrochemical electrode with an increase of the perturbation amplitude was already observed by Diard and coworkers [53, 62] and is consistent with their theoretical formulation [48].

In short, the perturbation amplitude has no significant effect on the spectra for low amplitudes. For these low amplitudes, the observed variability in the obtained spectra is due to the variability inherent to the measurement, which is closely related to the signal-to-noise ratio. While for high amplitudes, the perturbation amplitude has a significant effect on the spectrum: an increase in the amplitude causes a distortion in the obtained spectrum; and can even modify the overall shape of the spectrum for very large amplitudes. This effect of the perturbation amplitude is due to the emergence of nonlinear effects for amplitudes larger than a critical perturbation amplitude.

The fact that the spectrum distortion is only observed in the intermediate/low frequency zone, and not in the high frequency zone, shows that the nonlinear effects only appear under a threshold frequency. On the one hand, for frequencies higher than the threshold the nonlinear effects are neglectable even for very large amplitudes: there will be no distortion of the spectrum in the frequency zone corresponding to frequencies larger than the threshold frequency. Thus this part of the spectrum can be used with no fear of introducing bias in the results of the analysis because of a distortion due to nonlinear effects. On the other hand, for frequencies below the threshold the nonlinear effects are not neglectable above a critical amplitude of the perturbation: for amplitudes above the critical amplitude, a significant distortion in the frequency zone corresponding to frequencies below the threshold frequency will be observed. Consequently, this part of the spectrum may introduce a bias in the results of the analysis because of the distortion due to nonlinear effects in the case that the used amplitude is above the critical amplitude. The existence of a frequency threshold above which nonlinearities are negligible was already observed by Orazem [38].

This frequency threshold has a physical explanation. On the one hand, in the studied system, the dominant processes at high frequencies are the electrolyte resistance and the diffusion in the porous network of the electrode [54]. The first process is governed by Ohm's law, while the second one is dominated by Fick's law. Both laws are linear laws. This explains why the system behaves linearly at high frequencies, even for high perturbation amplitudes. On the other hand, in the studied system, the dominant

process at low frequencies is the charge transfer [54], which is governed by Butler-Volmer equation. This equation is a highly nonlinear equation. This is the reason why the system exhibits a nonlinear behavior at low frequencies. The change with frequency of the dominant process, from a linear process at high frequencies to a nonlinear process at low frequencies, explains why a threshold frequency arises in the studied system. Obviously, only the electrochemical systems that present such dominant process switch will exhibit a threshold frequency.

### 3.2. Qualitative analysis of the effect of the perturbation amplitude on the fitting parameters

In order to quantify the effects of the nonlinearity of the EIS spectra, the evolution of the parameters of an equivalent circuit model with the perturbation amplitude was studied. Figure 4 shows the equivalent circuit proposed by Herraiz-Cardona and co-workers for this system [54]: the proposed circuit is composed by three resistances and two constant phase elements (CPEs). The physical explanation of this equivalent circuit was widely described by Herraiz-Cardona [54-56, 63]. This two-time-constant model was introduced by Chen and Lasia [64]; and was used later by Birry and Lasia [65]. One of the time constants $(Q_2; R_3)$ is related to the Hydrogen Evolution Reaction (HER) kinetics; while the other time constant $(Q_1; R_2)$ is related to the diffusion of $H_2$ through the porous network of the electrode. Finally, the unbalanced resistance, $R_1$, is associated to the electrolyte resistance.

In this work, the spectra obtained for the different perturbation amplitudes, presented in section 3.1, were fitted to the equivalent circuit shown in figure 4. The obtained fittings are displayed as dashed lines in figures 2.a. and 2.b. Figures 5 and 6 give the obtained fitting parameters for each perturbation amplitude, with the corresponding 95.4% error bars; and figure 7 gives the fitting goodness parameter for each amplitude.

As it can be seen in figures 2.a. and 2.b. the selected equivalent circuit is able to perfectly fit the experimental spectra obtained for perturbation amplitudes lower than 8 mA; whereas it does not fit correctly the spectra obtained with perturbation amplitudes higher than 8 mA. This is due to the fact that the spectrum distortion is so significant for amplitudes above 8 mA that it modifies the overall shape of the spectrum.

On the one hand, figure 5 shows the value of the resistance parameters of the model $(R_1, \ R_2 \ and \ R_3)$ obtained from the fitting of each experimental spectrum. It can be observed that the value of parameter $R_1$ does not vary significantly with the perturbation amplitude. Parameter $R_1$ corresponds with the intercept of the real axis at high frequencies. As seen in section 3.1, the amplitude does not modify significantly the high frequency part of the spectra; and thus, it does not have a significant effect on $R_1$.

Conversely, the fitted values of parameters $R_2$ and $R_3$ vary significantly with the perturbation amplitude. It can be observed that for low amplitudes (from 0.5 mA to 3 mA), the fitted values are nearly constant with the amplitude of the perturbation. For very low amplitude (0.1 mA), the fitted value of parameters $R_2$ and $R_3$ vary significantly with respect to the fitted values obtained from the spectra obtained in the 0.5 mA to 3 mA range. This variation of parameters $R_2$ and $R_3$ for the lowest amplitude is due to a very low signal-to-noise ratio for that amplitude. This ratio is so low in the 0.1 mA case that the measurement variability due to noise causes a bias in the fitted values of these parameters. Besides this exception for the lowest amplitude, the fitted values of parameters $R_2$ and $R_3$ can be considered as practically constant for low amplitudes (up to 3 mA). For amplitudes larger than 3 mA, it can be observed that the values obtained for these resistances vary significantly with the perturbation amplitude: an increase in the amplitude leads to a lower fitted value for resistance $R_2$, and a higher fitted value for resistance $R_3$. This is due to the distortion of the spectra for high perturbation amplitudes, observed in the previous section: an increase in the amplitude causes the contraction of the high frequency semicircle (associated to $R_2$), and the expansion of the intermediate frequency semicircle (associated to $R_3$). This trend is broken at 10 mA. As stated in section 3.1, the spectrum obtained for perturbation amplitude of 10 mA is so distorted that the general shape of the spectrum is modified. This modification of the overall shape of the spectrum causes the change in the trend of the fitted values of parameters $R_2$ and $R_3$. In short, the fitted values of parameters $R_2$ and $R_3$ vary significantly for perturbation amplitudes greater than 3 mA.

On the other hand, figure 6 shows the values of the parameters associated with the constant phase elements (CPE) of the model obtained from the fitting of each experimental spectrum: figure 6.a shows the pseudo-capacitance, while figure 6.b is related to the exponent. The parameters of the CPE associated to the high frequency semicircle $(Q_1$ and $\alpha_1)$ fluctuate without a clear trend for amplitudes lower than 8 mA. These fluctuations are due to the small weight of the high frequency semicircle, which causes a high fitting variability of these parameters. Consequently, it can be considered that the values of $Q_1$ and $\alpha_1$ do not vary significantly with the amplitude of the perturbation for amplitudes lower than 8 mA: the observed variations in these parameters are due to the variability introduced in the fitting, because of the low weight of the high frequency semicircle. As it was stated in section 5.1, an increase in the perturbation amplitude does not distort significantly the high frequency zone of the spectra, so it is logical that the parameters of the CPE associated to the high frequency semicircle are not significantly affected by the perturbation amplitude. However, for very high amplitudes it was observed that the overall shape of the spectra varied: this change in the general shape causes a significant variation of the values of $Q_1$ and $\alpha_1$ when increasing amplitudes above 8 mA. In the case of the parameters of the CPE associated to the intermediate frequency semicircle $(Q_2$ and $\alpha_2)$, the fitted values are

approximately constant for amplitudes lower than 4 mA. The exponent associated to this semicircle, $\alpha_2$, is equal to 1 for amplitudes lower than 4 mA: therefore, the intermediate frequency semicircle is a perfect semicircle, associated to a pure capacitive element. In contrast, when the perturbation amplitude is increased above 4 mA the fitted value of $\alpha_2$ drops significantly. Therefore, the intermediate frequency semicircle gets depressed when the amplitude is increased above 4 mA on account of the nonlinear effects. Finally, for amplitudes larger than 8 mA, the values of $Q_2$ $and$ $\alpha_2$ vary markedly, due to the change of the general shape of the spectrum. In short, it can be considered that there is a significant variation of parameters $Q_1$ $and$ $\alpha_1$ for amplitudes greater than 8 mA; while the fitted values of $Q_2$ $and$ $\alpha_2$ vary significantly for perturbation amplitudes above 4 mA.

A common approach used to analyse circuits with CPEs is to work with pseudocapacitances, rather than with the CPE parameters themselves. Macdonald [66], and Hsu and Mansfeld [67], obtained the following expression for the pseudocapacitance of the parallel association of a CPE and a resistor:

$$C_{eq} = \frac{(R \cdot Q)^{\frac{1}{\alpha}}}{R} \qquad (2)$$

The above equation was used to determine the pseudocapacitance of each one of the CPEs of the considered equivalent circuit (figure 4). It was observed that the pseudocapacitances display the same trends with the perturbation amplitude, than the CPE parameters. Consequently, the conclusions extracted from figure 6 can be extrapolated to the pseudocapacitances.

Finally, figure 7 shows the fitting goodness parameter, $\chi^2$. It can be observed that the goodness parameter remains approximately constant for amplitudes ranging from 0.5 mA to 8 mA. It can be deduced that despite the distortion of the spectrum, in the 0.5 mA to 8 mA range the distortion is not enough to make the equivalent circuit model unable to fit the spectrum. On one side, the parameter $\chi^2$ is slightly higher for 0.1 mA, because of the noise-related variability of the points of the spectrum for an amplitude of 0.1 mA. On the other side, for amplitudes larger than 8 mA, the parameter $\chi^2$ increases with the amplitude of the perturbation: the spectrum distortion is so significant for amplitudes above 8 mA that it modifies the overall shape of the spectrum, causing that the equivalent circuit is no longer able to model the shape of the spectra. This results in a higher fitting goodness parameter (worst overall fitting). This is consistent with the observations extracted from the fittings of the experimental spectra represented in figures 2.a. and 2.b.

### 3.3. Quantitative analysis of the effect of the perturbation amplitude on the fitting parameters

After analysing qualitatively the effect of the perturbation amplitude on the fitted parameters, the next step is to quantify that effect. In previous works it was determined that the optimum amplitude (maximum perturbation amplitude that does not generate significant nonlinear effects) for measuring impedance spectra of the experimental system used in this work was of 2 mA. The methodology used to determine the optimum perturbation amplitude was presented in FDFC 2015 [68], and in a previous paper [69]. This methodology consists in measuring the spectrum of the system for different perturbation amplitudes in the time domain (as in this work). Using a Fast Fourier Transform (FFT) algorithm the response signals in the frequency domain are obtained; and the total harmonic distortion (THD) parameter of the response signal is calculated for each perturbation amplitude. This parameter quantifies the level of non-fundamental harmonics in the output signal. The optimum perturbation amplitude corresponds with the amplitude that minimizes the THD value, and therefore the non-fundamental harmonic content of the output signal. Further details can be found in [70].

Consequently, the fitted values obtained from the spectrum measured using an amplitude of 2 mA were taken as the reference values. Therefore, a relative error was defined for each model parameter $X_i$ as:

$$\varepsilon_{X_i} = \frac{|X_i - X_i(ref)|}{X_i(ref)} \qquad (3)$$

Where $\varepsilon_{X_i}$ denotes the relative error of parameter $X_i$ ( $R_1$, $R_2$, $R_3$, $Q_1$, $Q_2$, $\alpha_1$, $\alpha_2$). $X_i(ref)$ stands for the reference value for parameter $X_i$. As it was just stated this reference value corresponds with the fitted value of parameter $X_i$ obtained from the spectrum measured at 2 mA.

This relative error parameter includes the error due to the distortion of the spectrum with respect to the reference case; but it also includes an error due to the fitting process. Since the goal is to quantify the error in the fitted parameters due to nonlinearity, the contribution of the fitting process should be eliminated. The fitting relative error in parameter $X_i$, $\xi_{X_i}$, can be determined from the fitting error of the corresponding parameter. These fitting errors are obtained from the fitting process along with the fitted values. Therefore, a normalized relative error was defined as:

$$\varepsilon'_{X_i} = \frac{\varepsilon_{X_i}}{\xi_{X_i}(ref)} \qquad (4)$$

Where $\xi_{X_i}(ref)$ stands for fitting relative error in parameter $X_i$ for the reference case. According to this definition a normalized relative error of 1 would indicates that the relative error in parameter $X_i$ can be entirely assigned to the fitting, and therefore the error due to nonlinearity is neglectable.

Finally, the mean normalized relative error of the fitted parameters, $\varepsilon'_{mean}$, was defined as the arithmetic mean of the normalized relative errors of the seven parameters of the model. Thus:

$$\varepsilon'_{mean} = \frac{1}{7} \cdot \sum_{i=1}^{7} \varepsilon'_{X_i} \qquad (5)$$

Figure 8 shows the mean normalized relative error of the fitted parameters for each perturbation amplitude. Obviously the mean normalized relative error for a perturbation of 2 mA is 0, since the 2 mA case has been selected as the reference case in this work. The dashed line marks a mean normalized relative error of 1: as explained previously, this corresponds to the situation where the mean error in the fitted parameters due to the distortion of the spectrum can be considered neglectable. Therefore the dashed line can be considered as a threshold: points below this line can be associated to situations where the mean error in the fitted parameters due to the distortion of the spectrum can be considered neglectable; whereas for points above the line the mean error in the fitted parameters due to nonlinear distortion cannot be neglected. It can be observed that for amplitudes between 0.5 mA and 5 mA, the mean error in the fitted parameters due to nonlinear distortion is not significant from a quantitative point of view: even if there is a variation in the fitted values, it is not important enough from a relative quantitative point of view. However for amplitudes above 5 mA the mean error in the fitted parameters due to nonlinear distortion cannot be neglected. In the range of amplitudes from 6 mA to 10 mA the mean error in the fitted parameters is quantitatively significant. In this amplitude range, the mean relative error (with respect to the reference fitted value) in the fitted parameters ranges from 100% (for 6 mA) to 760% (for 10 mA). These values show the sharp effect of the distortion of the spectrum due to nonlinear behavior on the fitted parameters; and give an order of magnitude of the errors that may arise in the results and conclusions of a study if these large amplitudes were used to measure the impedance spectra.

4. Conclusions

In conclusion, it has been observed experimentally that the EIS spectra of the studied cathodic electrode of an alkaline electrolyser present significant distortions for high perturbation amplitudes (above 5 mA), due to the nonlinearity of the system. It has been shown experimentally that the non-fulfilment of the linearity condition may lead to significant distortions in the measured EIS spectra; and thus, to significant errors in the parameters obtained from the experimental spectra. However, not all the model parameters have the same sensitivity to nonlinear distortions: the parameters associated with the high frequency zone of the spectrum are nearly not affected by the violation of the linearity condition; whereas, the parameters related to the intermediate and low frequency zones of the spectrum are highly sensitive to nonlinear distortions. This is due to the fact that nonlinearity only arises under a frequency threshold: for frequencies above the threshold, the system behaves linearly even for very high perturbation amplitudes.

These results highlight the importance of the linearity condition fulfilment: failing to achieve this condition (high perturbation amplitudes) may lead to dramatic distortions of the spectra, and significant bias and errors in the obtained model parameters, especially in the parameters related to the frequency zone below the characteristic threshold frequency.

## 5. Nomenclature

### *Normal letters*

| | |
|---|---|
| $f$ | Frequency / $Hz$ |
| $I$ | Current / $A$ |
| $Q_o$ | Constant phase element pseudo-capacitance / $F \cdot s^{\alpha-1}$ |
| $R$ | Resistance / $\Omega$ |
| $U$ | Potential / $V$ |
| $X_i$ | i-th model parameter |
| $X_i(ref)$ | Reference value for the i-th model parameter |
| $Z$ | Complex impedance / $\Omega$ |
| $Z'$ | Real part of complex impedance / $\Omega$ |
| $Z''$ | Imaginary part of complex impedance / $\Omega$ |

### *Greek letters*

| | |
|---|---|
| $\alpha$ | Constant phase element exponent |
| $\Delta I$ | Galvanostatic perturbation amplitude / $A$ |
| $\varepsilon_{X_i}$ | Relative error of parameter $X_i$ |
| $\varepsilon'_{mean}$ | Mean normalized relative error of the fitted parameters |
| $\varepsilon'_{X_i}$ | Normalized relative error of parameter $X_i$ |
| $\xi_{X_i}$ | Fitting relative error in parameter $X_i$ |
| $\xi_{X_i}(ref)$ | Fitting relative error in parameter $X_i$ for the reference case |
| $\chi^2$ | Fitting sum of squares parameter / $\Omega^2$ |

## 6. Acknowledgments

7. Bibliography

[1] M.E. Orazem, B. Tribollet, Electrochemical impedance spectroscopy, John Wiley & Sons, New Jersey, **2008**.

[2] N. Wagner, K.A. Friedrich, Fuel Cells **2008**, 9, 237.

[3] D. Kaewsai, H.L. Lin, T.L. Yu, Fuel Cells **2015**, 15, 361.

[4] P. Gallo Stampino, L. Omati, C. Cristiani, G. Dotelli, Fuel Cells **2010**, 10, 270.

[5] K. Su, X. Yao, S. Sui, Z. Wei, J. Zhang, S. Du, Fuel Cells **2015**, 15, 449.

[6] M.S. Çögenli, S. Mukerjee, A. Bayrakçeken Yurtcan, Fuel Cells **2015**, 15, 288.

[7] R.E. Silva, F. Harel, S. Jemeï, R. Gouriveau, D. Hissel, L. Boulon, K. Agbossou, Fuel Cells **2014**, 14, 894.

[8] R. Mohammadi, M. Sogaardm T. Ramos, M. Ghassemi, M.B. Mogensen, Fuel Cells **2014**, 14, 645.

 [9] R.R. Mosbaek, J. Hjelm, R. Barfod, J. Hogh, P.V. Hendriksen, Fuel Cells **2013**, 13, 605.

[10] S. Hershkovitz, S. Balianski, Y. Tsur, Fuel Cells **2014**, 12, 77.

[11] P. Leone, T. Matencio, M.E. Garciä, Z.R. Domingues, A. Lanzini, M. Santarelli, Fuel Cells **2013**, 13, 733.

[12] A. Mohammed Hussain, B.R. Sudireddy, J.V.T. Hogh, N. Bonanos, Fuel Cells **2012**, 12, 530.

[13] X. Sun, A.D. Bonaccorso, C. Graves, S.D. Ebbesen, S.H. Jensen, A. Hagen, P. Holtappels, P.V. Hendriksen, M.B. Mogensen, Fuel Cells **2015**, 15, 697.

[14] A. Baricci, M. Zago, A. Casalegno, Fuel Cells **2014**, 14, 926.

[15] F.J. Pinar, M. Rastedt, N. Pilinski, P. Wagner, Fuel Cells **2015**, 15, 140.

[16] S.J. Abdreasen, J.L. Jespersen, E. Schaltz, S.K. Kaer, Fuel Cells **2009**, 9, 463.

[17] F. Chen, Y. Gao, Fuel Cells **2015**, 15, 337.

[18] S. Chevalier, B. Auvity, J.C. Olivier, C. Josset, D. Trichet, M. Nachmoum, Fuel Cells **2014**, 14, 416.

[19] M. Gasperin, P. Boskoski, A. Debenjak, J. Petrovcic, Fuel Cells **2014**, 14, 457.

[20] H. Haghighat Ghahfarokhi, A. Saatcgi, S.M. Monirvaghefi, Fuel Cells **2016**, 16, 356.

[21] S. Keller, A. Popenheim, M. Hempel, K. Glasker, Y. Manoli, Fuel Cells **2014**, 14, 758.

[22] D.D. Macdonald, E. Sikora, Electrochimica Acta **1997**, 43, 87.

[23] G.S. Popkirov, R.N. Schindler, Review of Scientific Intruments **1993**, 64, 3111.

[24] J.E. Garland, C.M. Pettit, D. Roy, Electrochimica Acta **2004**, 49, 2623.

[25] F. Fasmín, R. Srinivasan, Journal of Solid State Electrochemistry **2015**, 19, 1833.

[26] M. Urquidi-Macdonald, S. Real, D.D. Macdonald, Electrochimica Acta **1990**, 35, 1559.

[27] J.M. Esteban, M.E. Orazem, Journal of the Electrochemical Society **1991**, 138, 67.

[28] E. Barsoukov, J.R. Macdonald, Impedance spectroscopy. Theory, experiment and applications, John Wiley & Sons, New Jersey, **2005**.

[29] P. Agarwal, M.E. Orazem, Journal of the Electrochemical Society **1995**, 142, 4159.

[30] J.L. Polo, C.L. Torres, E. Cano, J.M. Bastidas, Revista Metalurgía **1999**, 35, 368.

[31] M. Kendig, F. Mansfeld, Corrosion **1983**, 39, 466.

[32] D.D. Macdonald, M. Urquidi-Macdonald, Journal of the Electrochemical Society **1985**, 132, 2316.

[33] C.C. Haili, The corrosion of iron rotating hemishperes in 1 M sulfuric acid: an electrochemical impedance study, Msc. Thesis University of California, Berkeley, **1987**.

[34] J.R. Macdonald, L.D. Potter, Solid State Ionics **1987**, 24, 61.

[35] B. Boukamp, Solid State Ionics **1993**, 62, 131.

[36] B. Boukamp, Journal of the Electrochemical Society **1995**, 142, 1885.

[37] B. Hirschorn, B. Tribollet, M.E. Orazem, Israel Journal of Chemistry **2008**, 48, 133.

[38] B. Hirschorn, M.E. Orazem, Journal of the Electrochemical Society **2009**, 156, C354.

[39] M.E. Orazem, J.M. Esteban, O.C. Moghissi, Corrosion **1991**, 47, 248.

[40] K.R. Sunil, H. Hagelin-Weaver, M.E. Orazem, Journal of Power Sources **2011**, 196, 3736.

[41] J.J. Giner-Sanz, E.M. Ortega, V. Pérez-Herranz, International Journal of Hydrogen Energy **2016**, 40, 11279.

[42] J.J. Giner-Sanz, E.M. Ortega, V. Pérez-Herranz, Electrochimica Acta **2016**, 209, 254.

[43] W. Aperador, J.H. Bautista Ruíz, O. Pardo Cuervo, Revista Mexicana de Ingeniería Química **2012**, 11, 145.

[44] K. Darowicki, Electrochimica Acta **1997**, 42, 1781.

[45] K. Darowicki, Electrochimica Acta **1995**, 40, 439.

[46] P. Wojcik, P. Agarwal, M.E. Orazem, Electrochimica Acta **1997**, 41, 977.

[47] S.N. Victoria, S. Ramanathan, Electrochimica Acta **2011**, 56, 2606.

[48] J.P. Diard, B. Le Gorrec, C. Montella, Journal of Electroanalitical Chemistry **1997**, 432, 27.

[49] E. Van Gheem et al, Electrochimica Acta **2004**, 49, 4753.

[50] G.S. Popkirov, R.N. Schindler, Electrochimica Acta **1995**, 40, 2511.

[51] R. Pintelon, E. Louarroudi, J. Lataire, IEEE Transactions on Intrumentation and Measurement **2013**, 62, 3361.

[52] R. Pintelon, E. Louarroudi, J. Lataire, Automatica **2015**, 51, 308.

[53] J.P. Diard, B. Le Gorrec, C. Montella, Journal of Electroanalitical Chemistry **1997**, 432, 41.

[54] I. Herraiz-Cardona, E.M. Ortega, V. Pérez-Herranz, Electrochimica Acta **2011**, 56, 1308

[55] I. Herraiz-Cardona, E.M. Ortega, J. García Antón, V. Pérez-Herranz, International Journal of Hydrogen Energy **2011**, 36, 9428.

[56] I. Herraiz-Cardona, E.M. Ortega, L. Vázquez-Gómez, V. Pérez-Herranz, International Journal of Hydrogen Energy **2011**, 36, 11578.

[57] J. García-Antón, A. Igual-Muñoz, J.L. Guiñon, V. Pérez-Herranz, Horizontal cell for electro-optical analysis of electrochemical processes, ES Patent P-200002526, **2000**.

[58] J.J. Giner-Sanz, E.M. Ortega, V. Pérez-Herranz. Electrochimica Acta **2015**, 174, 1290.

[59] A. Battistel, M. Fan, J. Stojadinovic, F. La Mantia, Electrochimica Acta **2014**, 135, 133.

[60] A.T. Tran, F. Huet, K. Ngo, P. Rousseau, Electrochimica Acta **2011**, 56, 8034.

[61] C.F. Coombs, Electronic instrument handbook, McGraw-Hill, New York, **2000**.

[62] J.P. Diard, B. Le Gorrec, C. Montella, Journal of Electroanalitical Chemistry **1997**, 432, 53.

[63] I. Herraiz Cardona, Desarrollo de nuevos materiales de electrodo para la obtención de hidrógeno a partir de la electrolisis alcalina del agua,  PhD thesis Universitat Politècnica de València, Valencia, Spain, **2012**.

[64] L.L Chen, A. Lasia, Journal of the Electrochemical Society **1992**, 139, 3214.

[65] L. Birry, A. Lasia, Journal of Applied Electrochemistry **2004**, 34, 735.

[66] J.R. Macdonald, Solid State Ionics **1984**, 13, 147.

[67] C.H. Hsu, F. Mansted, Corrosion **2001**, 57, 747.

[68] J.J. Giner-Sanz, E.M. Ortega, V. Pérez-Herranz, 6th International Conference on Fundamentals and Development of Fuel Cells (FDFC 2015), Toulouse, France, **2015**.

[69] J.J. Giner-Sanz, E.M. Ortega, V. Pérez-Herranz, Fuel Cells DOI 10.1002/fuce.201500141.

[70] J.J. Giner-Sanz, E.M. Ortega, V. Pérez-Herranz, Electrochimica Acta **2015**, 186, 598.

LIST OF TABLES.

LIST OF FIGURES

**Table 1.** EIS measurement parameters

| Measurement parameter | Value |
|---|---|
| Integration time | 1.0 $s$ |
| Number of integration cycles | 1 $cycle$ |
| Number of stabilization cycles | 10 $cycles$ |
| Maximum stabilization time | 3.0 $s$ |
| Minimum stabilization cycle fraction | 0.00 |

**Table 2.** Experiment order

| Order | Block | Experiment | Order | Block | Experiment | Order | Block | Experiment |
|---|---|---|---|---|---|---|---|---|
| 1 | | 0.1 mA | 13 | | 3 mA | 25 | | 9 mA |
| 2 | | 5 mA | 14 | | 9 mA | 26 | | 7 mA |
| 3 | | 4 mA | 15 | | 2 mA | 27 | | 4 mA |
| 4 | | 1 mA | 16 | | 0.5 mA | 28 | | 2 mA |
| 5 | | 0.5 mA | 17 | | 5 mA | 29 | | 0.1 mA |
| 6 | 1 | 7 mA | 18 | 2 | 10 mA | 30 | 3 | 6 mA |
| 7 | | 3 mA | 19 | | 7 mA | 31 | | 0.5 mA |
| 8 | | 2 mA | 20 | | 8 mA | 32 | | 1 mA |
| 9 | | 6 mA | 21 | | 0.1 mA | 33 | | 10 mA |
| 10 | | 8 mA | 22 | | 4 mA | 34 | | 8 mA |
| 11 | | 9 mA | 23 | | 1 mA | 35 | | 5 mA |
| 12 | | 10 mA | 24 | | 6 mA | 36 | | 3 mA |

REF

CE

Gases outlet

Refrigeration outlet

Refrigeration inlet

KOH electrolyte

DEA

W

S

Metrohm

a

10 kHz

50 Hz

5 Hz

2 Hz

$-Z'' / \Omega$

$Z' / \Omega$

Legend:
+ 0.1 mA — Fit 0.1 mA
■ 0.5 mA — Fit 0.5 mA
● 1 mA — Fit 1 mA
▲ 2 mA — Fit 2 mA