Identification and performance analysis of a fractional order impedance model for various test solutions

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Abstract
This paper presents a fractional order impedance for modelling and identification of electrical properties in test solutions by means of electrochemistry. Various solutions are tested, including different concentrations and granulations. The results indicate the proposed model is suitable to capture the implicit variations in the impedance values.

Key words: electrochemistry, impedance model, fractional order impedance

1 Introduction

Electrical impedance spectroscopy (EIS) measures the electrical impedance of a material over a given range of frequencies [1]. The term bioimpedance refers to the impedance of biological tissues and biochemical materials and has been widely used for characterizing tissues/fluids composition and to assess "in vivo" conditions of plants and animals [2, 3]. In practical terms, EIS involves exciting the material under the study by means of electric sinusoidal signals and registering the system's frequency response.

A considerable and relevant volume of research addressed these topics, selected hereafter. Aberg et al. [4] investigated the electrical impedance spectra to distinguish between skin injuries. Ivorra et al. [5] used the bioimpedance model parameters for monitoring the intra/extra-cellular volume balance and tissue structural alterations.

EIS has also been applied to assess the electric properties of plant tissues, such as roots, leaves, stems, vegetable and fruits. Cao et al. [2] used EIS to estimate the size of the specimen root system and they reached to the conclusions that EIS is a useful non-destructive method for assessing root surface area. The electrical impedance of fruits and vegetables was studied by Jesus et al. [3, 6] and they proposed equivalent circuits models, emphasizing their fractional order behavior. Variations have been observed in all impedance parameters and were related to the rooting ability.

There are several standard model structures to characterise the electrical impedance of systems under observation. For instance, the Cole-Cole impedance model is a generalization of the Debye equation [7] and these models can be described in term of fractional order-differential equations [8, 9] often referred to as fractional calculus (FC). FC denotes the branch of calculus that extend the concepts of integrals and derivatives to non-integer and complex orders. FC was found to play a fundamental role in modelling many important physical phenomena and emerged as an important tool which have been adopted in
a wide range of topics, from dynamics of financial markets and biological structures, up to mechanical and electrical systems [10].

In this paper we investigate whether electrical properties change with variations in concentrations and granulation of several test solutions. The proposed model is a generalization of fractional order impedance models proposed in [11].

The paper is structured as follows: In section two the materials and methods used to this study are presented. In this section the theoretical background as well as the identification protocol and design are given. In Section 3 the results are presented and discussed. In this section a statistical analysis of the fractional order model parameters is given. The conclusions are given in section 4.

2 Materials and Methods

2.1 Theoretical background

The impedance of a system is generally determined by applying a voltage perturbation with a small amplitude and detecting the current response. The impedance is a complex value, since the current can differ not only in terms of the amplitude but it can also show a phase shift \( \phi \) compared to the voltage-time function. Thus, the value can be described either by the modulus and the phase shift or alternatively by the real part and the imaginary part of the impedance. If multisine signals are used for excitation, then the impedance is a representation of the frequency response of the system under observation.

An impedance spectrum is obtained such that will allow the characterization of surfaces, layers or membranes as well as exchange and diffusion processes. To achieve this, the impedance spectrum is often analyzed using an equivalent circuit. This circuit, which commonly consists of resistances and capacitances, represents the different physico-chemical properties of the system under investigation. Alternatively, the system can be described based on transfer functions derived from the basic laws of the processes involved, such as electrokinetics, diffusion, partition, etc. However, it is not only possible to describe a system of interest, but the technique can also be used for analytical purpose. In this case, the change of one impedance element, a resistance or a capacitance, as a function of the solution composition is evaluated. In some cases it is also possible to correlate the overall impedance to a change in concentration. This can simplify measurements, since it is often sufficient to determine the impedance at just one selected frequency or within a limited frequency window (where the relative changes are largest) in such cases. In electrochemical impedance spectroscopy, where the electrolyte solution is one component of the system to be investigated, four elements are usually used to describe the impedance behaviour: ohmic resistance, capacitance, constant phase element and Warburg impedance [12].

One of the most used techniques is the Cole-Cole impedance [13]. However, in this paper we go one step further and employ emerging tools from fractional calculus, i.e. fractional order impedance models. Diffusion process has been characterized as a fractional order differentiator. The molecular diffusion undergoes a spatial and temporal alteration as it passes through the medium. Independently, the lumped impedance model has been shown to be of the form:

\[
Z(j\omega) = D(j\omega)^\alpha
\] (1)

\[
543
\]
with $D$ the diffusion constant and the fractional order parameter value related to the diffusion rate. The total augmented model used to characterize the diffusion process has the following form:

$$Z(j\omega) = R + L(j\omega)^\alpha + D(j\omega)^\beta$$

(2)

where $0 < \alpha < 1$ and $-1 < \beta < 0$. This model is a generic model able to characterize any frequency dependence (increasing or decreasing) [11].

### 2.2 Identification protocol and device

For the identification purpose, multi frequency voltage and corresponding current (multi-sine input-output signals) signals are collected. To extract only the linear contributions of the excited system, the non-parametric method of best linear approximation is employed, as described in [11]. This method has the advantage of giving a statistically meaningful analysis of the noise and bias present in the system, therefore extracting the best linear approximation that can be extracted from the available data.

From this graphical information of the impedance, a parametric representation is obtained by fitting the frequency response data to the parameters of a parametric model. This step is then a parameterization of the measured signals. It has been shown in [11] that this method is just as good as a full optimization procedure.

Sample measurements were performed with a Solatron modulabXm impedance analyzer (Solatron Analytical, UK), see figure 1. The impedance cell consisted of a plastic cylindrical tank with an inner diameter of 20 mm and a length of 30 mm. Artificial samples of potassium have been prepared and impedance has been measured. Through the Solatron analyzer we applied a 100 mV r.m.s. sinusoidal voltage to the outer couple of electrodes of the measurement probe which was immersed into the glass tube containing the analyzed sample. We analyzed the impedance of the samples in the 1 Hz - 0.1 MHz frequency range.

![Software interface](image)

**Figure 1**: Solatron ModulabXm impedance analyzer.

For the identification purposes two study cases were considered: 1) solutions of differ-
ent concentrations (i.e. 4.6 mmol K⁺/L, 4.7 mmol K⁺/L, 4.8 mmol K⁺/L and 4.9 mmol K⁺/L) have been prepared and impedance has been measured; 2) in the same solution granules of silica have been added and the impedance has been measured.

3 Results and discussion

This section enumerates the results obtained using the fractional order model given in (2). Additional statistical analysis of the parameters is also reported.

In figure 2 the polar plot for four different concentrations are shown. Figure 3 represents the polar plot for the same concentration but in which granule of silica have been added. This last step is to detect whether or not our model has the sensitivity to capture these fine changes in the properties.

As observed, there is a clear difference in impedance for the case where no granules of silica are presented in the samples (continuous line) and the case when the granules have been added in the samples (dashed line). To this data, fractional order impedance modeling has been employed and the results are presented in figure 4. The results indicate a very good fitting performance between measured impedance and the estimated impedance. Blue lines represent the estimated impedance and the red lines represent the measured impedance for the case when no granules are presented in the sample solution. In yellow and purple, the estimated and the measured impedance for the second study case (i.e. with granulation) are shown.

![Figure 2: Polar plot of the measured impedance for four different concentrations in the frequency range 1Hz-0.1MHz.](image)

In figure 5 the evolution of the R, L and D parameters is presented and in figure 6 the evolution of α and β parameters is shown. From these figures, it can be noticed that the trend for the two cases is similar. There is a amplitude difference in the case of granules
Figure 3: Polar plot of the measured impedance for four different concentrations in the frequency range 1Hz-0.1MHz.

Figure 4: Real and Imaginary part for a concentration of 4.6 mmol/L K⁺.

(red dots) and no granules (blue dots) in the samples. Also the results suggest that R, L and β parameters are well characterized, for the other two parameters the suitable experiment to characterize them has not been yet identified.
Figure 5: Evaluation of R, L, and D parameters as a function of sample concentration and influence of silica granules (blue-samples without silica granules, red-samples with silica granules).

Figure 6: Evaluation of α and β parameters as a function of sample concentration and influence of silica granules (blue-samples without silica granules, red-samples with silica granules).
Statistical analysis has been employed in order to see if is possible to differentiate between the two cases. The Kruskal-Wallis test has been applied to the data to compare two or more independent samples of equal or different sizes. Since it is a non-parametric method, the Kruskal-Wallis test does not assume a normal distribution of the residuals, unlike the one-way analysis of variance. The function returns a p-value for the null hypothesis that all samples are drawn from the same population. If the p-value is near zero, this casts doubts on the null hypothesis and suggests that at least one sample mean is significantly different than the other sample mean. A p-value of less than 0.05 or less than 0.01 is a common value to determine whether the results are statistically different. From figures 8 and 7 it can be seen that there is a significant difference between the fractional order model parameters and the influence of granulation. From these one may conclude that the fractional order model presented in this paper is a suitable candidate to detect variations in concentrations but also in granulations.

Figure 7: Boxplot of R (p << 0.02), L (p << 0.1), and D (p << 0.04) parameters. Left: samples without silica granules; Right: samples with silica granules.

4 Conclusions

In this paper, a generic model for capturing electrical properties of test solutions has been proposed. The model is a fractional order impedance bale to characterize well frequency dependence of system’s dynamic response. The statistical analysis on the obtained results suggest the model is adequate for detecting variations in concentrations and in granulations of our test-solutions.
Figure 8: Boxplot of $\alpha$ (p $<< 0.07$) and $\beta$ (p $<< 0.04$) parameters. Left: samples without silica granules; Right: samples with silica granules.

References


