FRACTIONAL MODELLING OF THE ELECTRICAL CONDUCTION IN NACL ELECTROLYTE

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Abstract
The fractional calculus (FC) constitutes a mathematical tool that presently is being applied in many emerging scientific areas, such as electricity, magnetism, mechanics, fluid dynamics and medicine. This paper describes the use of an electrolytic process for developing fractional order capacitors. The study includes several experiments for measuring the electrical impedance of the devices. The results are analyzed through the frequency response revealing capacitances of fractional order.

Key words
Fractional calculus, modelling, electrical conduction, electrolyte.

1 Introduction

Fractional calculus (FC) is a generalization of the integration and differentiation to a non-integer order. The fundamental operator is ${}_aD_t^\alpha$, where the order α is a real or, even, complex number, and the subscripts a and t represent the two limits of the operation [Oldham, Keith and Spanier, 1974a, 1974b; Loverro, 2004; Miller and Ross, 1993].

Recent studies brought FC into attention revealing that many physical phenomena can be modelled by fractional differential equations [Samko, Stefan, Kilbas, Oleg and Marichev, 1993; Debnath, 2002; Machado and Jesus, 2005; Jesus, Machado, Cunha and Silva, 2006a]. The importance of fractional order models is that they yield a more accurate description and lead to a deeper insight into the physical processes underlying a long range memory behaviour.

Capacitors are one of the crucial elements in integrated circuits and are used extensively in many electronic systems [Samavati, Hajimiri, Shahani, Nasserbakht and Lee, 1998]. However, Jonscher [Jonscher, 1993] demonstrated that the ideal capacitor cannot exist in nature, because an impedance of the form 1/[($j\omega C$)] would violate causality [Bohannan, 2002a, b]. In fact, the dielectric materials exhibit a fractional behavior yielding electrical impedances of the form 1/[(j$\omega C_F)^\alpha$], with $\alpha \in \Re^+$.

Bearing these ideas in mind, this paper analyzes the fractional modelling of several electrical devices and is organized as follows. Section 2 introduces the fundamental concepts of electrical impedances. Sections 3 and 4 describe the fractal geometries and capacitors, respectively. Section 5 presents the experiments results for the study of the fractional order capacitors. Finally, section 6 draws the main conclusions.

2 On the electrical impedance

In an electrical circuit the voltage $u(t)$ and the current $i(t)$ can be expressed as a function of time t:

$$u(t) = U_0 \cos(\omega t) \tag{1}$$

$$i(t) = I_0 \cos(\omega t + \phi) \tag{2}$$

where U_0 and I_0 are the amplitudes of the signals, ω is the angular frequency and ϕ is the current phase shift. The voltage and current can be expressed in complex form as:

$$u(t) = Re\left\{U_0 e^{j(\omega t)}\right\} \tag{3}$$

$$i(t) = Re\left\{I_0 e^{j(\omega t+\phi)}\right\} \tag{4}$$

where Re{ } represents the real part and $j = \sqrt{-1}$.

Consequently, in complex form the electrical impedance $Z(j\omega)$ is given by the expression:

$$Z(j\omega) = \frac{U(j\omega)}{I(j\omega)} = Z_0 e^{j\phi} \tag{5}$$

Fractional order elements occur in several fields of engineering.

A brief reference about the Constant Phase Element (CPE) and the Warburg impedance is presented here due to their application in the work. In fact, to model an electrochemical phenomenon it is often used a CPE due to the fact that the surface is not homogeneous [Barsoukov and Macdonald, 2005].

With a CPE we have the expression:

$$Z(j\omega) = \frac{1}{(j\omega C_F)^{\alpha}} \tag{6}$$

where C_F is a fractional order capacitance and the fractional order $0 < \alpha \leq 1$ is a parameter, occurring the classical ideal capacitor when α = 1. It should be noted that, the SI base units of the C_F element are $[m^{-2/\alpha} kg^{-1/\alpha} s^{(\alpha+3)/\alpha} A^{2/\alpha}]$ [Jesus, Machado and Cunha, 2006b; Jesus, Machado and Cunha, 2007].

Table 1 shows the polar plots of the impedance Z(jω) and the admittance $Y(j\omega)$ = $Z^{-1}(j\omega)$ for simple series and parallel *RC* associations of integer and fractional order, where G = Re$\{Y\}$ is the conductance and B = Im$\{Y\}$ is the susceptance.

It is well known that, in electrochemical systems with diffusion, the impedance is modelled by the so-called Warburg element [Barsoukov and Macdonald, 2005; Jesus, Machado and Cunha, 2007). The Warburg element arises from one-dimensional diffusion of an ionic species to the electrode. If the impedance is under an infinite diffusion layer, the Warburg impedance is given by:

$$Z(j\omega) = \frac{R}{(j\omega C_F)^{0.5}} \tag{7}$$

where R is the diffusion resistance. If the diffusion process has finite length, the Warburg element becomes:

$$Z(j\omega) = R\frac{\tanh{(j\omega\tau)}^{0.5}}{(\tau)^{0.5}} \tag{8}$$

with $\tau = \delta^2/D$, where R is the diffusion resistance, τ is the diffusion time constant, δ is the diffusion layer thickness and D is the diffusion coefficient [Jesus, Machado and Cunha, 2007].

Based on these concepts, in the following sections some fractional order electric impedances are presented.

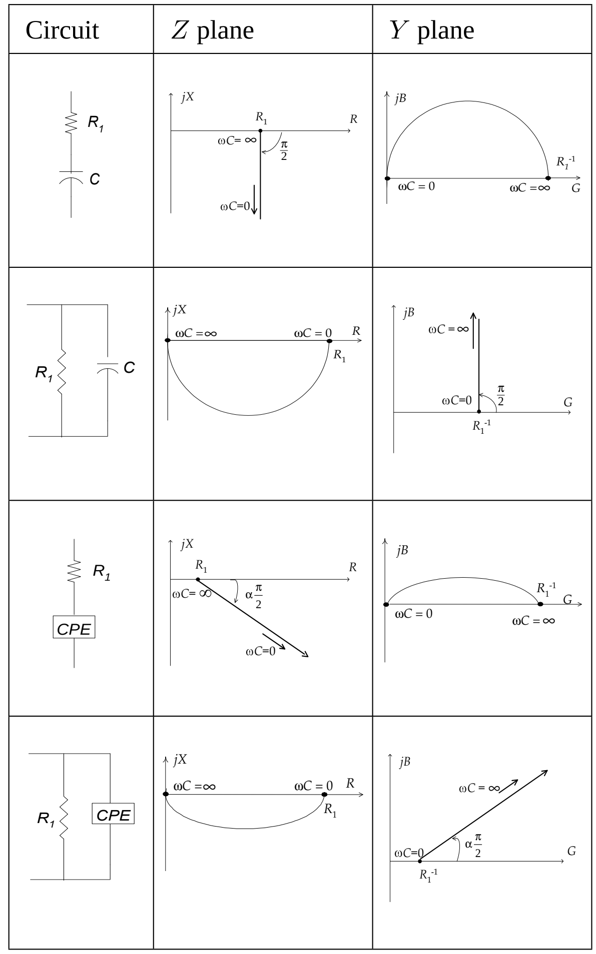


Table 1. Impedance $Z\,(j\omega)$ and admittance $Y\,(j\omega)$ loci of RC circuits of integer and fractional order.

3 Fractal geometries

Fractals can be found both in nature and abstract objects. The impact of the fractal structures and geometries, is presently recognized in engineering, physics, chemistry, economy, mathematics, art and medicine.

The concept of fractal is associated with Benoit Mandelbrot, that lead to a new perception of the geometry of the nature [Falconer, 1990]. However, the concept was initially proposed by several well known mathematicians, such as George Cantor (1872), Giuseppe Peano (1890), David Hilbert (1891), Helge von Koch (1904), Waclaw Sierpinski (1916), Gaston Julia (1918) and Felix Hausdorff (1919).

An geometric important index consists in the fractal dimension (*FDim*) that represents the occupation degree in the space and that is related with its irregularity. The *FDim* is given by:

$$FDim \approx \frac{\log{(N)}}{\log{(1/\eta)}} \tag{9}$$

where N represents the number of boxes, with size $\eta(N)$ resulting from the subdivision of the original structure.

This is not the only description for the fractal geometry, but it is enough for the identification of groups with similar geometries.

Some of the classical fractals adopted in this work are the curve of Koch, triangle of Sierpinski, carpet of Sierpinski, curves of Hilbert and Peano {*CK*, *TS*, *CS*, *CH*, *CP*}, depicted in the Table II.

The dielectric absorption in the capacitors is difficult to characterize accurately, due to the high value of the involved time constant, and the necessity of high precision measuring equipment [Jesus, Machado and Silva, 2008].

The simplest capacitors are constituted by two parallel electrodes separated by a layer of insulating dielectric. There are several factors susceptive of influencing the characteristics of a capacitor. However, three of them have a special importance, namely the surface area of the electrodes, the distance among them and the material that constitutes the dielectric.

This work examines other aspects that can also influence the capacity of a capacitor, namely the wrinkling of theirs electrodes, and a non-homogenous dielectric structure.

In this line of thought, in the electrodes are printed the fractal structures presented in Table 2. The choice of these fractals is due to the value of *FDim* that it is intended to evaluate cases from 1 up to 2.

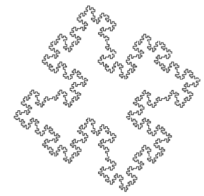
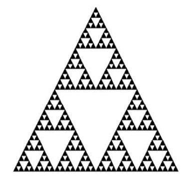
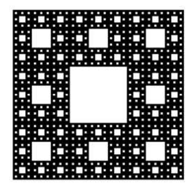
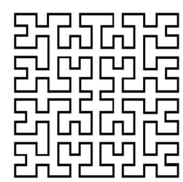
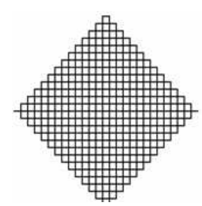
Fractal Name	*FDim*	Structure
Curve of Koch	1.262	
Triangle of Sierpinski	1.585	
Carpet of Sierpinski	1.893	
Curve of Hilbert	2.000	
Curve of Peano	2.000	

Table 2. Fractal structures adopted in the electrodes.

4 Experimental results

In the experiments (Fig. 1) we apply sinusoidal excitation signals $v(t)$ to the apparatus, for several distinct frequencies ω, and the impedance $Z(j\omega)$ between the electrodes is measured based on the resulting voltage $u(t)$ and current $i(t)$.

We study the influence of several factors such as *FDim*, different concentrations (Ψ) of sodium chloride (NaCl) and the type of fractal materials in the solution, namely gravel or sand. Moreover, we test also the linearity and the variation of the impedance $Z(j\omega)$ with the amplitude V_0 of the input signal.

In each experiment we use two identical single face electrodes. The voltage, the adaptation resistance R_a and the distance between electrodes d_{elec} are kept identical during the different experiments namely, $V_0 = 10\ V$, R_a = 1.2 kΩ and d_{elec}= 0.13 m. This methodology help us to understand the influence of the relevant factors in the impedance $Z(j\omega)$ and, consequently, the behaviour of the fractal capacitor.

In a first experiment, the electrolyte process consists in an aqueous solution of NaCl with Ψ = 5 gl^{-1} (AS5) and two single face copper electrodes with the carpet of Sierpinski printout and area S = 0.423 m^2.

Figure 2 presents the amplitude and phase Bode diagrams for the resulting $Z(j\omega)$ and the corresponding approximations. The electrical element reveals a fractional order impedance. In fact, approximating the experimental results in the amplitude Bode diagram through a power function $Z_{app} = |Z(j\omega)| = a\omega^{-b}$, we obtain $(a,\ b)$ = (227.97, 0.537) and $(a,\ b)$ = (54.80, 0.097), at the low and high frequencies, respectively. We verify that $Z(j\omega)$ has distinct characteristics according with the frequency range. For low frequencies it is clearly a fractional order of impedance, but for high frequencies, the impedance is approximately constant.

In a second case, with the purpose of studying the effect of the dielectric, we introduce gravel into the aqueous solution of Ψ = 5 gl^{-1} (AS5G). We use the same electrodes and the gravel covers completely the electrodes.

In this case we obtain a dielectric having fractal characteristics. The values of the voltage and the adaptation

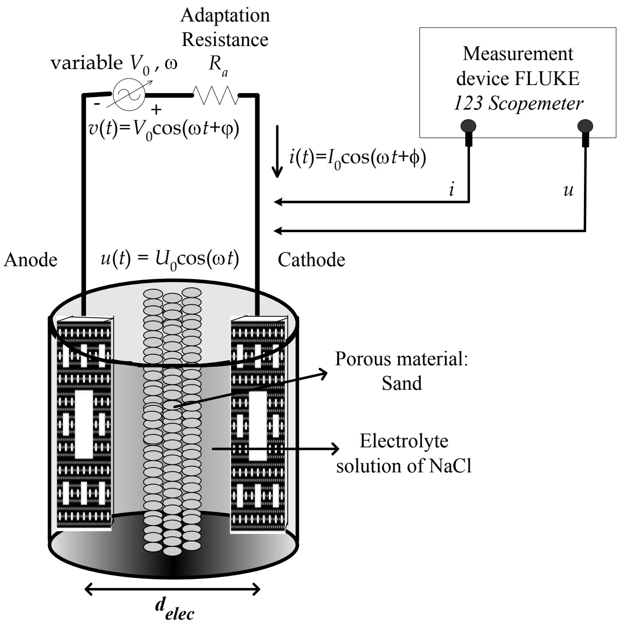


Figure 1. Electrolyte process.

resistance are identical to the previous experiment, ($i.\ e.$, V_0 = 10 V, R_a = 1.2 kΩ) leading to the approximations (a, b) = (323.25, 0.317) and (a, b) = (147.66, 0.099) at the low and high frequencies, respectively.

In a third experiment the gravel is replaced by sand (AS5S) leading to (a, b) = (322.64, 0.347) and (a, b) = (152.44, 0.058) at the low and the high frequencies respectively. Figure 3 illustrates the amplitude and phase Bode diagrams of $Z(j\omega)$ and the corresponding approximations. The results reveal a good fit between the experiment data and the approximation model.

The fourth experiment studies the influence of the fractal surface by using two electrodes printed with the carpet of Sierpinski having an area of S‘=1/3 S. In this case the values of the voltage, the resistance of adaptation and the solution remain unchanged, namely V_0 = 10 V, R_a = 1.2 kΩ and Ψ = 5 gl^{-1}, and a dielectric without gravel or sand. The resulting asymptotic approximation for $|Z(j\omega)|$ are (a, b) = (442.24, 0.075) and (a, b) = (564.27, 0.130) for the low and high frequencies.

Figure 4 compares the amplitude and phase Bode diagrams of the resulting $Z(j\omega)$ and the corresponding approximations for the first and for fourth experiments.

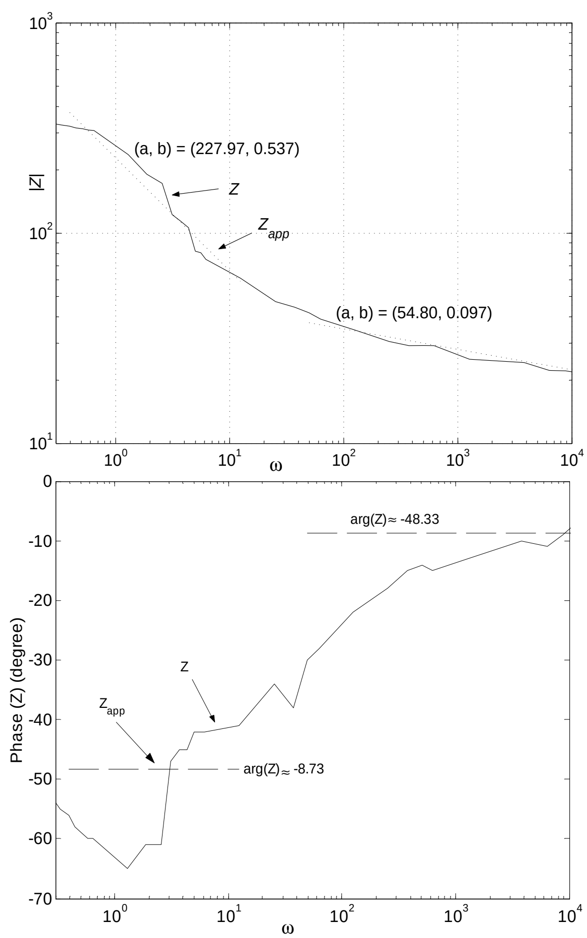


Figure 2. Amplitude and phase Bode diagrams of the impedance $Z(\mathrm{j}\omega)$ for Ψ = 5 gl^{-1} and electrodes with the carpet of Sierpinski.

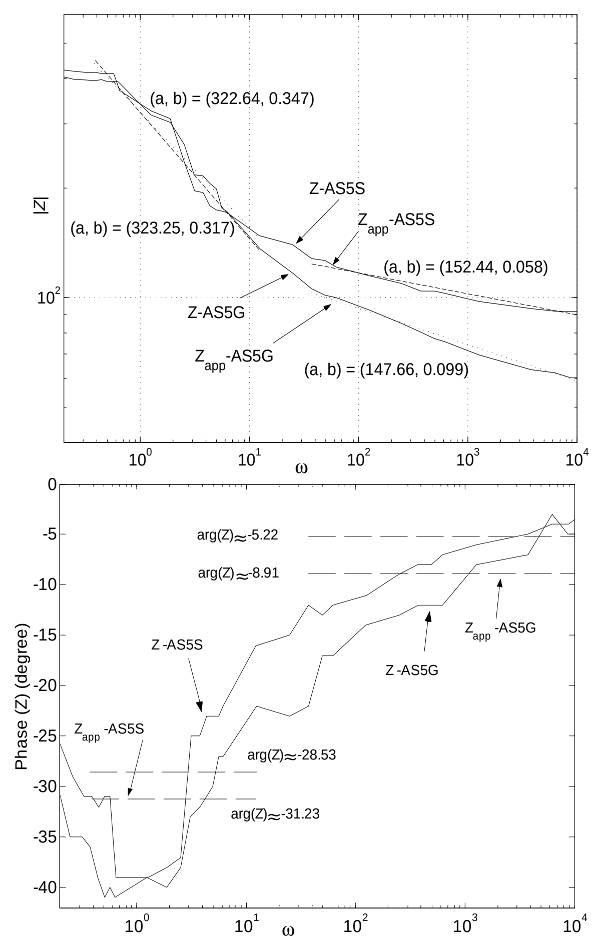


Figure 3. Amplitude and phase Bode diagrams of the impedance $Z(j\omega)$ for electrodes with the carpet of Sierpinski and the dielectrics: AS5G and AS5S.

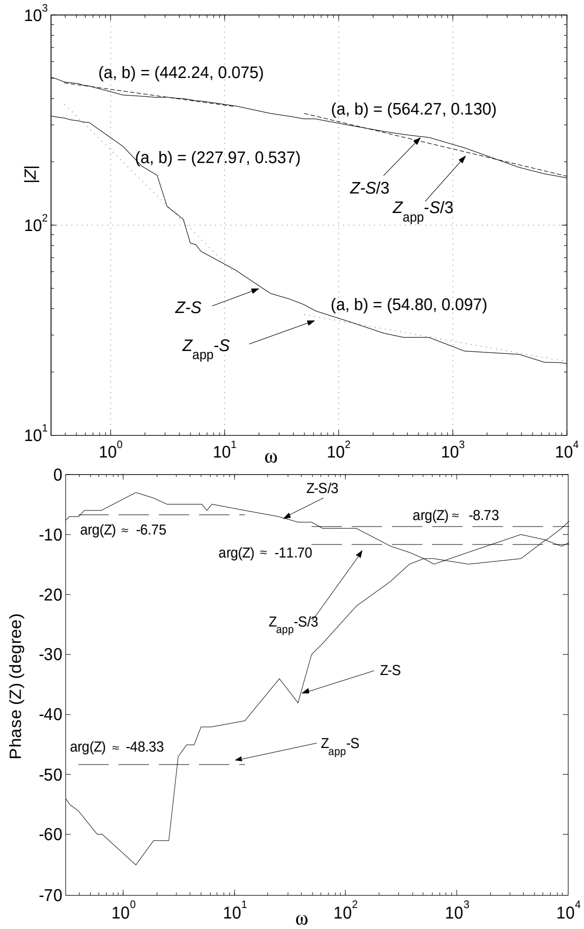


Figure 4. Amplitude and phase Bode diagrams of the impedance $Z(j\omega)$ for electrodes with the carpet of Sierpinski fractal, and dielectric AS5 for $S = 0.423$ m^2 and $S` = 1/3\,S$.

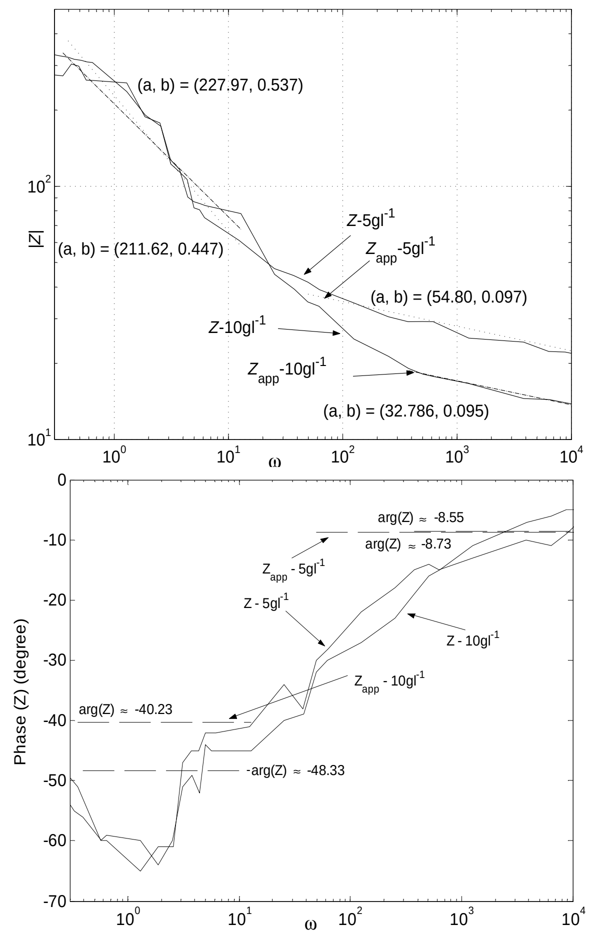


Figure 5. Amplitude and phase Bode diagrams of the impedance $Z(j\omega)$ for electrodes with the carpet of Sierpinski, the AS5 and AS10 dielectrics and S = 0.423 m^2.

In the case of $S` < S$, the electrical element reveals a smaller fractional order.

In a fifth experiment $Z(j\omega)$ is evaluated for the initial electrodes with the carpet of Sierpinski and $S = 0.423\ m^2$, but with a aqueous solution concentration of the Ψ = 10 gl^{-1} (AS10). The voltage and the resistance of adaptation remain the same. The asymptotic results for $|Z(j\omega)|$ yields: (a, b) = (211.62, 0.447) and (a, b) = (32.79, 0.095) at the low and high frequencies, respectively.

Figure 5 compares the amplitude and phase Bode diagrams of $Z(j\omega)$ and the corresponding approximations for the first and fifth experiments. The electrical elements reveal only a small variation at the high frequencies.

Table 3 displays the values of the approximations of the real and imaginary parts of $Z(j\omega)$, for all experiments described previously, at the low frequencies range, where the fractional behavior occurs.

When we compare the experiments with distinct dielectrics (experiments 1, 2 and 3), we conclude that the introduction of the gravel or sand in the solution, decreases the fractional order b, in both parts of Z. In Re$\{Z\}$ the parameter a increases, but in Im$\{Z\}$ we verify a small sensitivity.

Bearing these results in mind, we organize similar experiments for the fractals presented in Table 2 in order to analyze their influence on the impedance. The values of the voltage amplitude V_0, the resistance of adaptation R_a and the dielectrics solution (AS5) remain identical to those used previously. Moreover, the size of the fractals was adjusted so that their surface yields identical values, namely S = 0.423 m^2.

Case	Surface	Ψ	Re$\{Z\}$		$-$Im$\{Z\}$	
			a	b	a	b
1	S	AS5	122.33	0.358	180.47	0.571
2	S	AS5G	253.76	0.258	188.52	0.437
3	S	AS5S	267.80	0.243	162.52	0.475
4	$1/3\,S$	AS5	442.10	0.082	45.42	0.235
5	S	AS10	129.88	0.407	132.64	0.414

Table 3. Comparison of Re$\{Z\}$ = $a\omega^{-b}$ and $-$Im$\{Z\}$ =$a\omega^{-b}$, at the low frequencies, for electrodes with the carpet of Sierpinski.

Fractal	Re$\{Z\}$		$-$Im$\{Z\}$	
	a	b	a	b
CK	188.97	0.409	177.44	0.381
TS	216.46	0.380	189.65	0.448
CS	122.33	0.358	180.47	0.571
CH	171.16	0.425	199.9	0.401
CP	182.28	0.438	185.38	0.512

Table 4. Comparison of Re$\{\mathrm{Z}\} = a\omega^{-b}$ and $\mathrm{tg}\mathrm{Im}\{\mathrm{Z}\} = a\omega^{-b}$, at the low frequencies, for electrodes with the fractals present in Table 2, and the solution AS5.

Table 4 depicts the values of the approximations of the real and imaginary parts of $Z(j\omega)$, for all fractal structures in the low frequencies range, where the fractional behavior occurs.

Figures 6 and 7 depict the amplitude and phase Bode diagrams of $Z(j\omega)$, for the curve of Koch, triangle of Sierpinski, curve of Hilbert and curve of Peano, and the corresponding approximations, respectively.

These charts reveal similarities with the previous ones and confirm that we can modify the fractional order behaviour of the electrical device through the structure of the electrodes.

5 Conclusions

The FC was developed mainly in a mathematical viewpoint, but presently it addresses a considerable range of applications.

In this paper the FC concepts were applied to the analysis of electrical fractional impedances. Were adopted fractal structures for the development of fractional electrical devices with the objective of creating alternatives to the classical integer order capacitors.

It was verified that it is possible to get fractional order elements by adopting non classical electrodes and dielectrics.

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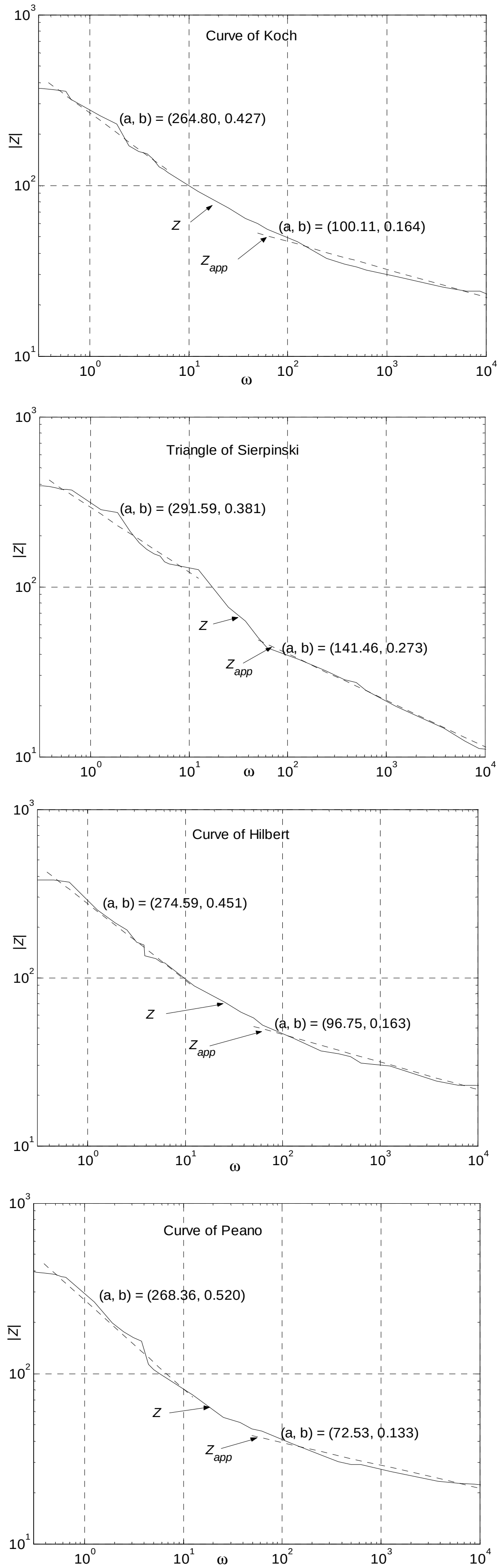

Figure 6. Amplitude Bode diagram of the impedance $Z(j\omega)$ and the corresponding approximations for electrodes with the fractal structures: Koch, triangle Sierpinski, Hilbert and Peano.

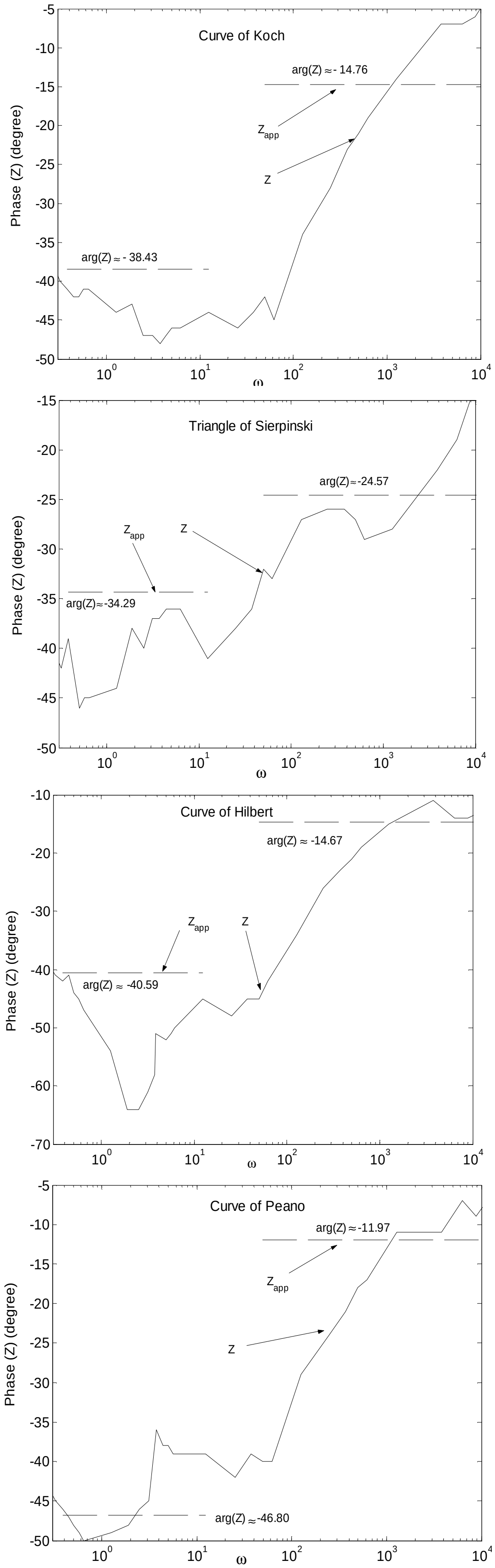

Figure 7. Phase Bode diagram of the impedance $Z(j\omega)$ and the corresponding approximations for electrodes with the fractal structures: Koch, triangle Sierpinski, Hilbert and Peano.

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