

Chapter 2

Devices

2.1 Introduction

In this chapter, we introduce some fractional-order devices (FOD). The successful recipes allowed for the construction of prototype devices and demonstrated the ease of designing circuits and systems using these devices. Some demonstrations of these devices in circuits are included in Chap. 3. No attempt will be made to discuss all possible approaches for fabricating such devices. The goal is to point the way to creating devices with stable, specific phase over broad frequency ranges.

To be specific, we are not looking at “fractal capacitors,” such as described in [40] where the area of the capacitor plates is increased by the use of fractal geometry. That technique makes better use of available surface area to achieve higher capacitance values. The devices discussed here exhibit “fractional-order dynamics” with both energy storage and dissipation properties being described by an impedance of non-integer order.

Electrical impedance spectroscopy (EIS) techniques have been steadily developing over the last century. By the middle of the twentieth century, the description of a constant phase element (CPE) had been invented [19]. The implications of this description were not readily apparent early on. Subsequent study suggested that analysis of CPE aspects might be useful for diagnostic purposes, such as corrosion detection, for example. As discussed in Chap. 1, by the turn of the millennium it was suggested that a material exhibiting CPE behavior in a might offer an approach to creating a new class of circuit elements.

We make the distinction between the CPE properties of materials forming fractional-order elements (FOE) and the ultimate fractional-order devices (FOD) made using these materials.

The reader should note that there are slight variations in the terminology used for the various FOE and FOD described herein. The authors came together to present their efforts from their perspectives. The state of the art is not yet ready for full standardization. The process of creating a new class of electronic device has been somewhat chaotic and has required each of us to consider many different approaches. Our overall goal is to pass on these perspectives and stimulate new approaches.

2.2 Discrete Element Approximations of Fractional-Order Elements

Numerous attempts have been made to approximate fractance response [10, 37, 44, 48], as well as multiple attempts at creating digital operators for control and signal processing [12, 14, 16, 17, 32, 34, 36, 49]. These approximations all are based on one or another self-similar arrangements, sometimes referred to as deterministic fractal scaling. A popular form is the continued fraction expansion,

$$Z(s) = R_1 + \frac{1}{C_1 s + \frac{1}{R_2 + \frac{1}{C_2 s + \dots}}}, \quad (2.1)$$

with $R_{n+1} = R_n \cdot R_{scale}$ and $C_{n+1} = C_n \cdot C_{scale}$, with R_{scale} and C_{scale} chosen to form a self-similar power-law spacing of the time constants. The ratio of R_{scale} to C_{scale} determines the phase angle. The values of R_1 and C_1 determine the upper frequency for the CPE range. For a given number of circuit elements, the closer R_{scale} and C_{scale} are to unity, the less the phase ripple, but with reduced bandwidth. The greater R_{scale} and C_{scale} , the broader the bandwidth, but greater phase ripple.

For example, an approximation of a -35° fractance circuit is shown in Fig. 2.1 and its impedance spectrum is shown in Fig. 2.2. Using such a circuit in practice is problematic for several reasons. Not the least of which is that the values of the elements given in the design are typically not readily available and often need to be built with parallel/series equivalent circuits, making the device even more complicated, bulky, and expensive.

Approximated FOD have been fabricated based on the self-similar scaling rules and exhibit the phase ripple as suggested in the example above [25]. Impedance spectroscopy texts offer a range of self-similar scaled equivalent circuit topologies that would produce CPE behavior in order to describe the observed data in disordered media [5].

The implication from this exercise is that if we could create a very broad distribution of time constants with a vast number of microscopic elements then we

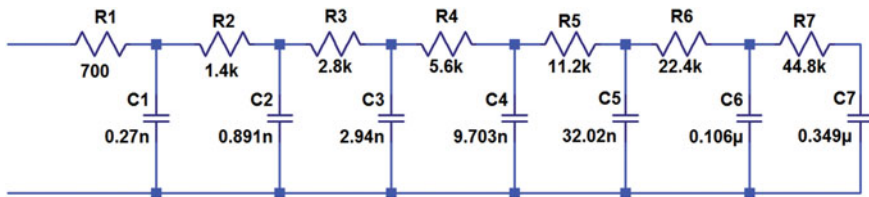
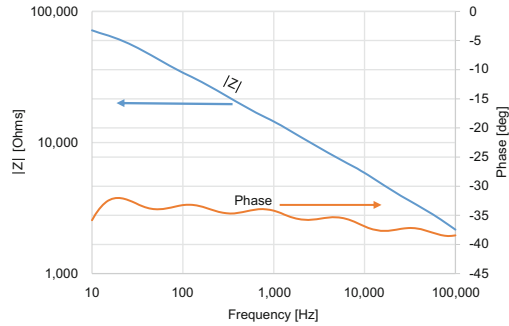


Fig. 2.1 Approximation of a -35° phase fractance using standard discrete R and C elements. For the circuit shown here: $R_1 = 700 \Omega$, $C_1 = 0.27 \text{ nF}$, $R_{scale} = 2.0$, $C_{scale} = 3.3$

Fig. 2.2 Phase and magnitude for a fractance approximation using standard discrete R and C elements. For the plot shown here: $R_1 = 700 \, \Omega$, $C_1 = 0.27 \, \text{nF}$, $R_{scale} = 2.0$, $C_{scale} = 3.3$. Note the phase ripple over the frequency band of $\Delta\phi \approx \pm 5^\circ$



could achieve low-phase ripple and wide effective bandwidth, if the natural distribution turns out to follow self-similar scaling. Fortunately, this self-similar scaling or random fractal scaling seems to be ubiquitous. The challenge is isolating the CPE behavior from the other processes.

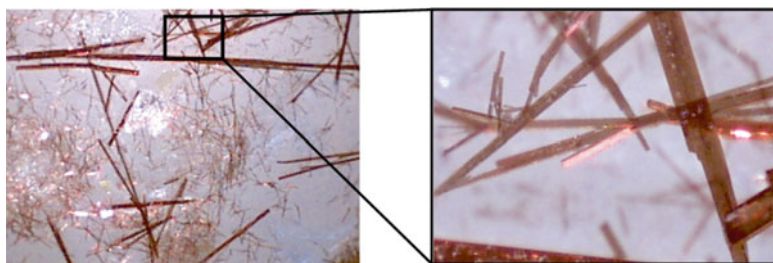
A device based on deterministic geometric fractal patterns on a silicon chip had been introduced by Haba et al. in [25], but the technique used applied only to high-frequency devices ($f > 100 \, \text{kHz}$) which would be appropriate for many signal processing applications but not to low-frequency motor control problems. To extend this design technique down to mHz would require many square meters of substrate. A different approach would be required; in this case, making use of intrinsic properties of disordered dielectric materials.

2.3 Early Fractional-Order Devices (FOD)

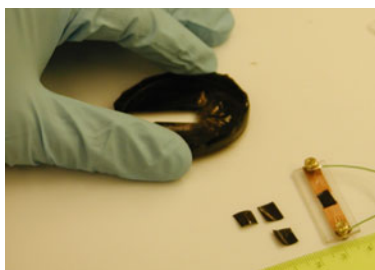
There have been several generations of attempts at creating single-element FOD. They virtually all start with the idea of creating some form of anomalous charge transport behavior. Free charges can flow in a material due to drift induced by an electric field or by concentration gradients where like charges repel each other resulting in diffusion. In either case, the sum of all the motions contributes to the net current. Randomizing the conduction and/or diffusion paths then creates the distribution of flow statistics. Many different conceptual models have been proposed, such as random walks with a distribution of waiting times due to combination of the charge carrier with a fixed ion then regenerating the mobile carrier.

2.3.1 Platinum Nanowire in Polymer

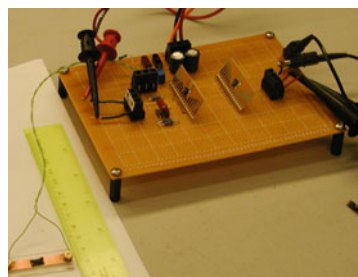
The initial attempt at creating a fractance was based on growing cross-linked conductive threads from conductive $\text{K}_2[\text{Pt}(\text{CN})_4\text{Br}_{0.3}]$ crystals in a nonconductive liquid polymer solution. After drying, the polymer film was cut and mounted against



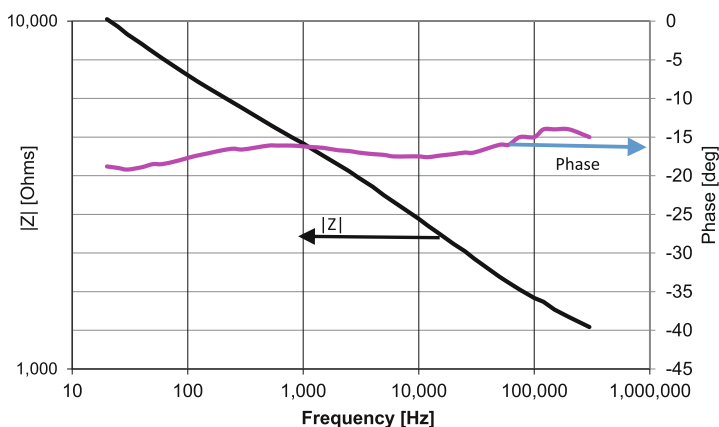
(a) Crystal Growth.



(b) Cut for testing.



(c) Mounted for impedance measurement.

Fig. 2.3 Growing and testing Pt chains in a polymer**Fig. 2.4** Impedance spectrum for a sample of the $K_2[Pt(CN)_4Br_{0.3}]$ crystals in polymer film

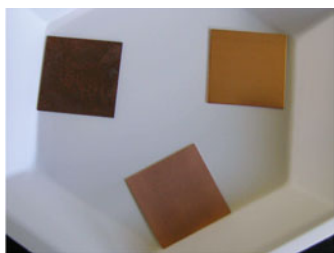
electrodes for impedance testing. Randomized conductive paths interspersed with capacitive cross-links did induce a CPE type of response. This first attempt showed that there was promise in isolating near constant phase over a fairly broad frequency range. This process showed promise, but it was expensive and the yield of samples showing fractance characteristics was less than 25% (Figs. 2.3 and 2.4).

2.3.2 Lithium-Ion Type

The next approach was to make use of anomalous diffusion rather than direct charge drift under the influence of an electric field while making use of the success of randomly cross-linked chains. This minimized the effect of the blocking and parasitic capacitances in Fig. 1.5.

In order to get the very broad frequency response desired, we looked at randomizing the structure of the charge transport pathways in the substrate. This was achieved in two steps. The randomization of the charge flow paths is enhanced by first roughening the inner plate, then dipping it into a suspension of the LiNO_4 , doped polyaniline in sulfonic acid and tetraethyl orthosilicate (TEOS). The roughening allowed the long polyaniline strands to twist around in random patterns. Each crossing of one strand to another generated a trapping/regeneration site. Each dipping was oriented 90° from the previous dipping. This further enhanced the randomization of the charge paths. The silicate gel was to stabilize the structure upon drying [35].

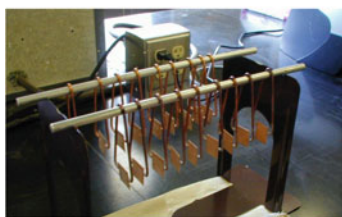
Figure 2.5a, starting at the upper right, shows a clean copper plate cut to ≈ 2.5 cm on a side. At the bottom is a roughened plate. At the top left is a plate after coating. After each dipping, the plates were dried for 30 to 50 min in a low temperature oven at $\approx 90^\circ\text{C}$. Higher temperatures tend to cause the plating to flake off. The rack is allowed for processing multiple samples at once. Twelve or more dipping and drying cycles



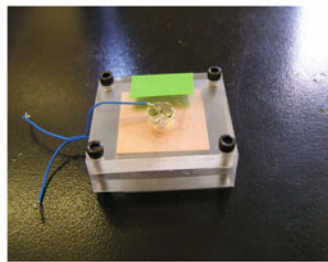
(a) Inner plate preparation.



(b) Plate Dipping.



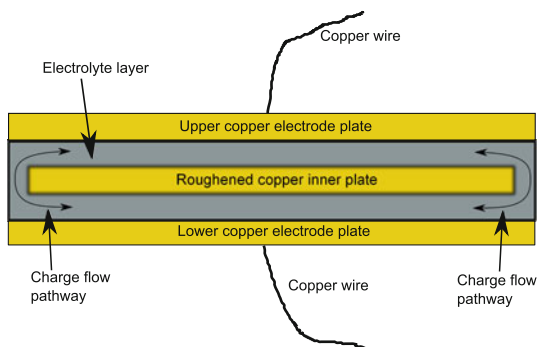
(c) The drying rack.



(d) Assembled Prototype.

Fig. 2.5 Fractor preparation process. The coated inner plate is mounted between two outer electrode plates. The copper plates act as insulators for the lithium ions and the nitrate radicals. The mobile electrons in the organic chains are bound to the chains. With this, there is no direct mobile charge flow from the *upper* to the *lower* electrode plates

Fig. 2.6 An edge view of the solid-state fractor assembly showing the current paths in the electrolyte layer. By having the charge carriers move orthogonally to the applied field, they exhibit diffusive charge transport as opposed to drift which they would exhibit if they moved directly with the applied field



were required to achieve the desired response. The coated plates were sandwiched between two outer electrode plates and the assembled device coated in a plastic dip to seal it from external moisture. The final product was dubbed the “fractor.”

In Fig. 2.6, the idea is to have the bulk of the charge carriers diffuse orthogonally to the applied field. Charges on edge will flow with the field around the central layer. It is this edge current that is seen as the external circuit. Because the charge becomes depleted or enhanced on the edges, the external circuit sees a decreasing or increasing current for a constant imposed potential. Charge diffuses out to the edges due to concentration gradients, not directly due to the applied field. This translates the anomalous diffusion statistics into a sum distribution in the current in the external circuit.

The randomization of the pathways gives rise to a broad distribution of “time constants” for trapping and recombination–regeneration of the carriers. The model of current flow (assumed to be Li^+ ions) around the edges of the inner plate was confirmed by grinding off the electrolyte around all the four edges, with only bare copper exposed. The resulting impedance was almost purely capacitive ($\alpha \approx 1$), as if the electrolyte had become a high-quality insulating dielectric. A typical impedance spectrum is shown in Fig. 2.7.

Unfortunately, these devices exhibited slow degradation over time, but not so quickly as to prohibit testing of these devices in physical circuits in a variety of applications to be discussed in Chap. 3. This will require more work on the recipes for fabricating the devices. Organic polymers are subject to deterioration and may be one contribution to the aging. Over the course of one to four years, the conductivity decreased substantially, with the impedance magnitude increasing by factors of 10^2 to 10^3 , as shown in Fig. 2.8. Interestingly, the phase did not seem to change, with the implication that the randomization statistics do not change over time. The most likely cause of the degradation is loss of Li^+ ion concentration due to interaction with oxygen forming an immobile Li_2O . The roll-off at the higher frequencies due to the parasitic capacitance of the copper plates becomes even more apparent.

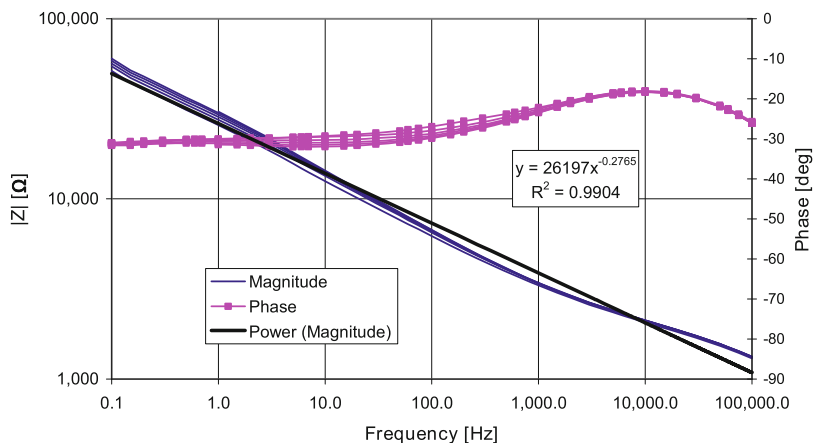


Fig. 2.7 Impedance plot. The phase roll-off at the *upper* frequencies is due to the parasitic capacitance of the electrodes. Thickening of the electrolyte layers pushes the roll-off to higher frequencies

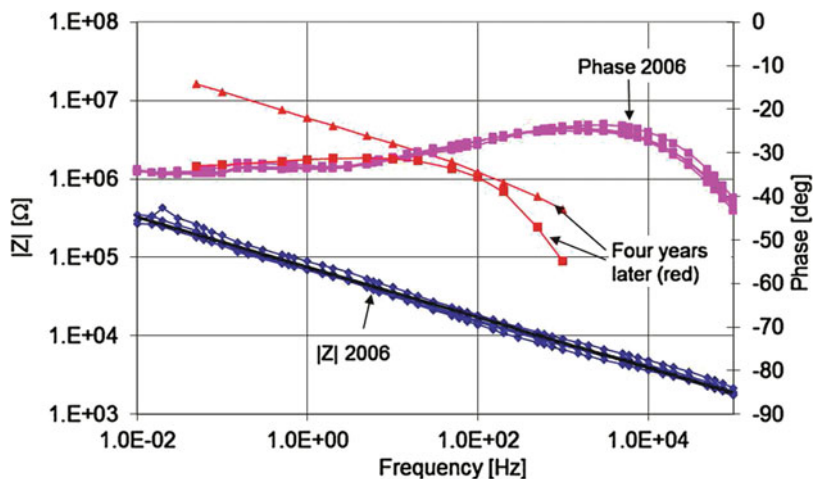


Fig. 2.8 Typical aging of solid-state fractor properties over a 4-year period. Impedance spectroscopy results of a fractor manufactured in 2006. The *pink line* represents the phase angle measurements while the *blue line* measures the impedance. The *red line* composed of triangles represents the impedance, where the *red-square line* represents the phase angle measurements, of the same fractor manufactured in 2006 measured again in 2010. The roll-off at the higher frequencies is due to the parasitic capacitance of the outer copper electrode plates

From there a manufacturing process will need to be invented that allows for production of predictable and consistent K and α values, with these values selectable on a batch-by-batch basis.

2.3.3 *Modified Lithium-Ion Type*

This second recipe was necessitated by the discontinued production of the polyaniline in sulfonic acid. Attempts to synthesize polyaniline in sulfonic acid locally proved the futile.

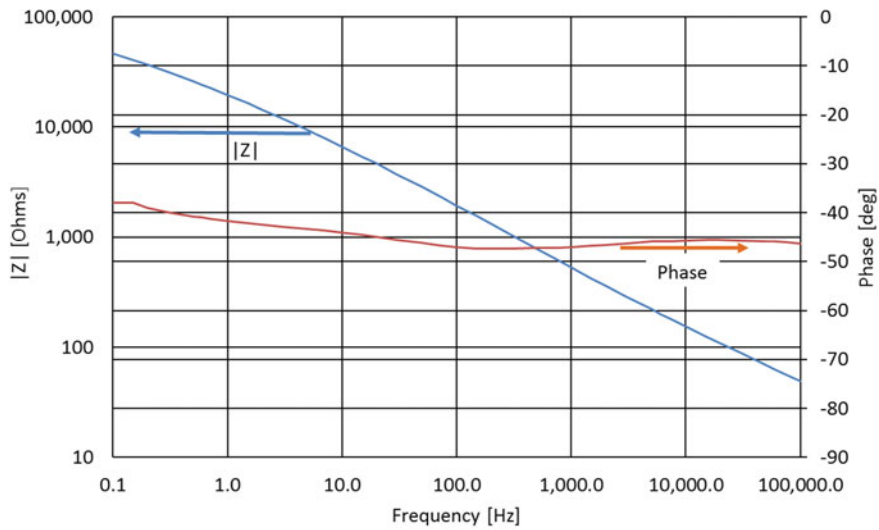
A revised recipe with cuprous mercuric iodide formed from potassium iodide, copper sulfate, mercuric nitrate, acetic acid, and acetone was tried with the intent to form a more consistent porous ionic gel. This proved to be very temperature dependent and was abandoned. The next step was to just try the earlier recipe without the polyaniline (Fig. 2.9).

The materials currently in use are lithium nitrate (LiNO_3), tetraethyl orthosilicate (TEOS, $\text{Si}(\text{C}_2\text{H}_5)_4$), distilled water (H_2O), 95% ethyl alcohol ($\text{C}_2\text{H}_5\text{OH}$), and nitric acid (HNO_3).

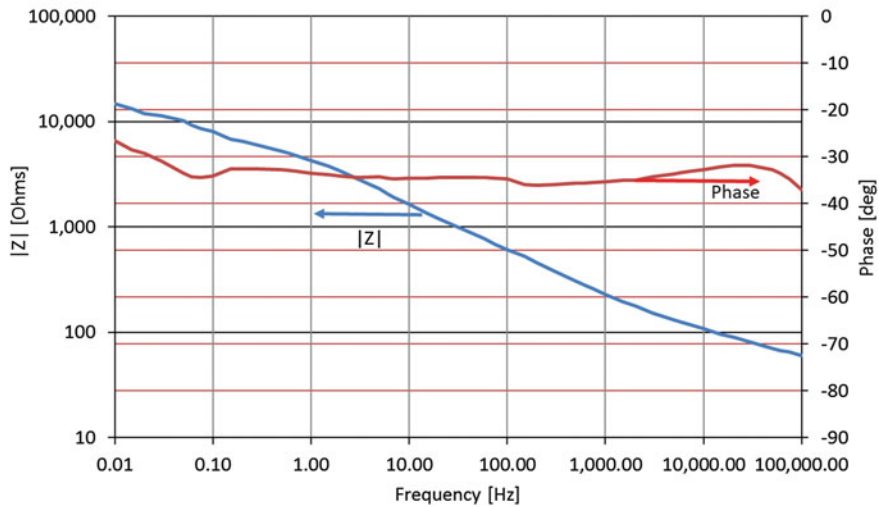
Ionic Gel Preparation: 7 mL of 95% ethyl alcohol was mixed with 7 mL of distilled water in a beaker with a magnetic stir rod and 0.7 g of lithium nitrate was added to it. The beaker was mounted on a stir plate and stirred the mixture until the entire lithium nitrate is solvated and removed the solution from the stir plate. Next, 3.5 mL of TEOS was added to the solution, at first the TEOS is not be soluble in the solution, so a drop or two of nitric acid must be added to the mixture. The beaker containing the solution was covered with a Petri dish to reduce degradation and evaporation and mounted back onto the stir plate and stirred on to a setting of approximately 300 rpm and left to stir for approximately 2 h. The beaker was tightly covered for storage. The solution must be used quickly as the compound degrades rapidly.

Again, we coated roughened square copper plates, approximately 3 mm thick, 2.5 cm on a side. The copper plates are dip coated and are held by their edges using bent copper wiring (“tweezer clamps”) and dipped in the solution, and then hung to dry on a rack. Once the coating has dried (approximately 5–15 min depending on how many coatings have already been applied), the copper plates were then removed from the clamps, rotated by 90° to ensure the sides of the plates are all coated, and placed back into the clamps, dipped and hung to dry again. This process was repeated to build up a minimum of 14 dip coatings on the copper plates in order to build appropriate ionic gel thickness.

Additional work needs to be done to determine the precise recipe variations lead to specific fractional-orders. Clues for varying the order can be developed from the IPMC, CBNC, and solution-based systems to be discussed in the next sections. Other clues could be taken from [22] in which it is shown that ionic conductivity is dependent on the concentration of the lithium ions and on the structure of the polymer electrolyte. Since fractors have been demonstrated with orders ranging between 0.27 and 0.5, it is possible that we have seen this concentration difference effect already merely in slight differences on a batch-to-batch basis.



(a) Prototype 1.



(b) Prototype 2.

Fig. 2.9 Impedance spectra for the second-generation fractor prototypes used later in the fractional harmonic oscillator demonstration

2.3.4 Other Lithium-Ion Attempts

We tried an idea for very low-cost fractance by just doping standard gelatin with lithium nitrate. There was evidence for CPE behavior, but the distribution of time constants was not adequate to get broad band phase consistency (Fig. 2.10).

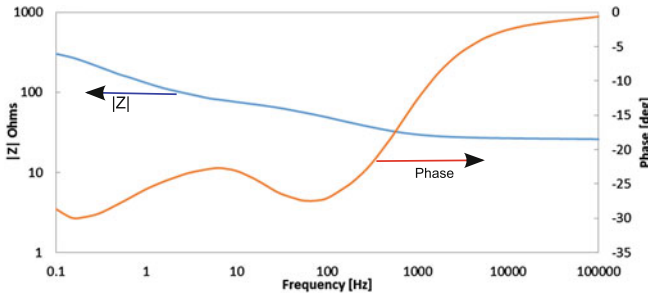


Fig. 2.10 An attempt using off-the-shelf gelatin doped with lithium nitrate exhibiting a mixture of CPE properties

2.4 Nanostructured Materials as Fractional-Order Elements

Ionic polymeric–metal composite (IPMC) and carbon-based nanocomposite (CBNC) are innovative nanostructured materials. The aim of this section is to show the fractional properties of IPMC and CBNC.

By varying some realization parameters, both for the IPMC and the CNNC, such as the geometrical dimensions, the duration of the electrodes deposition, the cation type, the solvent, the carbon percentage, and the curing temperature, it seems possible to obtain models, integrators, and derivators, whose non-integer order is strictly related to such parameters.

The interest of current investigation in fact is focused on the possibility to use IPMC and CBNC to realize fractional-order elements (FOE) able to implement a fractional-order device.

2.4.1 IPMC Structure and Working Principles

Ionic polymer–metal composites (IPMCs) as electroactive polymers (EAPs) have the very useful capabilities to transform electrical energy into mechanical energy, and vice versa [41, 42], making them privileged candidates for the implementation of actuators or sensors with features as low applied voltage, high compliance, softness, etc., thus creating great interest in future applications in very different fields such as aerospace, biomedics, and robotics [18, 38, 43].

In [15], the possibility of modeling the IPMC actuators via gray-box model based on fractional-order systems was presented, paving the path for a new approach to such materials seen as fractional-order electronic elements (FOEs) and not only as electromechanical transducers.

This new approach is suggested by IPMC electrochemical and structural properties. In fact the dendrites on the interfacial landscape between the metal electrodes

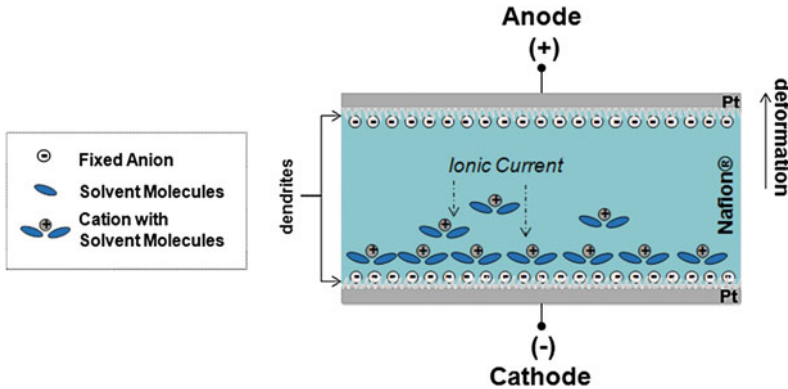


Fig. 2.11 Structure and working principle of IPMC

and the polymer layer show fractal dimensions, and a fractional electrical behavior might be due to the anomalous diffusion of ions and solvent through metal/polymer surface, see [28]. Furthermore, IPMCs fit in the research area working on FOE implementation processes which assesses the interaction between ionic phenomena and fractal structures as possible starting point for FOEs' realization.

IPMCs are based on polymer-containing ions, ionomers, or ionic polymers, that are weakly linked to the polymer chain and metallized via a chemical process, on both sides, with a noble metal, to realize the electrodes. There are a number of different types of ionic polymers available but the typical IPMC used in many investigations is composed of a perfluorinated ion-exchange membrane, Nafion 117, which is surface-composited by platinum via chemical process, see Fig. 2.11.

The platinum electrodes usually consist of small, interconnected particles of metal which are made to penetrate into the ionic polymer membrane. This allows the formation of electrodes with dendritic structures [28, 41], which extend from the surface into the membrane.

Working as an actuator, when an external voltage is applied across the thickness of the IPMC, mobile cations H^+ in the polymer will move toward the cathode. If a solvent is present in the sample, the cations will carry solvent molecules with them. The cathode area will expand while the anode area will shrink. If the tip of the IPMC strip is free the polymer will bend toward the anode; thus a force will be delivered. On the other hand, when the IPMC works as a sensor, it exploits the mechanical displacement of the polymer for the generation of a ionic current inducing a potential difference.

2.4.1.1 Manufacturing

Nafion 117 film, by DuPont™, Sigma-Aldrich Group, with thickness $t_{Naf} = 180 \mu m$, and sizes $4 cm \times 4 cm$, was pretreated by successive boiling for 30 min in HCl_2N and deionized water.

Fig. 2.12 IPMC sample

Ethylene glycol (EG) was used as the solvents and Platinum as the electrodes. Two platinum metallizations were obtained after the immersion of the Nafion117 membrane in a solution of $[Pt(NH_3)_4]Cl_2$, with $MW = 334.12$, and immersion time will be here referred to as absorption time.

The platinum solution was obtained by dissolving 205 mg of the complex in 60 ml of deionized water and adding 1 ml of ammonium hydroxide at 5%.

In order to increase the performance of the device, a dispersing agent (polyvinyl pyrrolidone with molecular weight 10000-PVP10) has been added. A secondary metallization was performed via deposition. Then, the samples were boiled in 0.1 M HCl for 1 h.

In order to obtain the IPMC with EG as solvent, Nafion117 membranes were soaked overnight in a beaker containing pure EG and, finally, heated to $60^\circ C$ for 1 h. Obtained IPMC was then cut into strips of size $1\text{ cm} \times 1\text{ cm}$ and dried for one week. Some IPMC samples are shown in Fig. 2.12.

Three different IPMC membranes have been fabricated with three different absorption times: 5, 10, and 20h in order to study the relationship between such a fabrication parameter and the fractional-order dynamics of the IPMC device.

The three membranes will be here referred, respectively, as $IPMC_{AbsT-5h}$, $IPMC_{AbsT-10h}$, and $IPMC_{AbsT-20h}$.

2.4.1.2 Geometry and Experimental Setup

In the experiments the IPMC device proposed as FOE consists of an IPMC sample ($1\text{ cm} \times 1\text{ cm}$) mechanically fixed within a plexiglas sandwich configuration in series with a resistor with $R = 46\ \Omega$ as shown in the schematic of Fig. 2.13.

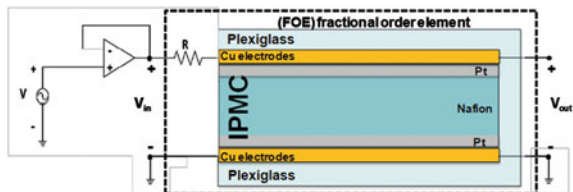
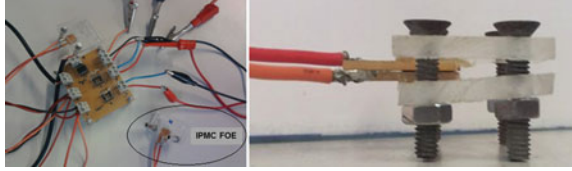
Fig. 2.13 IPMC FOE sandwich configuration schematic

Fig. 2.14 Experimental setup (left), IPMC FOE setup (right)



The input voltage signal V_{in} , applied to perform the frequency-domain identification, was forced by a waveform generator Agilent 33220A, through a conditioning circuit made of an operational amplifiers, ST TL082CP, in buffer configuration. The output voltage V_{out} was measured through a pair of electrodes $1\text{ cm} \times 1\text{ cm}$ and thickness $35\text{ }\mu\text{m}$ printed on a PBC board and in direct contact with the platinum electrodes.

Both the input V_{in} and output V_{out} signals were acquired using a National Instrument NI USB-6251 board and processed by the LabView software.

A schematic of the experimental setup is reported in left part of Fig. 2.14, while details on the IPMC FOE are in right part of Fig. 2.14.

Measurements have been performed on the three membranes $\text{IPMC}_{AbsT-5h}$, $\text{IPMC}_{AbsT-10h}$, and $\text{IPMC}_{AbsT-20h}$. A set of sine voltages with amplitude of 4 V_{pp} was applied as V_{in} .

For each membrane, different measures were performed varying V_{in} frequency in the range from 10 mHz to 10 kHz with 10 Hz step. MATLAB tools were used to estimate the modulus and phase of the acquired signals.

2.4.2 Linearity Study

As reported in literature [11], IPMC membranes working as transducers present a nonlinear component in the electromechanical model and show an hysteretic behavior in the relationship between applied voltage and absorbed current, and therefore the hypothesis of linearity must be verified in order to consider the frequency response as a coherent characterization for IPMC. Moreover, being the system nonlinear, such characterization is valid only for the given input voltage amplitude 4 V_{pp} .

Lissajous curves have been studied in order to characterize the linearity of the IPMC as FOE. A Lissajous curve was obtained at each frequency for the entire experimental range. Figures 2.15, 2.16, 2.17, and 2.18 show such curves for the device $\text{IPMC}_{AbsT-5h}$. Moreover, Fig. 2.19 shows zoomed curves for the sample frequencies: $f = 50\text{ mHz}$, $f = 1\text{ Hz}$, $f = 9\text{ Hz}$, and $f = 4\text{ kHz}$.

At low frequencies, the nonlinear component dominates and the Lissajous curves have a non-elliptic shape. In particular under the 1 Hz frequency, the curves show nonlinearity, while 1 Hz is a frequency of transition from nonlinearity to linearity. For frequencies higher than 1 Hz the shape of the Lissajous curves can be considered elliptic.

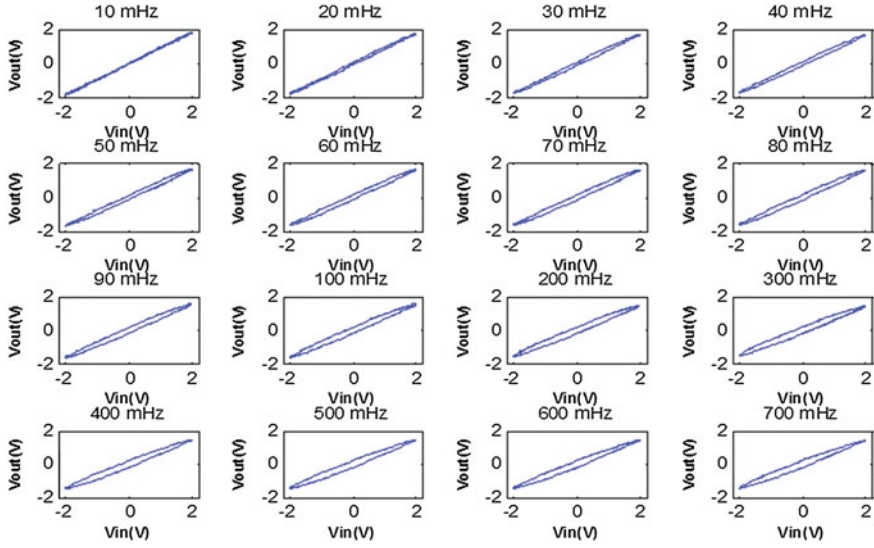


Fig. 2.15 Lissajous curves on measured input V_{in} and output V_{out} voltages in the frequency range between 10 and 700 mHz for the device $IPMC_{AbsT-5h}$

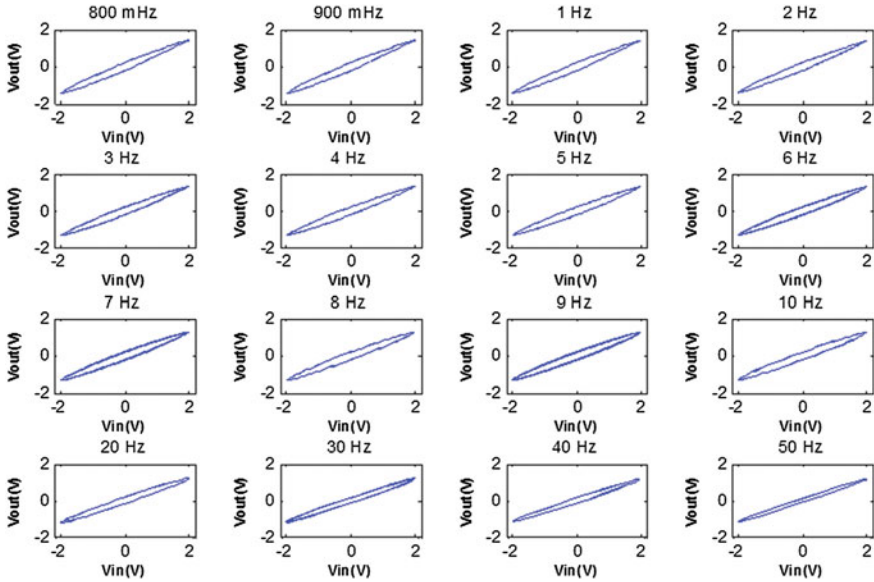


Fig. 2.16 Lissajous curves on measured input V_{in} and output V_{out} voltages in the frequency range between 800 and 50 Hz for the device $IPMC_{AbsT-5h}$

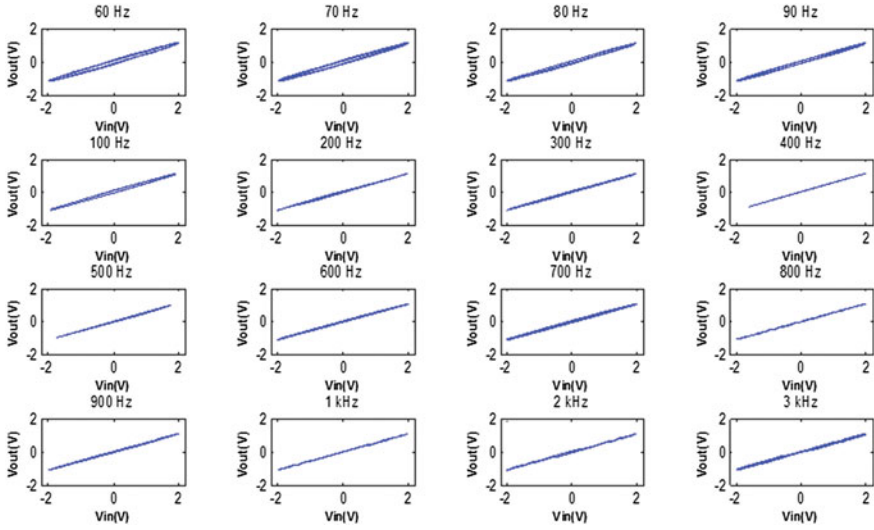


Fig. 2.17 Lissajous curves on measured input V_{in} and output V_{in} voltages in the frequency range between 60 Hz and 3 kHz for the device $IPMC_{AbsT-5h}$

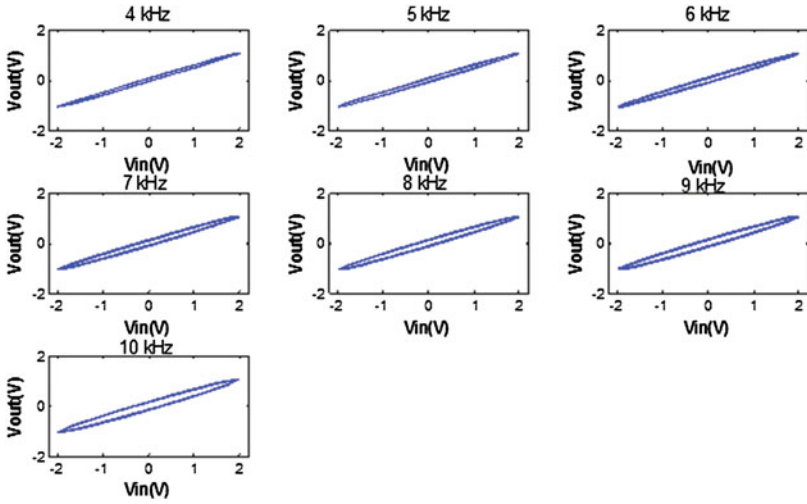


Fig. 2.18 Lissajous curves on measured input V_{in} and output V_{in} voltages in the frequency range between 4 and 10 kHz for the device $IPMC_{AbsT-5h}$

The $IPMC_{AbsT-10h}$ and $IPMC_{AbsT-20h}$ show the same trend in the Lissajous curves, and therefore the conclusion about $IPMC_{AbsT-5h}$ linearity will be extended to them.

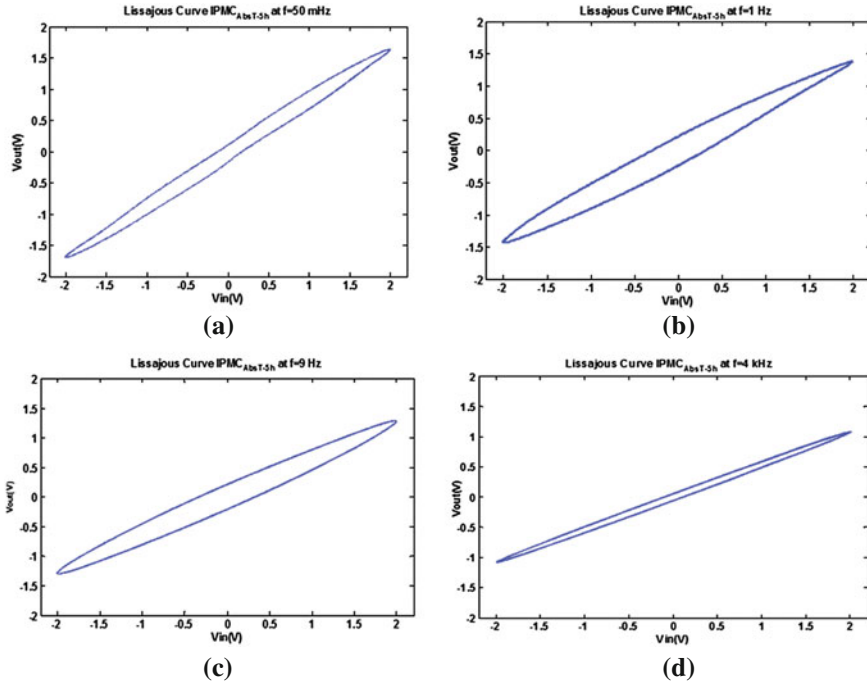


Fig. 2.19 Shape analysis of Lissajous curves on measured input V_{in} and output V_{in} voltages for the device $IPMC_{AbsT-5h}$: **a** non-elliptic shape at $f = 50$ mHz, **b** transition between non-elliptic to elliptic shape at $f = 1$ Hz, **c** elliptic shape at $f = 9$ Hz, **d** elliptic shape at $f = 4$ kHz

At low frequencies, a capacitance is considered an open circuit and the nonlinearity dominates the global behavior. As the frequency increases, the linear capacitive effect of IPMC becomes significant and dominant with respect to the nonlinear component.

Concluding, in this stage, IPMC FOE will be approximated as linear in a frequency range from 1 Hz to 10 kHz.

2.4.2.1 IPMC Frequency Analysis

The modulus and phase diagrams, see Figs. 2.20, 2.21, and 2.22 of the ratio between V_{out} and V_{in} signals at each frequency, have been obtained using the experimental data in the frequencies range between 10 mHz and 10 kHz for all the devices $IPMC_{AbsT-5h}$, $IPMC_{AbsT-10h}$, and $IPMC_{AbsT-20h}$.

Given the conclusion on linearity assessed by the Lissajous curves, such curves can be considered as the system's frequency response in terms of Bode diagrams of the transfer function in the linearity range from 1 Hz to 10 kHz. In such a range, it was observed that both IPMC devices show a fractional-order behavior in a limited span of frequencies where the modulus of the Bode diagrams presents a slope equal to $\alpha \times$

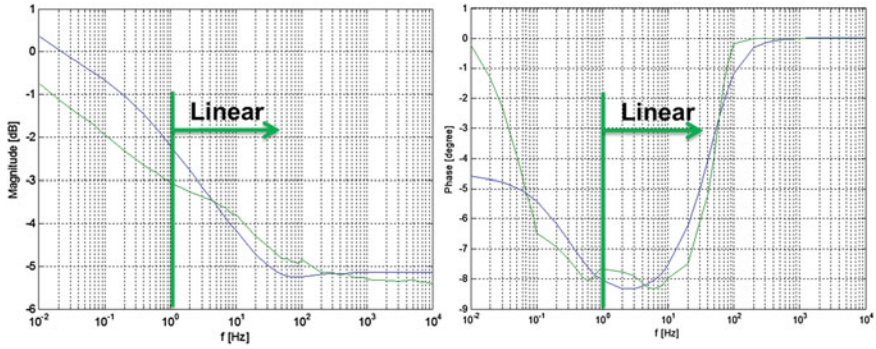


Fig. 2.20 Modulus (a) and phase (b) diagrams of the ratio $\frac{V_{OUT}}{V_{IN}}$ in the complete experimental frequencies range: 10 mHz to 10 kHz for the IPMC device at 5 h absorption time

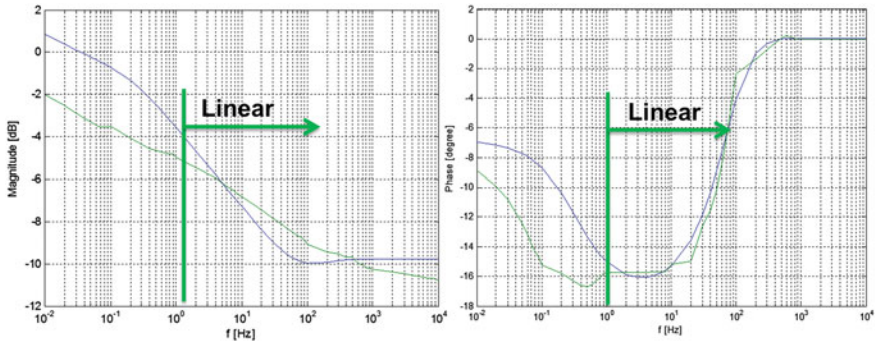


Fig. 2.21 Modulus (a) and phase (b) diagrams of the ratio $\frac{V_{OUT}}{V_{IN}}$ in the complete experimental frequencies range: 10 mHz to 10 kHz for the IPMC device at 10 h absorption time

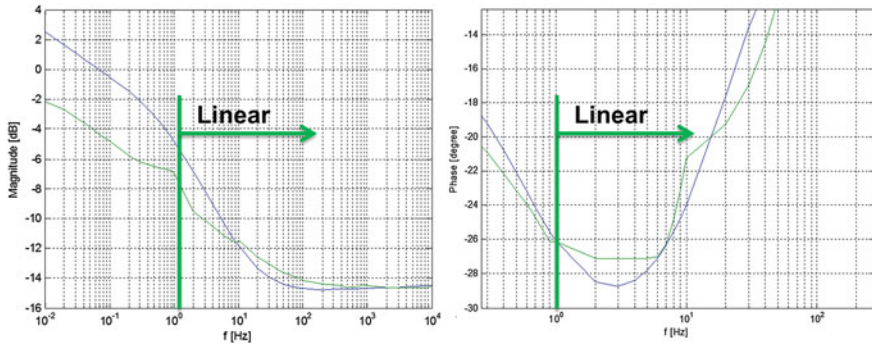


Fig. 2.22 Modulus (a) and phase (b) diagrams of the ratio $\frac{V_{OUT}}{V_{IN}}$ in the complete experimental frequencies range: 10 mHz to 10 kHz for the IPMC device at 20 h absorption time

20 dB/decade, and the phase presents a lag equal to $\alpha \times 90^\circ$, where α is identifiable as the fractional-order exponent.

With respect to the three IPMC devices, the following comparisons can be made:

- $\text{IPMC}_{AbsT-5h}$: IPMC device with 5 h of absorption time
The IPMC with 5 h of absorption time has shown an average slope in the modulus diagram of 1 dB per decade in the frequency range between 1 and 10 Hz, determining $\alpha = 0.05$. The phase diagram showed an average phase of -4.5° in the same frequency range being coherent with the fractional exponent related to the modulus $-\alpha \times 90^\circ = -4.5^\circ$.
- $\text{IPMC}_{AbsT-10h}$: IPMC device with 10 h of absorption time
The IPMC with 10 h of absorption time has shown an average slope in the modulus diagram of 1.6 dB per decade in the frequency range between 1 and 10 Hz, determining $\alpha = 0.075$. The phase diagram showed an average phase of -6.7° in the same frequency range being coherent with the fractional exponent related to the modulus $-\alpha \times 90^\circ = -6.7^\circ$.
- $\text{IPMC}_{AbsT-20h}$: IPMC device with 20 h of absorption time
The IPMC with 20 h of absorption time showed an average slope in the modulus diagram of 6 dB per decade in the frequency range between 1 and 10 Hz, determining $\alpha = 0.3$. The phase diagram showed an average phase of -27° in the frequency range between 1 and 10 Hz showing, in that range, coherence with the fractional exponent related to the modulus $-\alpha \times 90^\circ = 27^\circ$.

Finally, Fig. 2.23 shows the trend of the fractional-order α while varying the absorption time.

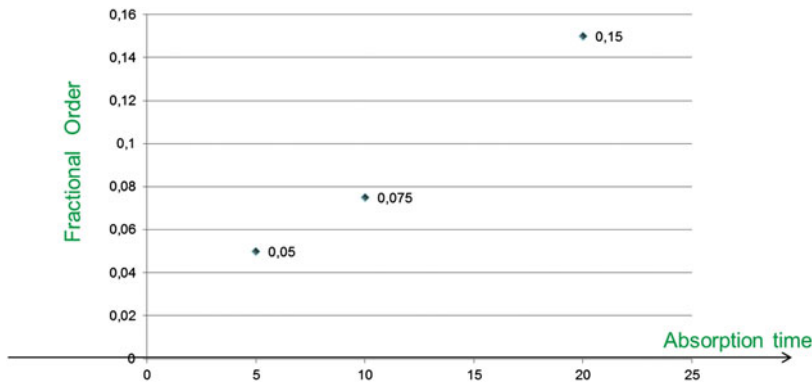


Fig. 2.23 Fractional-order versus absorption time

2.4.3 Carbon Black-Based FOE

The focus of this paragraph is on the possibility to exploit nanostructured material, in particular carbon black (CB)-based composite, to realize non-integer order devices. Such elements can be modeled as FOE whose experimentally acquired frequency response fit the following model:

$$Z(s) = \frac{K}{(1 + \tau s)^\alpha}. \quad (2.2)$$

It is known in the literature that by adding a conductive filler to an insulating matrix, generally a polymeric matrix, both the electrical and mechanical properties of the composite can change. Such phenomenon has been studied for realizing polymer conducting composites, with application, such as thermistors, deformation sensors [23], pressure sensors [20], and gas sensors [50].

Here, the possibility to use carbon black to realize nanocomposites with dielectrics properties is investigated.

2.4.3.1 Materials

Sylgard₁₈₄, the host matrix of interest in this research, is a thermally curable silicone rubber.

Its formulation consists of two parts: vinyl-terminated polydimethylsiloxane (PDMS) chains (part A) and a mixture of methylhydrosiloxane copolymer chains with a Pt catalyst and an inhibitor (part B).

Parts A and B are viscous liquids, 5000 cSt and 110 cSt at 25 °C, respectively, usually mixed together in a 10:1 ratio.

Addition of a catalytic amount of the SiH of methylhydrosiloxane (part B) to the double bond of the vinyl-terminated PDMS species (part A) leads to a cross-linked network through the formation of Si–C covalent bonds.

The described, nanomaterial CB-based polymer, is in fact the dielectric of the CB–FOE under investigation. The resulting structure of the CB–FOE is given in Fig. 2.24.

The obtained dielectrics have been used to realize cylindrical capacitors, whose geometry is shown in Fig. 2.25. More specifically, capacitances considered in the following had copper-based shell with height $h = 8$ cm, internal diameter $a = 0.6$ cm, and external diameter $b = 1.2$ cm.

2.4.4 FOE Under Test and Experimental Setup

The samples have been prepared by mixing the PDMS and the cross-linking agent in a ratio of 1:10 in a Teflon crucible.

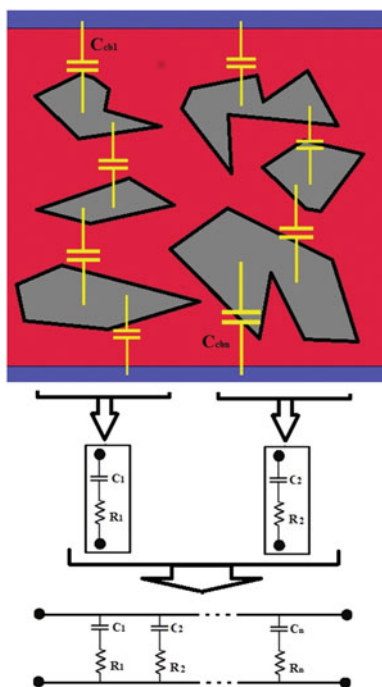


Fig. 2.24 Carbon black-based fractional-order element (CB-FOE) structure

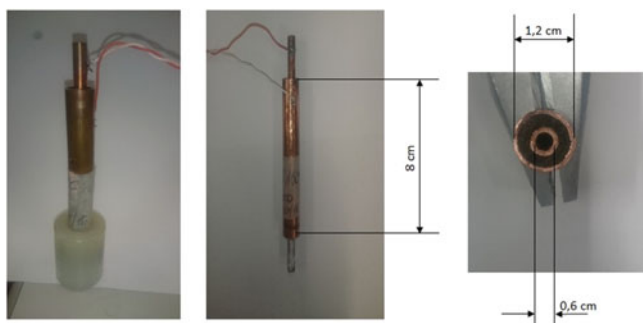


Fig. 2.25 Sample of the CB-FOE under investigation

The mixture was mixed for 10 min and at this point has been added the required amount of carbon black to achieve the desired concentration.

It is continued to stir for 10 min to enhance the dispersion of the carbon black, and then the viscous mixture was poured into the device and it is made reticular at 25 °C for 2 days or at 150 °C for 28 min.

Table 2.1 List of the realized CB-FOE

Carbon black %	Curing temperature	Characteristic (pF)
1%	Room	≈ 25
2%	Room	≈ 30
8%	100 °C	≈ 76.6
8%	125 °C	≈ 207
8%	150 °C	≈ 150
5% xiline solvent	Room	≈ 137
5% CHCL3 solvent	Room	≈ 50

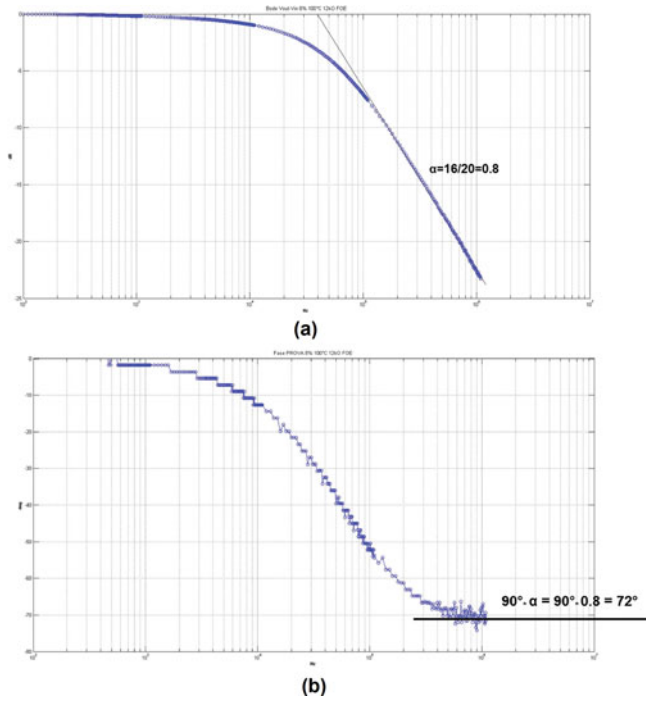


Fig. 2.26 Frequency-domain identification, device 8% @ 100 °C

The carbon black percentage, the curing temperature, and the solvent type have been changed according to Table 2.1. The capacitors, during the acquisition phase, were connected in series configuration with a resistor of 12 kΩ.

A sinusoidal input voltage V_{in} was produced using a waveform generator Agilent 33220A. The sinusoidal signal was applied through an operational amplifier, ST TL082CP, in buffer configuration.

The investigated frequency range was from 10^2 to 10^7 Hz; moreover, 100 points per decade were considered, see Figs. 2.26, 2.27, and 2.28.

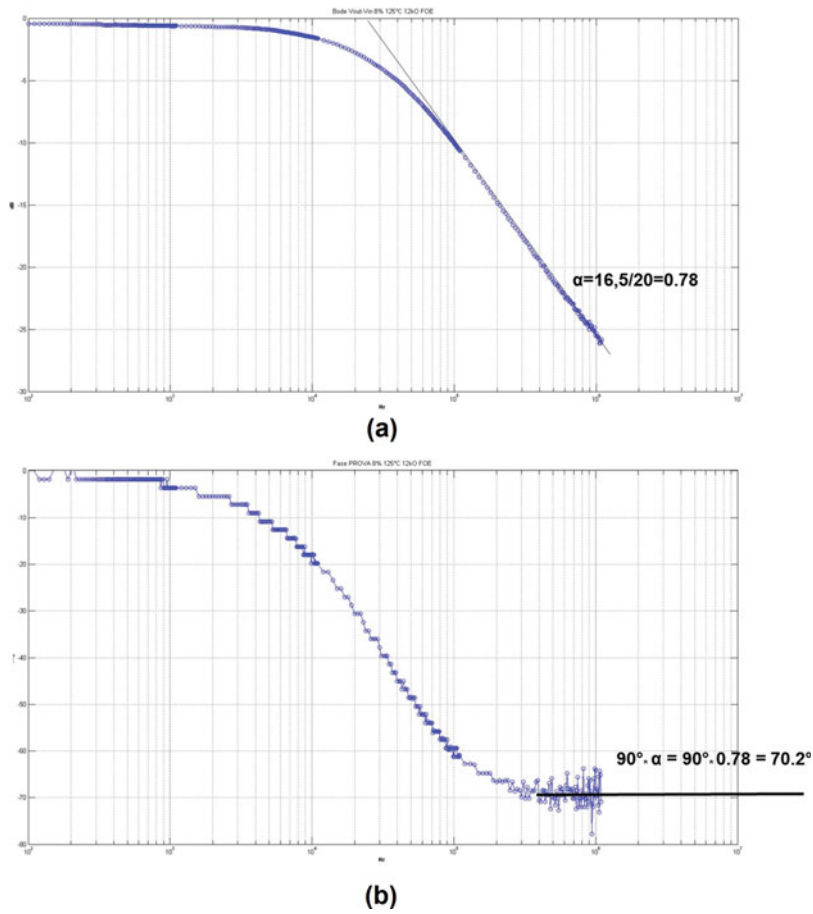


Fig. 2.27 Frequency-domain identification, device 8%@125 °C

The obtained result allows to foresee a dependence of the order α with the curing temperature.

In fact, in Table 2.2 it is possible to note that α decreases from 0.8 to 0.7 via 0.78 when the curing temperature raises from 100 to 150 °C.

2.5 Other Solid-State Devices

In addition to the fractional-order elements mentioned above, a few other solid states devices have been reported in literature. One such system is based on the *Fractal structure*. In 1997, Haba et al. developed a fractal structure with three levels of iterations which gives a prominent CP zone [24]. Later, they studied this fractal

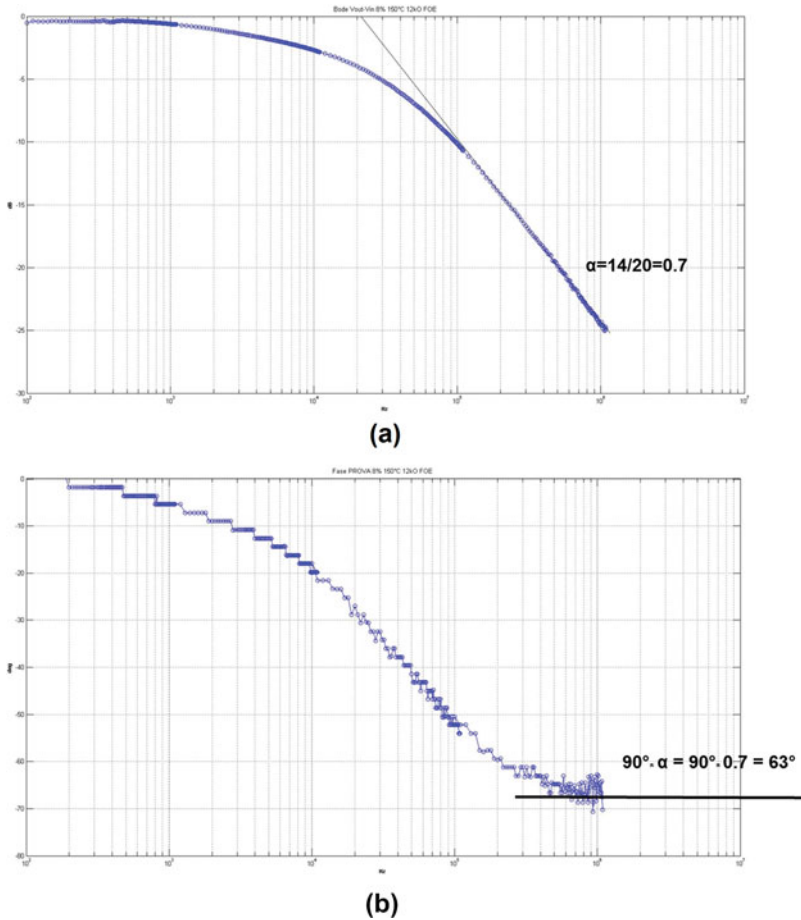


Fig. 2.28 Frequency-domain identification, device 8%@150°C

structure for varying fractal resistances and capacitances and showed how CP zone can be varied using those resistance and capacitance [25]. It shows CP in 10^5 Hz to 10^{10} Hz zone with CP angle = 36° (i.e., $\alpha = 0.4$) and fabricated by photolithography using Si substrate. The reported CPZs are usually three to five decades long. These devices are lightweight and dry fractors with a phase ripple of $<\pm 2.7^\circ$.

Another solid-state FOE worth to be mentioned is based on a graphene-polymer composite. Here, fractal or porous structures were introduced to bring the effect of dispersive RC blocks, as pursued in different multicomponent techniques. In this work, dielectric of conventional parallel-plate capacitor is replaced by a polymer composite, percolated with reduced graphene oxide [21]. The properly dispersed graphene sheets in the polymer gives a number of RC blocks of different relaxation times, which ultimately give FO nature. This FOE shows different α values (0.33–

Table 2.2 Determination of the α value using the asymptotic phase calculus

Curing temperature (°)	Asymptotic value (deg)	α	Magnitude slope (dB/dec)
100	$\simeq -72$	$\simeq 0.8$	$\simeq 16$
125	$\simeq -70.2$	$\simeq 0.78$	$\simeq 16.5$
150	$\simeq -63$	$\simeq 0.7$	$\simeq 14$

0.73) for different graphene loads (12%–2% respectively). This device is small in size, compatible to microfabrication, but could be realized for very small CPE zone (400 kHz–2 MHz only). The fabrication procedure is complicated and costly.

2.6 Solution-Based Systems

There has been significant research in electrochemistry verifying the validity of the CPE model describing embedded dynamics. The performance of these materials, depending on the processes of the electrolytes, has been described, and the physical origins of the model parameter have been established in many cases. However, the influence of the electrodes was not a subject of study and only recently this problem became relevant in the viewpoint of fractional calculus.

In this section, fabrication details of porous polymer-based electrolytic fractor and its potential for use in realizing fractional-order systems will be discussed. Our efforts in solution-based FOE were preceded by Jesus and Machado [26].

Fractal electrode-based electrolytic FOE: In 2008, Jesus and Machado [26] used the concepts of using both the fractal structure and electrolyte to realize FOE. Here, electrodes are Cu-clad PCB with a typical fractal geometry (carpet of Sierpinski) and electrolyte is NaCl solution. A sand stand within the NaCl solution is used as the fractal material. It is shown how α increases with the increase of effective area of fractal structure as well as solution molarity. Here, α values from 0.2 to 0.6 have been realized. The main limitation is the bulky structure and potential for spillable; thus limiting application in various FO systems.

Porous polymer-based electrolytic fractor: This prototype device was first reported by Biswas et al. [8]. It is made of porous PMMA-coated Cu or Pt electrodes, dipped in an ionic solution. Later, such fractors are packaged by replacing the ionic solution by ionic gel (made by agar-agar powder) [31]. Different α values between 0.1 and 0.85 have been achieved. The realized FOE covers the frequency zone from 100 Hz to 1 MHz. Initially, the constant phase zone (CPZ), i.e., the bandwidth of the FOE was maximum two decades long [30]. Later by introducing the CNT in the coating polymer (in this case coating polymer is BPADA–mPD) the bandwidth could be extended to five decades (20 Hz–2 MHz) [1]. The packaged FOE is smaller than the fractal FOE, cheaper, and simpler to fabricate. It is successfully used in developing

many FO systems [8, 31, 45–47]. This FOE has been studied for different system parameters, i.e., dipping length, coating thickness, the solution pH, and conductivity. It is shown that CP zone can be moved to high-frequency zone by increasing solution pH or conductivity, and CPZ can be widened by decreasing coating thickness. Though a definite equation between α and the system parameters could not be established yet, the study elaborates how we can design the system parameter to get a particular value of α and are detailed in the next section.

2.6.1 Fabrication Details of the Solution-Based FOE

It has been reported in the literature that when a porous electrode is dipped in an electrolyte then diffusion takes place through the electrode surface. If the surface is smooth then ordinary diffusion takes place; that is, the mean free path of the diffusing particles follows the ordinary linear law of diffusion [6],

$$r^2 \propto t, \quad (2.3)$$

where r is the mean free path displacement and t is the time constant. But for a porous surface the above-stated ordinary diffusion equation does not hold accurately. For this anomalous diffusion to take place, the mean square displacement of the diffusing particles shows a PL distribution on time as expressed by

$$r^2 \propto t^\alpha, \quad (2.4)$$

where α is fractional in nature. Considering the Fick's law of diffusion, continuity equation, and modified laws for anomalous diffusion, the impedance of diffusion process can be modeled by "Transmission Line" which has the similarity with the infinite RC ladder network mentioned by the researchers in the field of circuit theory [27, 33, 39] to realize FOE.

To get the porous surface, a thin coating (5–50 μm) was provided by dipping the probe in PMMA solution and the probes exhibit constant phase behavior with an angle much less than 90° when dipped in ionic solution. This can be explained as the relaxation time at the metal–PMMA electrolyte interface gives a fractional exponent α much less than the value 1. The probe shown in Fig. 2.29 is made of about 6-mm-wide strip cutout from about 1.6-mm-thick plate generally used as double-sided printed circuit boards (PCB). The copper claddings on the two external faces serve as the two electrodes of the probe. The construction of PCB ensures sufficient rigidity to the probe. The fabrication of PMMA-coated probes is reported in [9]. For 1% PMMA solution, 0.44 g of PMMA flex is fully dissolved in 30 mL of chloroform to prepare the coating solution. The copper-coated epoxy strip is then dipped into this solution. Thus, a layer of PMMA solution is coated over the copper surface.

The insulation process of the metal electrodes of the probe by the above-mentioned procedure forms a thin porous film of PMMA on the metal electrodes. This may be

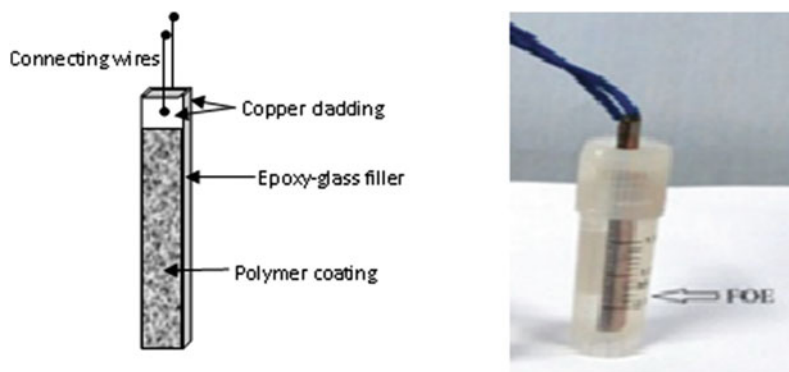


Fig. 2.29 Schematic of the polymer-coated probe and the solution-based FOE

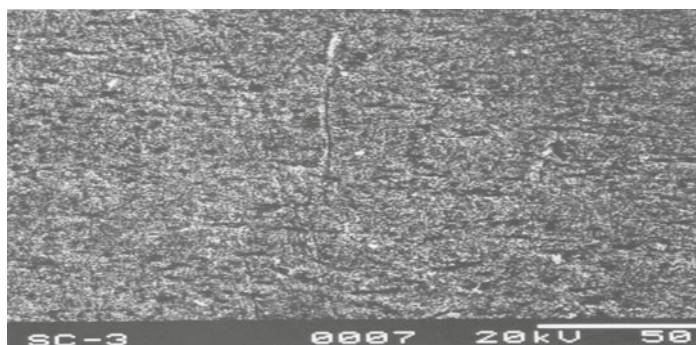


Fig. 2.30 The SEM picture of the surface of copper electrode of the probe without coating

due to the fact that when the solvent chloroform evaporates, nanopores are formed on the surface. This can be seen in the scanning electron microscope (SEM) pictures of the surface of the copper electrodes taken before coating and after the coating by PMMA. Figure 2.30 shows a SEM picture of the bare surface of the electrodes at a magnification of 500 and Fig. 2.31 shows the same for a PMMA-coated surface with coating thickness of 5 μm . The regular porous nature of the surface is similar to the “Transmission Line” model as described by Bisquert et al. [7] and results “CPA” behavior of the process. The CPA behavior for such probes are shown in Figs. 2.33 and 2.34.

In place of PMMA other polymer can also be used if they are soluble in a solvent which evaporates during drying, leaving the porous polymer surface on the electrodes. One such polymer is BPADA–mPD. It is a composition of 4,4’-(4,4’-isopropylidene di phenoxy) bis (phthalic anhydride) (BPADA) and m-phenylene diamine (mPD). The FOE realized using BPADA–mPD is elaborated later.

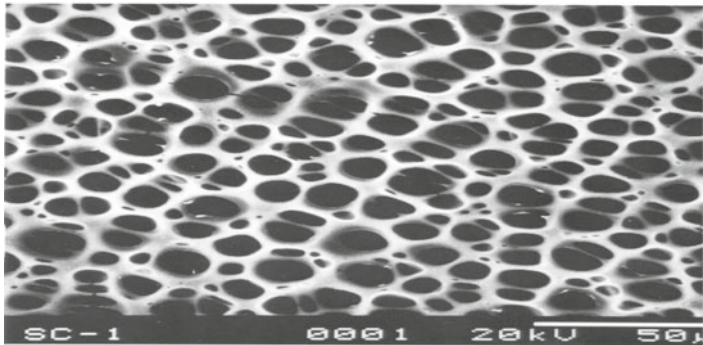


Fig. 2.31 The SEM picture of the surface of PMMA coating of 5 μm (2.5%) thickness at a magnification of 500

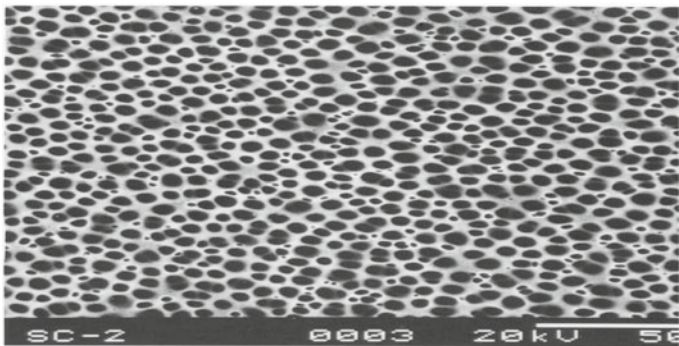


Fig. 2.32 The SEM picture of the surface of PMMA coating of about 12 μm (5%) thickness at a magnification of 500

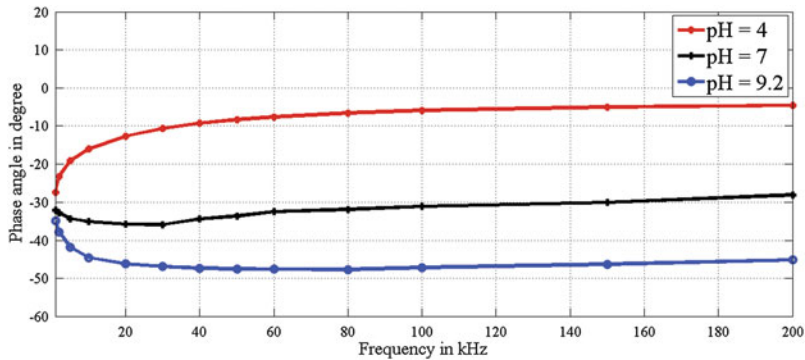


Fig. 2.33 Constant phase angle of the FOE realized by dipping the PMMA-coated probe in three buffer pH solutions

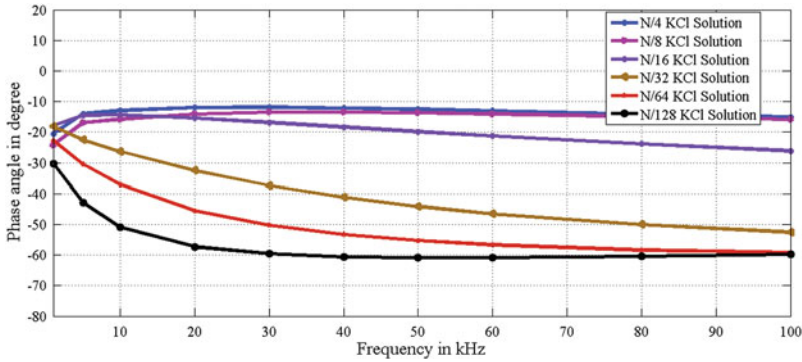


Fig. 2.34 Constant phase angle of the FOE realized by dipping the PMMA-coated probe in six different aqueous solutions of KCl

2.6.2 The Parameter Dependence of the FOE

The characteristics of FOE are mainly dependent upon the fractional exponent α in (1.1), that means on the constant phase angle θ which is being measured by the LCR meter. The constant phase angle depends on a number of parameters. This has been investigated experimentally and from the experimental observation we can say

$$\theta_{FOE} = f(t, A, \sigma), \quad (2.5)$$

where t is the thickness of the insulation on the electrode, A is the area of contact of the electrodes with the polarizing medium, and σ is the ionic concentration of the polarizing medium.

2.6.2.1 Dependence of Phase Angle on the Ionic Concentration, “ σ ”

The exponent α of (1.1) varies with the ionic concentration of the solution in which the polymer-coated probe is dipped. This is illustrated by the graphs of Fig. 2.33. It can be seen from the figures that when the same probe is dipped in three different buffer solutions of pH (pH 4, pH 7, and pH 9.2), they result in different phase angles and hence different values of the exponent, α . Similar observation also can be found in Fig. 2.34, wherein different concentrations of KCl solution result in different phase angles.

2.6.2.2 Dependence of Phase Angle on “ t ”

The fractional exponent α is very much dependent upon the coating thickness of the porous polymer on the surface of the metal electrode. It has been observed

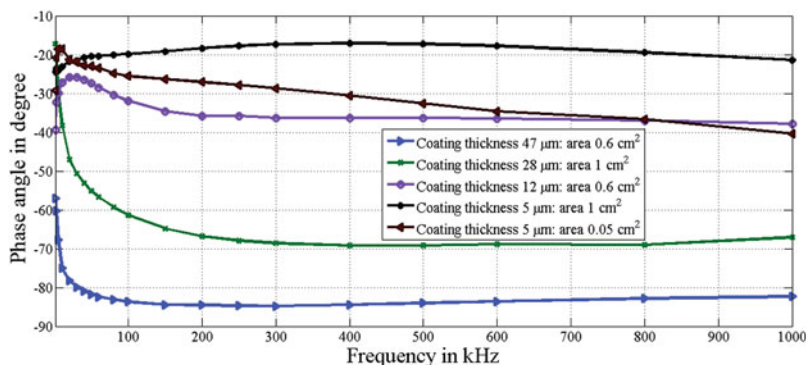


Fig. 2.35 Behavior of constant phase angle characteristics of probes constructed with varying coating thickness, length, and width when immersed 1 cm in ionic medium (conductivity = $250\mu\text{S}/\text{cm}$); for coating thickness = $47\text{ }\mu\text{m}$, area in polarizable medium is 0.6 cm^2 ; for coating thickness = $28\text{ }\mu\text{m}$, area in polarizable medium is 1 cm^2 ; for coating thickness = $12\text{ }\mu\text{m}$, area in polarizable medium is 0.6 cm^2 ; for coating thickness = $5\text{ }\mu\text{m}$, area in polarizable medium is 1 cm^2 ; for coating thickness = $5\text{ }\mu\text{m}$, area in polarizable medium is 0.05 cm^2

that for a thick coating it acts as a capacitor with the phase angle near about 90° and as the coating thickness decreases the fractional exponent also decreases and gives lower phase angle in the impedance measurement of the probe by LCR meter. Figure 2.35 shows the dependence of the phase angle on the thickness of the coating. For coating thickness 47 and $12\text{ }\mu\text{m}$, the area in contact with the polarizing medium is same but different coating thicknesses results in a wide difference in the measured constant phase angle. The same observation is also true for coating thickness of 28 and $5\text{ }\mu\text{m}$. This is because, with the increased number and size of pores (for lesser coating thickness); the electric current density takes less time to follow the change of the electric field in the dielectric region. As a result, the phase angle of the impedance is less than the case when the size and number of the pores are less. This phenomenon can be further illustrated by the “SEM” picture taken for two different coating thicknesses and shown in Figs. 2.31 and 2.32. So, from the above observations, it can be said that coating thickness becomes a design parameter for realizing different FOEs.

2.6.2.3 Dependence of Phase Angle on “A”

The dependence of constant phase angle, θ , on the area of contact with the polarizing medium can be observed in Fig. 2.35. From the graphs of Fig. 2.35, it is apparent that when the coating thickness is $5\text{ }\mu\text{m}$ the CPA is nearly 30° for 1 cm^2 contact area and CPA is nearly 20° for contact area of 0.05 cm^2 ; thus the area of contact can be varied to get different FOEs.

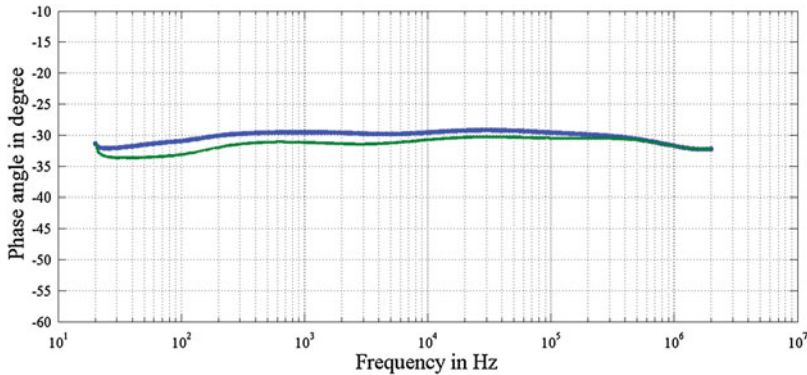


Fig. 2.36 Constant phase angle of the FOE realized by dipping the probe coated with BPADA–mPD + 1% CNT in pH 9.2 buffer solution

2.6.3 CNT–Polymer Composite-Based Wideband FOE

This wideband FOE was reported in [1]. It has similar structure like that of solution-based system discussed above [8], the difference is that the electrodes are now coated with carbon nanotube (CNT)–polymer composite instead of porous PMMA. The coating polymer is BPADA–mPD. It is a composition of 4,4'-(4,4'-isopropylidene di phenoxy) bis (phthalic anhydride) (BPADA) and m-phenylene diamine (mPD). Carbon nanotube (CNT) has been introduced to coating polymer, to achieve dispersive resistive–capacitive blocks, that is, the physics behind the realization technique of ladder-realized fractors. That means, now, CNT loading is also a design parameter which enhances the design flexibility [1].

In PMMA-based FOE, the effect of porosity does not become prominent until the coating thickness is low. So, the bandwidth is small in [8]. This problem is overcome by adding 1.5% CNT loading in the polymer. This CNT-based FOE shows five decades long bandwidth ranging from 20 Hz to 2 MHz with $\alpha = 0.35$. The main advantages are as follows: long bandwidth, low-phase ripple ($\pm 2^\circ$ only), and high yield rate. The main limitation is that any variation in α is yet not explored in this work. Phase plot of one such FOE is shown in Fig. 2.36.

2.6.4 Fractance-Based Sensor

It will be worth to mention here that the FOE can be used for sensing purposes by correlating the phase angle with the concentration of components in the electrolyte.

In Sect. 2.6.2, it is mentioned that the phase angle of a FOE changes with the change of ionic concentration of the polarizing medium. This change of phase angle behavior leads to the concept of a new type of sensor, where the phase angle changes

with the process variables. Characteristics of a fractance sensor differ from a conventional “Impedance Sensor” in a way that the phase angle introduced by the sensor is measured (as in the present case); as a result the measuring circuit becomes simpler. A signal conditioning circuit, based on phase detection, can be developed which gives linear output with the phase angle change. Discussion on the sensing phenomenon based on the fractance properties is an active area of research and may help in our understanding of how to model time-varying order parameters.

2.7 Lesson Learned

This chapter introduced a few approaches to developing FO devices. The most important point is that we can use the ubiquity of the “universal dielectric response” to create such devices using different materials and methods, solid state and liquid based, all well modeled by the fractional calculus. In the next chapter, we see a sampling of the applications of such devices in actual physical demonstrations. In the following chapter, we make connections with living organic matter, looking at the kind of FO dynamics nature creates.

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