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Ferroelectric Fractional-Order Capacitors

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Abstract: Poly(vinylidene fluoride)-based polymers and their blends are used to fabricate electrostatic fractional-order capacitors. This simple but effective method allows us to precisely tune the constant phase angle of the resulting fractional-order capacitor by changing the blend composition. Additionally, we have derived an empirical relation between the ratio of the blend constituents and the constant phase angle to facilitate the design of a fractional order capacitor with a desired constant phase angle. The structural composition of the fabricated blends is investigated using Fourier transform infrared spectroscopy and X-ray diffraction techniques.

Introduction

Any electrical circuit element can be classified as passive or active. Inductors, resistors, and capacitors are passive circuit elements whose impedance Z can be expressed as

$$Z(\omega) = A(j\omega)^\alpha \quad (1)$$

where ω is the cyclic frequency, A is a constant coefficient, j is the unit imaginary number, and α represents the phase angle of Z . Three integer values of α , -1, 0, and 1, lead to the pure inductor, pure resistor, or pure capacitor, respectively. If α takes non-integer values, the element is called a fractional-order element, which can also be described as a constant phase

element with phase angle, $\phi = \pm \frac{\alpha\pi}{2}$ [1-3]. The concept of a

fractional-order element provides an additional degree of freedom in modeling, characterizing, and implementing novel circuit components in a wide spectrum of disciplines: viz. energy-storage and generation device modeling^[4-5], supercapacitor modeling^[6-7], sensor design^[8-9], corrosion modeling and characterization^[10-11], neural-system modeling^[12-14], bio-impedance characterization^[15-16], control-system design^[17-18], heat diffusion control^[19-20], electromagnetic system design^[21-22] and electronic circuit design^[23-28].

In particular, a fractional-order element with $0 < \alpha < 1$ (i.e. $-90^\circ > \phi > 0^\circ$) is called a fractional-order capacitor (FOC)^[1]. An FOC facilitates circuit configurations that would be impractical or impossible to implement with conventional capacitors. For example, replacing an integrator capacitor with an FOC in a temperature controller virtually eliminates the overshoot and windup effect due to the time spent in actuator saturation and drastically reduces the time required to stabilize the

temperature^[17]. It may be possible to design a circuit with the desired α between 0 and 1 by connecting pure capacitor and resistor, but it gives the desired α only at certain frequency. In general, it is highly desirable to have an FOC that is dielectric-based and printed-circuit-board (PCB) compatible^[1, 29], and that could operate over a wide frequency band with a precisely tunable and constant phase angle (CPA) and minimum phase-angle ripples.

Previously reported theoretical models and realized FOCs can be classified into five main categories: 1) liquid electrode-based (LEB) FOCs^[30-32], 2) geometry-related fractal (FT) FOCs^[33], 3) resistor-capacitor (RC) ladders FOCs^[34-35], 4) CMOS-based emulator FOCs^[36-37], and 5) composite FOCs^[1]. LEB FOCs are fabricated by dipping capacitive, parallel-plate electrodes coated with a porous film of polymers into an ionic medium. The operating principle of LEB FOCs is anomalous diffusion of ions through a porous surface at the electrode-electrolyte interface. The CPA depends on the depth of immersion of the electrodes into the ionic medium, the thickness of the polymer film, and the conductivity of the ionic medium^[30]. Their large dimensions, lack of portability, and the need for a liquid ionic medium prevent their integration in microelectronic circuits. On the other hand, FT FOCs can be easily integrated with microelectronic circuits since they use fractal structures created with metal traces on silicon wafers. The CPA of the resulting circuit depends on the fractal shape and how many times it is iterated^[33]. An RC ladder FOC is designed by using a network of different resistors and capacitors, which cumulatively represents non-integer-order transfer function, to approximate the term $(j\omega)^\alpha$ in Equation 1^[35]. One disadvantage of this approach is that an accurate approximation of the desired fractional behavior requires a very large number of resistors and capacitors. A CMOS-based emulator FOC uses a differentiator and a voltage-to-current converter to emulate the constant phase element and operational transconductance amplifier and grounded capacitors to tune the equivalent CPA. This operation requires external power. Furthermore, for the last three models discussed above, namely FT-FOCs, RC ladders FOCs, and CMOS-based emulator FOCs, the fractional-order behavior is generated by the resulting circuit impedance rather than by a physical capacitor. It is important to mention that none of the above approaches offer a dielectric-based FOC that is printed-circuit-board (PCB)-compatible, has a precisely tunable CPA over a wide band of frequency, and does not suffer from large variations in CPA within this band.

Our previous study proposed a dielectric-based, PCB-compatible, microscale electrostatic FOC with a wideband CPA. Fractional-order behavior is obtained through the use of a reduced graphene oxide (rGO) reinforced polymer composite^[1]. The conductive rGO sheets dispersed in the composite behave as a network of resistors and capacitors (as done in RC ladders FOCs), which leads to a tunable phase angle controlled by the volume ratio of the rGO in the composite. However, the difficulty in controlling this ratio limits to use of the resulting

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Figure 1. (Left panel) Schematic shows FOC with P(VDF)-based polymer dielectric. The next bottom image shows the P(VDF) molecular structure and arrows indicating polarization vectors. Arrows in the bottom image show the random nature of polarization in the polymer films. (Right panel) Permittivity (real and imaginary parts) and ϕ plotted against frequency. The inset in the graph shows ϕ against frequency in CPZ. The color bands show three regions in the frequency dispersion. The next bottom image shows dipole response to the frequency in the three regions. The bottom image shows the visualization of ϕ between current (I) and voltage (V) in the three regions.

FOC in commercial electronics. Additionally, this approach of designing and fabricating FOCs does not benefit from the fact that the polymer also contributes to the fractional-order behavior and can be used to control the CPA.

Polymers such as polyethyleneterephthalate, polyethylene, polystyrene, polytetrafluoroethylene, and polycarbonate are routinely used in the fabrication of capacitors in the electronic industry due to their electrical properties, ease of processing, and cost-effectiveness^[38]. Unfortunately, they cannot be used to fabricate FOCs because of their low dielectric constant (<4 at 100 Hz), low dissipation factor (<0.002 at 100 Hz), and low dielectric loss (<0.0072 at 100 Hz)^[39]. An FOC requires a polymer with high dielectric constant, dissipation factor, and dielectric loss to introduce the fractional-order behavior in the impedance $Z(\omega)$ in a given frequency band. One potential candidate with such electrical properties is ferroelectric poly(vinylidene fluoride) P(VDF): Its dielectric constant, dissipation factor and dielectric loss at 100 Hz are 11, 0.011, and 0.12, respectively^[39]. The control over polar and nonpolar molecular structures adds freedom in controlling the electrical properties of P(VDF)^[40]. For instance, adding trifluoroethylene (TrFE) molecules to P(VDF) yields a copolymer P(VDF-TrFE)

with improved dielectric constant, dissipation factor, and dielectric loss. Similarly, adding chlorofluoroethylene (CFE) molecules to P(VDF-TrFE) yields a terpolymer P(VDF-TrFE-CFE) with even further improved dielectric constant, dissipation factor, and dielectric loss^[41].

Several P(VDF)-based polymers are commercially (and easily) available in the market, which is a good reason to explore the

Figure 2. Illustration showing a PCB compatible FOC fabrication from the polymer. Photograph showing the final device.

possibility of using P(VDF)-based polymers in FOC fabrication^[42-44].

Additionally, from a physics perspective, one can expect that P(VDF)-based polymers are good candidates for FOC fabrication after a closer look at the behavior of the phase angle ϕ in P(VDF)-based polymers. This behavior can be tracked by studying the relaxation phenomenon due to polarization—such as orientational (or dipolar), ionic and interfacial polarization—in polymer dielectrics^[45]. For instance, ferroelectric polymers such as P(VDF), P(VDF-TrFE), P(VDF-TrFE-CFE) contain permanent dipole moments (Fig.1), and when a time-dependent electrical field is applied, the permanent (or induced) dipoles tend to align along the direction of the applied electric field. The frequency of the applied field determines how the dipoles behave: if the frequency is small, the dipoles are easily polarized, and the material behaves as close to the ideal capacitor ($\phi = -90^\circ$)^[46]. However, at higher frequencies, the dipoles do not have enough time to respond to the electrical field and therefore remain relaxed ($\phi = -90^\circ$)^[47-48]. At intermediate frequencies, friction accompanies the polarization, resulting in a conductive electrical current and a complex permittivity (with an imaginary part). Consequently, the phase angle satisfies $-90^\circ < \phi < 0$, which allows us to design FOC. This phenomenon is called orientation (or dipolar) relaxation.

Herein, we present, for the first time, a simple but effective approach to fabricating a PCB-compatible FOC using P(VDF)-based polymers. We use a solution-casting method to fabricate FOCs. This method allows us to easily blend different P(VDF)-based polymers providing a mechanism to tune the CPA. We should note here that our blend approach is distinct from the molecular modifications of P(VDF) by rigorous chemical synthesis methods^[49]. Polymer-based dielectrics, simple and low-cost fabrication processes, PCB compatibility, CPA that is precisely-tunable within a wide range of values, and a wideband of operation frequency make our device one of the top potential candidates for advanced electronics. It could pave the way for completely new applications.

Results and Discussion

A simple drop-casting method is used to form a dielectric layer of P(VDF)-based polymers and their blends. The FOC fabrication process is depicted in Figure 2. The final PCB-mountable chip contains nine individual capacitors. We measured the phase angle ϕ and the magnitude of the impedance Z of the individual capacitor.

Figure 3 plots the measured ϕ and the measured magnitude of Z versus frequency for P(VDF), P(VDF-CFE), and P(VDF-CFE-TrFE) (hereafter abbreviated as P, CP, and TP, respectively). The phase angle, ϕ increases with frequency, saturates in the MHz range and decreases in the high-frequency range (the high-frequency range is not covered completely in the figure). Compared to state of the art, we report broader, constant phase zone (CPZ) between 100 kHz and 10 MHz as shown in Fig.3a. In this range, the constant phase angle (CPA) is -83° , -79° , and -65° for P, CP, and TP, respectively. Figure 3b plots Z

versus frequency in logarithmic (log) scale. In this figure, the slope of the lines represents the exponent of the element constant α .

Using least-squares fit on the experimental data for Z between 100 kHz, and 10 MHz, the values of the line slopes/ α are found to be 0.90, 0.85 and 0.69, which is equivalent to a CPA of -81° , -77° , and -63° for P, CP, and TP, respectively. The values of α from Fig.3b confirm the measured CPA values given in Fig.3a. These results clearly demonstrate that a P(VDF)-based polymer can be used as a dielectric in an FOC. We further extend this concept to the P(VDF)-based polymer blends.

A simple mixing approach is used to formulate these blends (Table 1 for the ratio of constituents in each blend). Figure 4 shows the measured ϕ and the measured Z versus frequency for P-TP, P-CP, and CP-TP blends in the CPZ. The ϕ and Z measured for P, CP, and TP are also provided in the respective graphs for comparison. Note that the values of the CPA for the blends (Figures 4a, 4c, and 4e) is clearly different than the CPA of the P, CP, and TP. Overall, the CPA for the blends lies in between that of their two constituent polymers. For example, blend M3 contains 75 vol% of TP (with CPA measured as -65°) and 25 vol% of P (with CPA measured as -83°), resulting in a CPA of -70° . It is important to note that the CPA can be tuned by simply changing the blend composition. Figures 4b, 4d and 4f plot Z versus frequency in log scale for P-TP, P-CP, and CP-TP blends in the CPZ. Similar to Fig.3b, values of the line slopes / α are obtained (Table 1). These values of α confirm the measured CPA values in Figure 4a, 4c, and 4e (Table 1).

Figure 3. (a) The measured ϕ versus frequency for P, CP, and TP. The inset shows the histogram of phase angle deviation from CPA. (b) The measured Z versus frequency for P, CP, and TP. The slope of the lines represents the exponent of the element constant, α .

Figure 4. The measured ϕ versus frequency for (a) P, TP and their blends, (c) P, CP, and their blends, and (e) CP, TP, and their blends. The inset shows a histogram of phase angle deviation from CPA. The measured Z versus frequency in the CPZ for (b) P, TP, and their blends, (d) P, CP, and their blends, and (f) CP, TP, and their blends. The slope of the lines represents the exponent of the element constant, α

The availability of a wide range of values for CPAs is important in designing diverse FOCs [3]. Figure 4 shows that the CPA depends on the blend composition. An explicit expression of this dependence is useful in the design process. Figure 5 plots the CPA versus the blend composition. The P-TP blend shows an average of 4° of CPA change for every 25 vol% change of TP (Figure 5a). The P-CP blend shows an average of 1° CPA change for every 25 vol% change of CP (Figure 5b). The CP-TP blend shows an average of 3° CPA change for every 25 vol% change of CP (Figure 5c). Additionally, we derive an empirical equation between the CPA and the blend composition using least-squares fit on the data points. These equations, which are provided in Figures 4b, 4d, and 4f, could be used to design an FOC with the desired CPA by simply choosing the appropriate composition in the blend.

The change in CPA and Z with composition might imply that the electrical properties of P, TP and CP are modified in the blend. To further investigate this, we studied the structure of P-TP series blends using Fourier transform infrared spectroscopy (FTIR) and X-ray powder diffraction (XRD) techniques (Fig. 6). The FTIR spectra of P, TP, and its blends show that the blends

contain signature peaks of P and TP per their volume percentage in the blend (Figure 6a). No additional peak arises due to the blending of two polymers; rather, individual polymers retain their characteristic molecular structures. The observed peaks in P are at 835 cm^{-1} (CF stretching vibration of PVDF), 880 cm^{-1} (C–C–C asymmetrical stretching vibration), 1096 cm^{-1} , 1183 cm^{-1} (C–C bond of P(VDF)), and 1403 cm^{-1} (CH_2 wagging vibrations)^[50–52]. TP shows a higher intensity of peaks confirming, thus the higher freedom for molecular vibrations due to the presence of CFE monomers in P(VDF-TrFE-CFE), which gives chemical confinement to the VDF-TrFE sequence and meanwhile expands the lattice spacing to cause local distortion^[45, 53]. Figure 6b shows the normalized XRD spectra of P, TP, and its blends. P shows a single broad peak at 20.5° that corresponds to (200) and (110) crystal planes, whereas TP shows intense peaks at 18.2° followed by a 16.5° peak corresponding to (111) and (100) planes. The higher d spacing in TP is due to the incorporation of TrFE-CFE molecules in P(VDF) chains^[45, 53–55]. The XRD peaks follow the P to TP trend as per the TP contained in the blend. FTIR and XRD confirm that the blends contain P and TP in their pristine forms,

Figure 5. The CPA versus volume ratio of (a) TP over the total volume of the P-TP blend, (b) CP over the total volume of the P-CP blend, and (c) TP over the total volume of the CP-TP blend. Dotted lines in the figures represent the data fit used to develop the empirical relation (provided in the inset) between CPA and volume ratio.

such that without forming any additional complex molecular structure in the blend. Nonetheless, the change in the microstructures in the blend, which are responsible for the change in electrical properties such as polar conformation, could not be discarded^[56].

Table 2 compares main features of P(VDF)-based FOCs with the other type of FOCs. It is clearly evident that P(VDF) based FOCs are superior to other FOCs in terms of CPA, CPZ, phase error, and tunability of the CPA. Apart from that our approach is compatible with the present industrial capacitor manufacturing process.

Conclusions

P(VDF)-based polymers, and their blends are used to fabricate PCB-compatible FOCs. A simple solution-mixing approach to form the blends facilitates manipulation of the electrical properties. Our approach ultimately controls the CPA of the FOC for, 100 kHz to 10 MHz. Furthermore, we derive an empirical

Figure 6. (a) FTIR, and (b) normalized XRD spectra for P, TP, and P-TP blends. XRD spectra are normalized with the main Au (111) peak at 38.3°. The inset in (b) shows 2θ in 15° to 23° range.

relation between blend composition and CPA, which gives immense freedom to designing FOCs with desired CPAs. FTIR and XRD confirm that the blends contain P and TP in their pristine forms, such that without forming any additional complex molecular structure in the blend. Polymer-based dielectrics, simple fabrication processes, PCB compatibility, a wide range of CPAs, fine-tuning of CPAs, a wide range of operational frequency bands, and a low cost of fabrication make our device one of the top potential candidates for advanced electronics.

Experimental Section

Materials

Polymer (P), P(VDF) (CAS No. 24937-79-9) and solvent N, N-Dimethylformamide (DMF) (CAS No. 68-12-2) was purchased from Sigma Aldrich. P(VDF)-based polymers such as copolymer (CP), P(VDF-TrFE) (composition of 70/30 % mol) and terpolymer (TP), P(VDF-TrFE-CFE) (composition 60/30/10 % mol) were purchased from PiezoTech, France.

Device fabrication

Initially, 200 mg of P(VDF), P(VDF-TrFE) and P(VDF-TrFE-CFE) were dissolved in 2 ml DMF under constant stirring at room temperature to obtain 0.1 mg/ml solution of individual polymers. These solutions were further used to obtain various volume-ratio blends to fabricate the polymer films, as given in (Table 2). Au-deposited, 2 cm × 2 cm Si/SiO₂ wafers were used to fabricate the fractional-order capacitors (FOC) by drop casting the polymer solutions. A 10 nm Ti followed by 190 nm Au was deposited on Si/SiO₂ wafers via DC sputter to define one of the electrodes. The polymer solutions were drop-casted, leveled and dried for 12 hours at 80 °C under a vacuum. The other Au electrode of defined

Table 1. Polymer content in the blends. The exponent of the element constant, α obtained from the slope in the line equations given in Figures 4b, 4d, and 4f. A comparison of the CPAs derived from the line equations in Figure 4b, 4d, and 4f with experimentally obtained values in Figure 4a, 4c, and 4e. A

Sample name		P(VDF) Volume ratio (%)	P(VDF-TrFE) Volume ratio (%)	P(VDF-TrFE-CFE) Volume ratio (%)	Measured α	Measured CPA ϕ (degree)
P-TP	P	100%	-	-	0.9	-83.0
	M1	75%	-	25%	0.85	-76.3
	M2	50%	-	50%	0.84	-73.4
	M3	25%	-	75%	0.76	-70.5
	TP	-	-	100%	0.69	-65.0
P-CP	P	100%	-	-	0.9	-83.0
	M4	75%	25%	-	0.88	-78.0
	M5	50%	50%	-	0.87	-77.5
	M6	25%	75%	-	0.86	-77.0
	CP	-	100%	-	0.85	-79.0
CP-TP	CP	-	100%	-	0.9	-79.0
	M7	-	75%	25%	0.85	-76.3
	M8	-	50%	50%	0.84	-74.5
	M9	-	25%	75%	0.76	-71.0
	TP	-	-	100%	0.69	-65.0

Table 2. A comparison of the different type of FOCs with this work

FOC type	FOC origin	CPA, ϕ [degree]	CPZ [Hz]	Pros and Cons
LEB [Krishna et al.]	electro chemical	-30	$9 \times 10^3 - 3 \times 10^5$	large dimension, liquid electrolyte, not PCB compatible
FT [Haba et al.]	fractal structures	-36, -44, -45	$3 \times 10^3 - 10^6$	fractal shapes large variation in CPA equivalent capacitor, PCB compatible,
RC ladders [Roy et al.]	resistors and capacitors in ladders	-30, -45, -60	$0.1 - 10^3$	needs large components, equivalent capacitor, PCB compatible
CMOS-based emulator [Tsirimokou et al.]	operational transconductance amplifier and grounded capacitors	-20, -45, -75	$10^1 - 10^3$	active device, equivalent capacitor, PCB compatible
Composite [Elshurafa et al.]	RC-ladder equivalent capacitors due to fillers	-30, -35, -45, -55, -67	$5 \times 10^4 - 2 \times 10^6$	filler ratio in the composite controls the CPA, equivalent capacitor, PCB compatible,
Polymer dielectric (This work)	polymer dielectric blends	-65, -70, -71, -73, -75, -76, ... -83	$1 \times 10^5 - 1 \times 10^7$	blend composition dependent CPA, actual capacitor, PCB compatible,

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geometry was deposited in a similar fashion using a shadow mask. The electrode is defined in a 3 mm circular form, which gives us the freedom to fabricate nine individual FOCs on a 2 cm by 2 cm sample area. The sample was further flip-bonded on a PCB board (Fig.2). The PCB board was designed in such a way that an individual capacitor gives a separate connection for the electrical measurements

Device characterization

An Agilent 4294A precision impedance analyzer was used for the electrical measurements. Individual FOCs were characterized for the impedance, Z , and phase angle, ϕ , in the 50 kHz to 10 MHz frequency range at 0.5 V. Fourier-transform, infrared-attenuated, total-reflection (FTIR-ATR) spectroscopy (Thermo Scientific NICOLET iSIO) was used to characterize the dielectric films with a wave number range of 4000 cm^{-1} to 550 cm^{-1} and with a spectral resolution of 0.2 cm^{-1} . Crystallographic analysis of samples was performed using a powder X-ray diffractometer (XRD; Bruker D8 Advance) with $\text{Cu K}\alpha$ (1.5418 Å) radiation. The instrument was operated at 40 kV voltage and 40 mA current. The dielectric films were analyzed from 10 to 60 °C in increments of 0.01 and 0.1 s/step scan speed. All spectra were normalized for the Au (111) peak to obtain the relative crystallinity of the polymers in the samples. Experimental Details.

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Keywords: Fractional order capacitor • constant phase element • constant phase angle • constant phase zone • Poly(vinylidene fluoride) polymer blends

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ARTICLE

A constant phase angle tunable fractional-order capacitor is fabricated from PVDF based polymers and their blends. The orientation polarization of abundant dipoles in PVDF, PVDF-TrFE, and PVDF-TrFE-CFE are used to design capacitor with constant phase angles. By blending the polymers, constant phase angle level is successfully tuned.

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