Microscale Electrostatic Fractional Capacitors using Reduced Graphene Oxide Percolated Polymer Composites

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We show that graphene-percolated polymer composites exhibit electrostatic fractional capacitance response in the frequency range of 50kHz – 2MHz. In addition, it is shown that by varying the loading of graphene within the matrix from 2.5\% to 12\%, the phase can be controllably tuned from $-67^\circ$ to $-31^\circ$, respectively. The fractional capacitors proposed herein are easy to fabricate, and offer integration capability on electronic printed circuit boards.

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The resistor ($R$), the inductor ($L$), and the capacitor ($C$) are three passive circuit elements whose impedance is given by:

$$Z(s) = Ds^{-\alpha},$$

(1)

where $D$ is a coefficient, $s$ denotes that the impedance is being evaluated in the Laplace domain, and $\alpha$ is ideally $-1$, $0$, or $1$. The impedance is also often described in the frequency domain by substituting $j\omega$ for $s$, where $j$ is the complex number and $\omega$ is the radial frequency; the impedance then becomes:

$$Z(j\omega) = D(j\omega)^{-\alpha},$$

(2)

and the magnitude and phase of this impedance are respectively $|Z| = D/\omega$ and $\varphi = -\alpha\pi/2$. For $\alpha = -1$, $0$, and $1$, the phase is $\pi/2$ (i.e. inductor), $0$ (i.e. resistor), and $-\pi/2$ (i.e. capacitor) respectively, which conforms to our prior knowledge of basic electric circuits. From a practical point of view, however, the value of $\alpha$ is not always an integer but can rather lie anywhere between $-1 \leq \alpha \leq 1$. If a component possessed $\alpha = 0.4$ for example, then this element would be referred to as a fractional element$^1$, or an element with fractional impedance$^2$. Equation 2 also suggests that this phase is independent of $\omega$. As such, a fractional element exhibits a constant phase behavior and is often referred to in the literature as a constant phase element (CPE). For the purposes of this paper, we will restrict the analysis to the range $0 < \alpha < 1$, i.e. the study of CPE with a phase $-90 < \varphi < 0$, or fractional capacitors$^3$. The concept of a CPE is an important one, and its importance stems from being heavily adopted in modeling, characterizing, and understanding the behavior of many systems; a few examples include studying microbial growth$^4$, biological tissues$^5$, relaxor ceramics$^6$, electrochemical energy storage phenomena$^7,8$, supercapacitors$^9,10$, characterizing the impedance of fruits and vegetables$^{11}$, and design and analysis of control systems$^{12,13}$. In electronic circuitry, fractional order circuits offer unique
benefits by enabling broader impedance matching\textsuperscript{14,15} allowing flexibility in shaping the frequency response of electronic filters\textsuperscript{2,16,17}. Despite its importance and useful applications, limited realizations exist in the literature of fractional capacitors; these realizations are either electrochemical-based or fractal-tree based. The former is bulky and not practical for use in commercial electronic system applications\textsuperscript{1,18}, while the latter does not yield a stable constant phase response, but rather a rippling one\textsuperscript{19}. This paper, on the other hand, presents a realization of compact and stable electrostatic fractional capacitors, i.e. based on an actual dielectric material. This is accomplished by using percolative polymer composites in which the matrix is a dielectric polymer and the filler is graphene nanosheets.

Some classical electrical networks have been used to realize fractional impedances like for example ladder networks (with its known variations), or parallel combination of series-connected $Rs$ and $Cs$\textsuperscript{21}. To approximate a desired value of $\alpha$, one can utilize Carlson’s Method, Matsuda’s Method, or Oustaloup’s Method\textsuperscript{3,12}, and the possible set of component values that yield a specific value of $\alpha$ is not unique. Practically, and for some values of $\alpha$, the capacitance magnitudes required may be achievable but not practical (i.e. $C \sim 2$ farads and $R \sim 0.1$ ohms), the number of stages in the network may be large, or both\textsuperscript{2}. Hence, a method that can provide simultaneously a large number of capacitors and a large capacitance value for these capacitors was sought. After surveying the literature, it was found that percolation serves our purposes well; by populating a polymer (dielectric) matrix with conductive fillers, it is possible to create a very large number of capacitors within that polymer\textsuperscript{20}. Moreover, because the conductive fillers are going to be within a very close proximity to each other, large capacitances can be achieved.

An illustration of the proposed concept is schematically shown in Figure 1. As can be seen, the capacitor comprises two electrodes representing the capacitor terminals (in blue), a
polymer serving as the dielectric (in red), and graphene sheets that reside within the polymer matrix (in gray). Note that neither the thickness of the graphene sheets nor the separation between them will be equal due to the nature of the graphene preparation process which will be explained shortly. The presence of the conductive graphene sheets if properly dispersed can create several capacitors that are connected in series \((C_{g1}, C_{g2}, \ldots)\), as shown in Figure 1a, and can be equivalently represented as \(C_1\). Practically, a dielectric loss will exist, which can be modeled as a series resistor \((R_{series-loss})\). The latter situation, i.e. a capacitor connected in series with a resistor, can be used repetitively to describe the rest of the structure of the capacitor as shown in Figure 1b. Ultimately, the overall capacitor can be modeled as a network very similar to a parallel-combination of series-connected Rs and Cs, and the fractional impedance of the network can be varied by varying the graphene loading. Other circuit models and/or configurations could be used to describe the behavior of this composite\(^{22,23}\), and some can actually account for the randomness in the filler orientation using appropriate algorithms\(^{24}\).

FIG. 1. (a) A conceptual front view and a 3D schematic of the proposed fractional capacitor showing the top and bottom electrodes, the polymer matrix, and the graphene sheets; note the capacitances present between each successive graphene sheet \((C_{g1}, C_{g2}, \ldots)\); (b) the approximate equivalent network comprising an equivalent capacitance \((C_1, C_2, \ldots)\) in series with a resistor that models loss \((R_1, R_2, \ldots, R_n)\). Ultimately, an overall network would approximate the structure. Horizontal fringing capacitances are ignored assuming that the thickness of the graphene sheet is very small.
To fabricate the composites and devices, graphite oxide (GO) was first prepared from graphite using an improved Hummer’s method\textsuperscript{25} followed by hydrothermal reduction\textsuperscript{26}. Briefly, 37.5 ml of 0.5 mg/ml GO aqueous solution, prepared by probe ultrasonication (160 W) for 1 hour, was sealed in a 50 ml teflon-lined autoclave and maintained at 180°C for six hours; it was then cooled to room temperature. The resultant reduced graphene oxide (RGO) powder was filtered, rinsed by de-ionized water until reaching a pH of approximately 7, and dried at 60°C for further use. After preparing the RGO powder, it was weighed according to the desired filler loadings, suspended in 3 mL DMF, and dispersed via ultrasonication for one hour. Then, 300 mg of the polymer Poly (vinylidene fluoride-trifluoroethylene- chlorofluoroethylene), P(VDF-TrFE-CFE), was dissolved onto the suspensions under continuous stirring at 80°C. The graphene/polymer solutions were then ultrasonicated for two additional hours and solution-cast directly onto platinum-coated silicon substrates (to a thickness of \(~50\ \mu m\)), air-dried overnight, and finally dried at 70°C in a vacuum oven for two days. For dielectric characterization, circular Al electrodes possessing a thickness of 200 nm and a radius of 250 \(\mu\)m were deposited on the films by thermal evaporation using a shadow mask.

The structural properties of the RGO are shown in Figure 2, where Figure 2a shows a scanning electron microscopy (SEM) image of the acquired RGO where wrinkles, which are characteristic of reduced graphene oxide nanosheets, are clearly present. The wrinkled morphology prevents agglomeration of the sheets and helps form a more stable dispersion in dimethylformamide (DMF), which is important for processing homogenous films. As mentioned earlier, the thickness of the graphene sheets will not be equal given that solution-based conversion of graphite to RGO, inherently, offers very little control over the final RGO thickness.
in the composite. Explicitly, due to sonicatoin time and power, annealing temperature, casting method, restacking, etc, the RGO sheets will possess different thicknesses.

Figure 2b shows X-ray diffraction (XRD) pattern for graphite, GO, and RGO. The sharp (002) peak at 26.5° for graphite shifts to 9.9° after oxidation indicating the expansion of interlayer spacing from 3.37Å to 8.93Å. After hydrothermal treatment, the (002) peak of GO reduces to 3.63Å signifying the conversion of GO to RGO. An SEM of a cross section of the prepared composite is shown in Figure 3 where stacks of the multilayered RGO sheets are clearly sandwiched within the polymer medium. Further, intercalation of thinner polymer layers is also observable within these stacks. Such morphology is conducive to creating a very large number of microcapacitors\(^{20}\) as illustrated in the conceptual illustration in Figure 1. On the right of Figure 3, the actual fabricated miniature device is shown. Note that fabricating this device does not require complex lithographic processing, and allows for creating compact surface-mount versions that are fully integratable on printed circuit boards.

![Figure 2a](image1.png)

**FIG. 2.** (a) SEM image of the wrinkled RGO structures, which is characteristic of graphene oxide nanosheets, and (b) XRD analysis the on the graphene oxide samples showing conversion to reduced graphene oxide.
FIG. 3. Cross-sectional SEM of the prepared composite where the reduced graphene oxide (RGO) sheets are clearly visible.

The fabricated capacitors were characterized with an Agilent 4980A LCR meter, and the measurements were performed up to 2 MHz, which is the maximum operating frequency of the meter. In total, there were five fractional capacitors that were fabricated, in which the graphene weight loading varied from 2.5% up to 12%. The measurement results are shown in Figure 4. As can be seen, the phase is near constant and stable for a considerably large frequency band. Further, we notice that the different graphene loading present in each capacitor provided a capacitor possessing a unique capacitance value and a unique phase value. The phase angles obtained using our capacitors varied from approximately −67 degrees to −31 degrees, corresponding to alpha values of 0.73 to 0.33, respectively. For further verification, the measured magnitudes were also plotted versus frequency in log scale to extract the alpha values; as shown
in Figure 5, the lines are seen along with the equation of their linear fit where the slope of the line corresponds to the value of alpha. As expected, the values extracted from this plot are in agreement with the values provided from the measurement in Figure 4.

FIG. 4. The measured phase angle versus frequency from 50 kHz up to 1 MHz for different reduced graphene oxide (RGO) loadings.

FIG. 5. The impedance magnitude versus frequency in log scale. The slope in the line equations represents the alpha, and the results confirm the measurement provided in Figure 4. Explicitly, the values of alpha are approximately 0.38, 0.52, 0.62, 0.66, and 0.74.
The design proposed in this paper offers several advantages over previously reported fractional capacitors. The electrochemical based capacitor\textsuperscript{1} for example, relies on electrodes that are immersed in a PMMA-chloroform solution, and enables phase variation from $-12$ degrees to $-6$ degrees only by controlling the depth of the electrode immersion. Clearly, this method does not allow integration with current microelectronic systems or printed circuit boards. As for the fractional capacitor proposed herein, the phase range attainable is much larger and the design process allows creating a compact device. Because of the small overall size, integration with other microelectronic circuits/systems and printed circuit boards becomes viable. Further, the proposed capacitors are electrostatic capacitors rather than electrochemical capacitors, which eliminates the hazards associated with chemical spills and electrode corrosion. We also note that percolation allows flexibility in changing the value of the phase by changing the loading of the filler material.

As for the other reported fractional capacitor, which relies on transmission line theory\textsuperscript{19}, fractal geometries are created on a circuit board, and these geometries act as stubs or transmission lines, which in turn yield a specific impedance based on this specific geometry. The values of $\alpha$ that were achieved in that case were only in the range of $0.46-0.5$, and the phase angle is not constant but rather rippled by approximately $6^\circ$. Note also that it is important to distinguish between fractional capacitors and fractal capacitors\textsuperscript{27,28,29}, where the term fractal relates to geometry only.

V. CONCLUSION

Using graphene-percolated polymer composites, we have demonstrated electrostatic fractional capacitance behavior. Contrary to previous fractional capacitor realizations, which were either bulky or impractical to be used in real commercial applications, the proposed
compact capacitors possess dimensions in the micrometer range enabling integration possibility with printed circuit boards. Percolated composites offer the advantage of creating a very large number of microcapacitors using simple processing methods, and also allow control over the number/density of these microcapacitors by varying the loading of the filler, which changes the phase of the impedance. We speculate that this method will be effective in enabling the realization of surface-mount fractional devices that will ultimately be used in commercial electronics.

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References