Organic microcantilevers based on reduced graphene oxide composite for electrostrictive energy harvesting

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Abstract. Electrostrictive materials are promising for mechanical energy harvesting applications because of their high power density, low cost and scalability. In this paper, strain sensitive nanocomposite materials based on reduced graphene (rGO) and PDMS are used for energy harvesting; they are characterized by a high electrostrictive coefficient (2.4×10⁻¹⁵ m²/V²) and a giant dielectric constant (ranging from 100 to 1000 at 100 Hz, depending of rGO concentration). Using these nanocomposite materials, electrostrictive MEMS microgenerators are fabricated with an innovative low-cost and environment friendly process in an all-organic approach. The fabricated microcantilevers exhibit excellent mechano-electrical performances in dynamic mode. With an acceleration of 1 g of the microcantilever base using a shaker, experiment at the first resonant mode (≈ 16 Hz) generates an electrical power density of 8.15 μW/cm³.

1. Introduction

To develop autonomous and self-powered electronic devices, increasing attention is focused on harvesting energy from ambient energy sources such as light, heat, and mechanical vibrations [1]. Among them, vibration energy has been widely and intensively studied because it exists almost everywhere in our living environment. In most cases, it can be converted to electricity by three different electromechanical transduction schemes: electrostatic, electromagnetic, and piezoelectric [2]. Nanocomposite electrostrictive materials have been recently introduced since they are suitable for low frequency, high-strain excitation owing to their flexibility. Because of the capacitive nature of nanocomposite electrostrictive polymers, it is possible to directly apply electrostatic cycle for energy harvesting when the materials are submitted to strain [3]. In this paper, we use nanocomposite electrostrictive materials made of near-percolated networks of reduced graphene oxide (rGO) as conducting fillers dispersed in a polydimethylsiloxane (PDMS) matrix which is a soft and deformable dielectric elastomer [4]. A MEMS microgenerator integrating the reduced graphene oxide nanocomposite is fabricated with an innovative low-cost and environment friendly process in an all-organic approach. Then, this original nanocomposite integrated into the MEMS is characterized by measuring the variation of the capacity under mechanical strain. The microdevices are finally mounted in a primitive continuous conditioning circuit to evaluate the electrical energy which can be harvested with these strain-sensitive nanomaterials.

2. MEMS fabrication

The micromachining process used in this work does not require the high-cost semiconductor manufacturing machines used for silicon microfabrication and thus reduces drastically the fabrication cost of the MEMS devices. The electrostrictive organic microcantilevers are fabricated in an all-organic approach thanks to a low-cost method allowing a rapid production rate. The fabricated microdevice is a simple microcantilever composed of the electrostrictive material sandwiched between two electrodes and deposited on a flexible substrate. Simple rectangular microcantilevers without seismic mass are first fabricated and tested in static mode to evaluate the change in capacitance of the electrostrictive material. Then, trapezoidal shaped micro-cantilevers incorporating a seismic mass at
their free-end are of particular interest for dynamic mode tests for their relatively low resonant frequency and high uniform strain. The cross-section and top view of the fabricated organic microcantilevers are given in figure 1.a and 1b. The first step of fabrication consists in the screen-printing of PEDOT:PSS conductive polymer on top of a 50 µm thick PolyEthylene Naphthalate (PEN) sheet used as supporting layer. This printed PEDOT:PSS layer is afterwards cured for 20 min at 120 °C and serves as bottom electrode. Subsequently, the electrostrictive rGO/PDMS layer is spin-coated and soft baked at 200 °C for 3 h. The average thickness of the deposited layer is about 50 µm. An additional PEDOT:PSS top electrode is printed by doctor-blade through a shadow-mask for patterning. Finally, the microcantilever shape is simply defined by xurography using a vinyl cutting machine (Graphtec Craft ROBO Pro) [5]. Note that the mask used for the top electrode printing is also fabricated by xurography. The seismic mass is based on epoxy loaded with Ag particles for higher density. A paste (ESL1901-SD from ElectroScience Laboratory) is used for this purpose and is deposited with a syringe on the tip-end of the trapezoidal microcantilever; it is afterwards dried for 30 min at 120 °C. The deposited mass is measured with a microbalance (~ 86 mg). Photographs of the fabricated multilayered microstructures are given in figure 1.c. The final dimensions of the trapezoidal microcantilevers are 10 mm long, 5 mm large base width, 2 mm small base width and 100 µm thick.

Figure 1. (a) (b) Cross-section and top-view scheme of a rectangular electrostrictive microcantilever (c) Top-view photograph of a trapezoidal electrostrictive microcantilever.

3. Results and discussion

3.1. Static mode
In this part, the organic rectangular microcantilevers are tested in static mode to evaluate the change in capacitance of the electrostrictive materials. Following that, the gauge factor, which gives an image of the electromechanical sensitivity of the material relatively to the strain, is calculated. Concretely, the rectangular microcantilever is bent intermittently by applying a force at its end using a microprobe while monitoring the evolution of both the capacitance and the resistance with an impedance analyser. Several graphene oxide concentrations are tested while pure PDMS is used as reference. The electrostriction coefficient \( M \) of the electrostrictive material as well as the capacitive and resistive gauge factor \( (F_G^C, F_G^R) \) respectively) are defined by the following equations:

\[
F_G^C = \frac{\Delta C / C_0}{\Delta \varepsilon} \\
F_G^R = \frac{\Delta R / R}{\Delta \varepsilon} \\
M = \frac{\Delta e}{2E\Delta \varepsilon}
\]

With \( \varepsilon \) being the mean top surface strain, and \( C, R, e \) and \( E \) being the capacitance, resistance, permittivity and Young’s modulus of the electrostrictive material, respectively. As shown in figure 2, an increase of the capacitance as a function of strain is observed for the sample prepared with pure PDMS (geometric effect, with \( F_G^C = 1 \)) while a decrease is observed for the rGO/PDMS microstructures with a maximum relative variation of 4 % for a strain of 0.55 % for the material composed of 3.7 wt% of rGO. In addition, it is worth noting a difference in samples response depending on their rGO concentration, as observed in nanocomposite electromechanical gauges. These results confirm that changes of capacitance are dominated by the strain dependence of the permittivity of the nanocomposite and not to geometrical variations. The best gauge factor of the MEMS capacitive sensor is obtained for the 3.7 wt% sample with a value of (-) 6.7 at low strain level (\( \varepsilon < 0.6 \% \)). Using the equation 1, the static electrostriction coefficient \( M \) of the best sample of rGO/PDMS is \( 2.4 \times 10^{-15} \) m²/V², with dielectric constant of 80 for 3.7 wt% sample and \( E = 1 \) MPa.
3.2. Dynamic mode

Here, the trapezoidal microcantilevers are tested in dynamic mode to evaluate the variation of the admittance of the electrostrictive material at the mechanical resonant frequency of the microcantilevers. A shaker drives the devices into resonance for this purpose. The admittance of the device is measured by impedance analysis, with an applied support acceleration of 1 g. During the measurement, a constant external bias voltage (8 V) is injected to polarize the material.

![Figure 3](image)

Figure 3. Experimental measurement and analytical calculation of the conductance (a) and susceptance (b) of the electrostrictive MEMS as a function of the frequency for 1 g acceleration.

A resonance peak is observed electrically at ~16 Hz and demonstrates the existence of a phenomenon of electrostriction at the resonant frequency of the microcantilever (figure 3). Near the resonant frequency, the equivalent electrical circuit of the device is a ‘capacitance’ $C$ in parallel with a ‘resistance’ $R$, the expression of $C$ and $R$ being expressed as follows (note that $R$ and $C$ are not real numbers but complex numbers due to the resonance phenomenon):

$$ C = C_0 \left( 1 + \frac{K_C}{1 + \frac{f}{f_0} - \frac{f^2}{f_0^2}} a_s \right) $$

$$ R = R_0 \left( 1 + \frac{K_R}{1 + \frac{f}{f_0} - \frac{f^2}{f_0^2}} a_s \right) \quad (2) $$

Where $f_0$ is the resonant frequency, $Q$ the quality factor, $C_0$ and $R_0$ the capacitance and resistance at rest, $a_s$ the support acceleration and $K_C$ and $K_R$ two constants expressing the dependence of the capacitance and resistance to the applied acceleration (these constants depend on the electrostrictive material and on the cantilever geometry and size).

With these two equations (2) it is possible to express both the conductance and susceptance. A fit, presented in figure 3 with $K_C = 0.1 \text{ s}^2/\text{m}$ and $K_R = 0.001 \text{ s}^2/\text{m}$, gives a good adequation with measurement. The high $K_C$ value reflect the electrostrictive effect. As proved by the measurement, the fabricated microdevices exhibit excellent electromechanical performances in dynamic mode. Moreover, they are characterized by a low resonant frequency (~16 Hz) which can be advantageous for use in human motion energy harvesting for instance.
The electrostrictive device is then connected to a resistance load $R_{\text{load}}$ with an external voltage source (20V), to evaluate the harvested energy of the resonant MEMS devices. Figure 4.a shows the existence of an optimal resistance $R = 166 \, \text{k}\Omega$, defined as $R_{\text{load}}$ in parallel with $R_{\text{oscilloscope}}$ (1 M$\Omega$). For this value, a maximum harvested power of $\sim 59 \, \text{nW}$ at 1 g is observed. In addition, the output power increases with the amplitude of the displacement of the microstructure with the largest power measured at the resonance, as expected (figure 4.b). Last, a linear increase of the maximal output power at resonance with the support acceleration (figure 4.c) is observed. It should be noted that a significant part of the harvested power is lost because of the quite low resistance of the electrostrictive layer (few MHz).

Figure 4: Output power of the electrostrictive micro-generator (a) as function of the resistance load at the resonant frequency; (b) around the resonant frequency (c) as function of the support acceleration

4. Conclusion
The present work shows a new organic electrostrictive MEMS for energy harvesting. A novel nanocomposite electrostrictive material based on reduced graphene oxide and PDMS has been integrated in all organic MEMS microcantilevers characterized by a low resonant frequency and a high strain at the resonance. This original electrostrictive micro-generator is an excellent candidate for energy harvesting applications, providing a power density of 8.15 $\mu$W/cm$^3$ at 1 g and $f_0 \sim 17\text{Hz}$. This output power density is in the same order of magnitude as the one extracted from the standard P(VDF-TrFE-CFE) electrostrictive material [6]. The next step will be to use charge pump with flyback return circuit to manage the converted energy in an optimal way.

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6. References
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