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Stretchable Helical Architecture Inorganic-Organic Hetero Thermoelectric Generator

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Abstract

To achieve higher power output from a thermoelectric generator (TEG), one needs to maintain a larger temperature difference between hot and cold end. In that regard, a stretchable TEG can be interesting to adaptively control the temperature difference. Here we show, the development of simple yet versatile and highly stretchable thermoelectric generators (TEGs), by combining well-known inorganic thermoelectric materials Bismuth Telluride and Antimony Telluride (Bi_2Te_3 and Sb_2Te_3) with organic substrates (Off-Stoichiometry Thiol-Enes polymer platform – OSTE, polyimide or paper) and novel helical architecture (double-arm spirals) to achieve over 100% stretchability. First, an OSTE-based TEG design demonstrates higher open circuit voltage generation at 100% strain than at rest,

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although it exhibits high internal resistance and a relatively complex fabrication process. The second, simpler TEG design, achieves a significant resistance reduction and two different structural substrates (PI and paper) are compared. The paper-based TEG generates 17 nW ($\Delta T = 75^\circ\text{C}$) at 60% strain, which represents more than twice the power generation while at rest (zero strain). On the other hand, polyimide produces more conductive TE films and higher power (~ 35 nW at $\Delta T = 75^\circ\text{C}$) but due to its higher thermal conductivity, power does not increase at stretch. In conclusion, highly stretchable TEGs can lead to higher temperature gradients (thus higher power generation), given that thermal conductivity of the structural material is low enough. Furthermore, either horizontal or vertical displacement can be achieved with double-arm helical architecture, hence allowing to extend the device to any nearby and mobile heat sink for continuous, effectively higher power generation.

Graphical Abstract

Keywords: Stretchable Electronics, Thermoelectric Generator, Finite Element Analysis, Paper substrate, Polyimide.

1. Introduction

The ability of materials to flex and stretch has increasingly become a relevant characteristic and game-changer in rising, novel technologies, especially where higher architectural complexity and moving components are involved. The challenge remains in the inherent rigidity of current conventional electronics and their integration with soft, flexible and stretchable materials, such as elastomers [1,2]. Intelligent architectural designs can aid to reach this gap by transforming such rigid materials, commonly used to build high performing electronic devices such as silicon, into flexible and stretchable platforms [3–12]. Consequently, by incorporating an out-of-the-ordinary mechanical behavior with high performing electronics, new and exciting technologies can be implemented for a large range of application such as bio-integrated systems, robotics, wearable electronics, among many others [13–26]. On the other hand, optimization in several materials via nanotechnology, as well as recent studies of novel, promising and potentially flexible 2-dimensional (2D) materials [27], have shown an important leap forward [28–38]; an energy harvesting device capable of electricity generation out of a temperature gradient, with the potential of reusing the high amounts of wasted heat as an alternative, environmentally friendly energy source [39–41]. In order to be able to employ these generators to power up integrated electronic systems, such as the aforementioned applications, they also need to be highly compliant and capable of adapting to constantly reconfigurable components and shapes. For instance, if we consider that in many applications (such as robotics, cybernetics and bio-integrated electronics), a hotter and a colder section might be constantly moving with respect to each other, stretchability would play a fundamental role to make the most out of such situation. With this in mind, researchers have explored the use of intrinsically flexible organic-based as

well as composite materials based on the 2D and nano-engineered materials mentioned earlier. Several organic-based TEG demonstrations can be found in the literature, however, their thermoelectric properties are still well behind their inorganic counterparts [42,43].

On the other hand, 2D and nano-engineered materials exhibit great potential with promising performance. For instance, phosphorene and silicene nanoribbons have been predicted to display figures of merit as high as 6.4 and 3.5 respectively [35,36]. Nevertheless, in terms of practical devices very few demonstrations have been carried out, such as the recent work presented by Oh *et al.*, in which a highly foldable and stretchable TEG was fabricated based on chemically exfoliated transition metal dichalcogenide (TMDC) nanosheets. Such device was able to produce 38 nW of output power at ΔT of 60°C, however this power was degraded down to two orders of magnitude at a 50% strain [44]. An interesting alternative consists of using both organic and inorganic materials, in such a way that an organic substrate can act as structural material on top of which inorganic materials can be deposited as thin films and thus rely on their superior thermoelectric properties. Moreover, with the aim of reaching stretchability, structural modifications at the device architecture level can be employed as discussed earlier, such that the inorganic materials experience less deformation and hence the impact on the device's performance can be minimized [3]. Structures such as serpentines, fractals, and coils have been demonstrated before, where helical design are of special interest due to the very high strain ratios that can be achieved [4,6,8]. More importantly, as a result of the high elongation capacity, the TEG's cold side can move further from the heat source, thus causing a larger temperature difference along the TEG and leading to a higher power generation. With this objective in mind, we have developed helical architecture TEG to demonstrate the versatility of novel architectures along with organic structural materials and inorganic thermoelectric (TE) materials.

2. Material and Methods

In order to implement our structurally stretchable TEG, we have evaluated the use of different materials and used slightly different designs. The first design consisted of a series of five helicals per TEG's leg fabricated on an Off-Stoichiometry Thiol-Enes (OSTE) material, on top of which the thermoelectric materials and metallic contacts were sequentially deposited. As will be discussed later on, long thermo-pairs and a not so simple fabrication method led us to re-design the TEGs to consist of a single helical/spiral (therefore shorter thermo-pairs and thus lower resistance) and more common and practical materials (such paper or polyimide) and simpler methods. In the following subsections we will discuss the design and fabrication related to both designs.

2.1 Stretchable OSTE based TEG

For the first stretchable TEG implementation we selected a spiral-based design envisioned with OSTE as structural material. OSTE features tunable mechanical properties, the ability of direct surface modification and bonding (for wettability control and others), as well as it presents an improved adhesion of sputtered materials compared to other polymeric materials. Additionally, changing the off-stoichiometry ratio in OSTE-polymers, allows to accurately tune the mechanical properties of the cross-linked material from rigid to rubber-like (e.g. $10 \text{ MPa} < E < 2000 \text{ MPa}$) [45]. For example, an OSTE formulation comprised of Thiol-Enes monomers with large stoichiometric differences (50 to 90% excess) produces rubber-like materials because the molecules of monomer in excess, have fewer crosslinks to the network [46].

Similarly, rigid materials are produced with closer off-stoichiometric ratios. In our experiments, OSTE-Thiol (80) with a large, 80% excess of thiol-functionality was

used to fabricate the stretchable structures. These spiral structures can be formed using a double molding fabrication process, by first micro-machining the desired shape in Poly(methyl methacrylate) (PMMA) using a CO₂ laser cutter (Universal PLS6.7S), following the procedure described in another work [47]. Then the stiff spirals are glued to a flat PMMA slide to form a hard mold (Figure 1a). A second mold is then casted in PDMS to serve as a flexible mold for the OSTE-Thiol (80) (Figure 1b). The flexibility of the PDMS mold improves the demolding process, while its optical transparency allows for uniform UV exposure of desired OSTE-spirals (Figure 1c). After the OSTE mix is prepared and poured into the mold (Figure 1d), a UV crosslinker (CL1000) with a 365 nm and 4 W UV light source is used to crosslink the structures, exposing them to 300 mJ/cm² energy dose. Next, the spirals are carefully removed from the soft-mold (Figure 1e). Using a PVD magnetron sputtering (Angstrom Engineering, NEXDEP CS-05), ~1 μm of Bi₂Te₃ and Sb₂Te₃, well known TE materials, are sequentially deposited (Figure 1a) (5 mTorr, 10 sccm Ar, 20 rpm rotation, 30 W and 20°C) onto the OSTE spirals with aid of shadow masks (Figure 1f). Finally, metallic contacts are deposited to interconnect the TE pairs together in series and as contact pads (Sputtered Ti/Au - 20 nm/300 nm). Figure 1g illustrates the device with dimensions of about 4.5 cm long, 4.5 cm wide and 1 mm thick, while Figure 1h shows the device stretched to a 100% ratio.

2.2. Stretchable polyimide-based vs. paper-based TEGs

Given the large resistance obtained with the first design, we built a second stretchable TEG device with a single spiral per thermoelectric leg and due to the relative complexity of OSTE's manufacturing and patterning. In fact, because of the small dimensions and shape of the spirals, it was really challenging to complete the double molding process with repeatable

success. Moreover, the mechanical properties of the resulting OSTE polymer were not as appropriate as expected. Its rigidity was not allowing for a proper elastic behavior, and hence deformation was permanent after certain displacement. A softer mixture of the polymer, on the other hand, would not produce a firm enough material. Optimization of its mechanical properties to fit the required needs might be possible, although its fabrication would still be challenging. Therefore, we have chosen two alternative materials, with a much simpler and practical fabrication approach, to be the structural mechanical support, polyester-paper and polyimide (PI) sheet. The polyester-paper, also known as permanent-paper, is a commercially-available, tear-resistant and stiffer paper, which also exhibits higher temperature stability, water-resistance, and much smoother surface compared to conventional fiber-based papers. Spiral shapes were first patterned on both materials using a CO₂ laser cutter (Universal PLS6.7S, 75-watt laser, maximum scanning speed of 300 mm/s) [48]. To cut the 0.05 mm polyimide film, a laser power of 45 W and a 150 mm/s were used. Similarly, the permanent paper was cut using 20 W and 220 mm/s scanning speed (Figure 2a,b) [49]. Shadow masks were made out the same permanent paper and were also patterned with the laser cutter tool. The masks were used to sequentially deposit the TE materials in a PVD magnetron sputtering tools as described before but for twice the thickness ($\sim 2 \mu\text{m}$) (Figure 2c,d). Furthermore, both sides of the substrate materials were coated, two depositions for Bi₂Te₃, top and bottom and same for Sb₂Te₃, in an effort to reduce the final TEG's internal resistance. Figure 2e-h show the 5-pairs stretchable TEGs on PI (Figure 2e resting and 2f being stretched) and on polyester-paper (Figure 2g resting and 2h being stretched). The fabrication of the spirals was performed in a precise micromachining laser cutter with final dimensions of $\sim 9 \text{ mm} \times 50 \text{ mm}$ for both materials. Next, micro-machined shadow masks, also defined in the laser cutter tool, were placed on the spirals followed by the deposition of the TE materials in a consecutively fashion by shifting the mask after each deposition. As

mentioned earlier, both sides of the structural materials were coated, which means that four consecutive depositions were needed.

3. Results

3.1 Stretchable OSTE based TEG

A 6 1/2-digit Agilent Multimeter was used to measure resistance, voltage and current while the gradient of temperature was set with a hot plate and a digital thermometer. Figure 2a shows the open circuit voltage vs. temperature difference in the OSTE-based stretchable TEG, exhibiting a voltage rate of 0.26 mV/K. As anticipated, the results show that the TEG does exhibit higher voltage generation when stretched and for a large temperature range (0.36 m/K, near 1.5 times higher). Due to the ability of stretching, the cold side of the TEG can move further away from the heat source and therefore a larger temperature gradient will be available across the TEG leading to a higher voltage drop. However, the internal resistance of this considerably long design remains a significant limitation (1.59 M Ω), which is further worsen at stretching (1.92 M Ω at 100% strain), thus impacting the current and power that can be generated (16 nA and ~0.1 nW at $\Delta T = 50^\circ\text{C}$ and matching load, Figure 2b). In conclusion, the total length of the device and the stretching capability should be controlled such that the impact on the resistance is reduced, but we can still benefit from a higher temperature gradient at stretch. Finally, a potential solution to mitigate the resistance degradation, including post-stretching cycling, would be the encapsulation of the TE thin films so they can rest at the neutral mechanical plane of the structure while stretched and flexed, thus improving the mechanical reliability, integrity and overall robustness of the device [15,50–52].

3.2. Stretchable polyimide-based vs. paper-based TEGs

In an effort to find for a simpler fabrication approach and significantly reduce the internal resistance, hence improving performance, the second design was built to be shorter and with a second layer of TE materials. As a result, even though the surface of the chosen substrate materials (PI and paper) were not optimized for deposition, the measured final internal resistance was greatly improved compared with the more complex OSTE-based device. The measured internal resistance for the PI-based device was 17.8 k Ω (35.5 k Ω at 140% strain) and for the paper-based device was 42 k Ω (49.3 k Ω at 60% strain). Figure 4 shows the cross-section and top view of Bi₂Te₃ deposited on PI and polyester-paper. As can be observed, the thin film on the PI substrate exhibits a much smoother surface than the irregular surface of the polyester paper. Thus, lower resistance is achieved with PI, although it is also noticeably more affected by stretching. A closer look into the morphology of both materials can shed some light on the reason behind this behavior. The irregular surface of the polyester paper, contrary to the PI surface, might help to distribute the stress and therefore reduce the impact on the electric conductivity of the thin film on top [52].

3.2.1 Mechanical simulation

The mechanical validation of our devices was performed through a Finite Element Analysis (FEA) simulation. COMSOL Multiphysics software package was used to perform this analysis. First, to create the three dimensional models, we used the exact same layout designs used for the fabrication that were drawn in CorelDraw. The 2D drawing file was imported in COMSOL as a DFX file, using the CAD import module. The software allows us to extrude the structures to accurately have a digital representation of the final device. To ensure compliance in the structure, a union operation was performed to obtain a single object to be analyzed. Setting several appropriate boundary conditions are needed to achieve accurate

results. As a mechanical structure the device boundaries were set up in the Solid Mechanics module: all the faces of the 3D model are free to move except for the two end of the spirals and a prescribed displacement was set to deform the structure. A swept mesh technique was used to divide the structure. First, a Free Triangular mesh pattern was created on the top face of the structure and then the pattern is propagated to the bottom face. The simulation analysis was performed using a Stationary Study, accounting for large deformations using geometric nonlinearities. An auxiliary sweep aid the simulation to deform the structure from its initial position, to an extended final position of 1 cm (in steps of 1 mm for each solution). The studies were created to be able to compare results of devices computed using different materials. For the first study, permanent paper was set as the structural material. The second study was set to use PI for the structural material and Bi_2Te_3 (1 μm) was the top coating of the structures in both studies. The simulation was set to deform the structure from its initial position, to an extended final position of 1 cm ($\sim 100\%$ stretch ratio). This analysis was performed accounting for such large deformations using geometric nonlinearities. Unlike PI [53], the mechanical properties of the permanent paper were unknown. Therefore, a mechanical characterization was required. The elastic modulus of the permanent paper was obtained following a conventional tension test that was setup in a Tabletop Instron 5900-Series. The dimensions of the specimen under test, were obtained from the ASTM standard for thin plastic sheeting [54]. A 1 kN load cell and self-tightening roller grips were selected to perform the measurements. In this test, the specimens were loaded from zero until their ultimate tensile strength, at a 10 mm/min strain rate while recording their stress-strain curve. The results of five experiments, showed an ultimate tensile strength of 135 MPa and a Young's Modulus of 250 MPa for the permanent paper.

The results from the simulation are displayed in Figure 4, showing both stress and strain distribution over the volumes of the polyimide and paper-based spirals. From the

figures we can infer that the maximum stress and strain occurs at the extremes of the spirals, as it is expected, since they correspond to the places where the forces are applied.

The maximum stresses that the spirals reached when fully elongated (at 1 cm or 100%) were 50 MPa and 58 MPa for the PI and paper respectively. These values are safely far below the ultimate tensile strength values of 172 MPa for PI [53], and the obtained 135 MPa for the permanent paper. Likewise, strain only reaches a maximum of $\sim 3\%$ along the spiral in both cases, particularly exhibiting spikes at the Bi_2Te_3 film on places of maximum deformation. This could also contribute to the increment on the resistance of the film, which was observed as mentioned above.

3.2.2 Mechanical characterization

In order to further the mechanical characterization of our flexible devices, we have performed a simple cycling mechanical test with the specific aim of exploring the long term functionality of the devices. It has been studied before that thermoelectric (TE) materials are strongly dependent on applied mechanical stress, which can directly affect the band-gap and carrier transport characteristics of the material [55]. That is the reason why such tests are critical to have a better picture of the devices' functionality in the long term. Single spirals with each TE material and substrate (Bi_2Te_3 and Sb_2Te_3 on PI and Paper) were manually stretched to a ratio of around 30% each time for a total of 500 cycles. A 6 1/2-digit Agilent Multimeter was used to measure the electric resistance after specific amount of bending cycles up to 500. Figure 6a shows the change in electric resistance of both TE films on paper showing an almost linear but small increment reaching up to around twice the original electric resistance for both Sb_2Te_3 and Bi_2Te_3 after the 500 cycles. Figure 6b shows the change for the case of PI substrate with a very similar behavior and increments in electric

resistance up to ~2 times and ~2.5 times the original value for Sb_2Te_3 and Bi_2Te_3 respectively after the 500 cycles.

Once more, a close look at the morphology of the thin films in each substrate might shed some light on the reason behind the resistance increment after cycling. Figure 6c and 6d show the SEM images of Bi_2Te_3 , the most affected film, on both paper and PI after the cycling test. As evident from the images, fractures appeared on the films, explaining the increase in resistance. It is also clear that the smoother film on PI is visibly more affected, which is also apparent from the higher resistance increment shown in the graphs. Thin films might be expected to be affected by the continuous mechanically stressful conditions and as such, it is very important to design a good packaging scheme, to not only reduce the applied stress and strain, for example by locating the TE film at the neutral mechanical plane, but also to protect the films from diverse environmental conditions

3.2.3 Power production

When comparing the power generation between the resting and stretched states, we found dissimilar results for the paper and PI-based TEGs (Figure 7a and 7b respectively). Although the overall power generated by the paper-based TEG (~6.5 nW) was smaller than the PI-based (~35 nW), the former actually showed an increase in power generation at a stretched state (~17 nW, 2.6 times higher power), whereas the PI-based one displayed a slightly smaller power while stretched (~30 nW) with nearly half the current generated (from 3 μA to 1.7 μA). This can be explained due to the higher thermal conductivity of PI (Kapton film) compared with paper (polyester paper film), ~1.5 W/m·K [56] vs. ~0.15 W/m·K [57] respectively. Therefore, the benefit of a higher temperature gradient due to a higher distance from the heat source, gets reduced due to the higher thermal conductivity in the structural material and also the fact that the internal resistance gets affected when the spirals are

stretched. In the case of PI this deterioration was higher, as observed before, and thus the current, and also power, were impacted more. In the case of the paper-based TEG there was an increment of about 2.6 times higher power generated while stretched at 60%, (~3 mm longer distance from the heat source). This validates the advantage of length adaption in a TEG, which creates a higher temperature gradient. Furthermore, either horizontal or vertical displacement can be achieved with the spiral design, thus allowing to extend the device to any nearby mobile heat sink and further increase the gradient and power.

3.2.4 Thermal imaging

In order to visually perceive the effect of thermal conductivity of the structural material in the thermal distribution along the spiral, we have taken thermal images of the structures for both materials at resting state and while stretched. OptoTherm - InfraSight MI320 infrared camera with both microscopic and wide angle lenses was used to take thermal images of the TEGs (stretched and at rest) while one end was attached to a hot plate and the other was being stretched. Figure 8 shows the comparison between the materials and it is evident that the PI-based spiral exhibits a more uniform heat distribution along the spiral, hence decreasing the maximum temperature gradient, even if the spiral is at rest. The paper-based spiral, on the other hand, acts as a better thermal insulator and thus a higher temperature gradient can be achieved when the structure is stretched, which concurs with the observed power generation at stretch state.

4. Conclusions

The objective of this work was to demonstrate a simple yet versatile and highly stretchable TEG, by relying mechanically on organic common substrates (such as PI and paper) structured with novel designs (double-arm spirals), and thermoelectrically on well-known

inorganic TE materials (Bi_2Te_3 and Sb_2Te_3). We learned from our first OSTE-based TEG design, that the leg's length (and number of spirals) should be kept low enough such that total resistance can be reduced, but it remains stretchable enough so it can still benefit from a higher temperature gradient at stretch. Based on this idea, a second, simpler TEG design was implemented with a significant resistance reduction (2 orders of magnitude), ensured by minimizing the leg's length and by depositing thicker TE thin films on both sides of the substrate. Two different structural substrates (PI and paper) were compared with this second design. A stiffer, tearless, polyester paper or "permanent paper" was used due to its smoother surface compared with standard fiber-based papers. It generated up to 17 nW at $\Delta T=75^\circ\text{C}$ and 60% stretching, which represented more than twice the power generated while at rest (zero strain). On the other hand, the polyimide produced more conductive TE films and higher overall power (35 nW at $\Delta T=75^\circ\text{C}$) but due to its higher thermal conductivity, compared to the one of the paper, its power was actually reduced at stretch. We conclude that the ability of length adaptation (stretchability) in this TEG's designs, can lead to a higher temperature gradient, and thus higher power generation, given that the thermal conductivity of the structural material is low enough. Furthermore, either horizontal or vertical displacement can be achieved with our double-arm spiral designs, hence allowing to extend the device to any nearby and mobile heat sink for continuous, effectively higher power generation.

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Vitae

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Figures

Figure 1. 3D schematics describing the fabrication process of the 1st design; (a) a PMMA hard mold is prepared with a laser cutter, then (b) PDMS is applied on top to form (c) a soft mold. (d) Next the OSTE mix is prepared, applied to the PDMS mold and cured under UV light. (e) The OSTE-spirals are then carefully removed from the soft-mold and finally (f) the TE materials are deposited sequentially. (g) Digital photographs of un-stretched OSTE-based TEG with 3 TE-pairs and (c) stretched to a 100% strain. (Scale bars are 1 cm).

Figure 2. 3D schematics describing the fabrication process of the 2nd design; (a) first the substrate (PI or paper) is laser cut, then (b) the cut structure, consisting of a series of spiral pairs, is separated from the substrate, and finally (c) the first leg is coated with Bi_2Te_3 , followed by (d) Sb_2Te_3 deposition on the other leg. (Shadows masks are used to protect the other leg). (e) Digital photographs of un-stretched PI-based TEG with 5 TE-pairs and (f) stretched to a maximum 140% ratio. (g) Paper-based un-stretched TEG with 5 TE-pairs and (h) stretched to a ~150% ratio. (All scale bars are 1 cm).

Figure 3. (a) Comparison of open circuit voltage vs. ΔT between un-stretched and stretched OSTE-based TEG. (b) Generated power vs. generated current of OSTE-based TEG stretched to 100% strain at $\Delta T = 50^\circ\text{C}$.

Figure 4. SEM images of Bi_2Te_3 deposited onto (a) Polyimide (PI) and (b) Polyester paper including zoomed in inset.

Figure 5. Finite element simulation showing (a) stress and (b) strain distributions along the spiral for polyimide-based and paper-based spirals stretched to 1 cm. (Axis dimension in axes are [m])

Figure 6. Resistance change of each TE material after continuous mechanical cycles on single (a) paper spirals and (b) PI spirals.

Figure 7. (a) Comparison of generated power vs. generated current between un-stretched and stretched PI-based TEG. (b) Comparison of generated power vs. generated current between un-stretched and stretched Paper-based TEG.

Figure 8. Infrared (IR) thermal images showing the thermal distribution along (a) paper-based and (b) polyimide-based spirals at resting state and while stretched.

Research Highlights

- Stretchable TEGs, capable of temperature-gradient adjustment, are demonstrated.
- Higher power is observed at stretching if thermal conductivity of base material is low.
- Reducing legs' length helps to reduce internal resistance and increase performance.

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