P(VDF–TrFE) based spiral thermo-magneto-electric generators for harvesting low grade thermal energy

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Abstract. Low-grade thermal energy harvesting remains a challenge because of the low Carnot efficiency. Among various thermal energy harvesting mechanisms available for capturing low-grade heat (hot-side temperature less than 100°C), thermomagnetic effect has been found to be the most promising. Developing a high power density thermo-magneto-electric generator (TMEG) requires developments at both materials as well engineering levels. In this study, we propose a novel P(VDF–TrFE) based spiral-shaped cantilever beam for TMEG. Numerical simulations were performed using COMSOL Multiphysics and it was found that spiral beam experiences higher stresses, and consequently exhibits higher voltage output, as compared to rectangular cantilever beam for the same magnitude of tip deflection. Experiments revealed that the spiral structure of dimension 2.5 mm x 2.5 mm generates output voltage of about 4.0 mV, when oscillation displacement is 0.5 mm and oscillation frequency is 1 Hz. The output voltage increases with increase in tip deflection as well as oscillation frequency and a peak voltage of 25 mV is obtained at oscillation frequency of 10 Hz.

Keywords: thermal energy harvesting; thermomagnetic; PVDF; piezoelectric.

1. Introduction
Thermomagnetic effect (TME) is described as the effect of heat on the magnetic behaviour of a ferromagnet. When temperature rises above Curie temperature, the ferromagnet becomes paramagnet and loses magnetization. The magnetization can be restored by cooling the material below the Curie temperature. This phenomenon of temperature dependent ferromagnetic to paramagnetic phase transition and vice-versa can be used to create mechanical work by combining the magnetic forces with elastic forces. Various studies related to thermomagnetic (TM) devices have been conducted in the last few years, well-summarized in reviews [1, 2]. Thermo-magneto-electric generator (TMEG) broadly consists of a cantilever-mass system, where mass is a thermomagnetic material [3-6]. TMEG is placed between a heat sink and a heat source that contains a permanent magnet. The specific power output, $P_{out}$, of TMEG can be expressed as [2]:

$$P_{out} = \mu_0 f \oint H \, dM$$

(1)

where $\mu_0$ denotes permeability of free space, $f$ represents frequency of oscillation and $H$ is external magnetic field causing change in magnetization $dM$ of the material.
Most TMEGs proposed, thus far, utilize piezoelectric material to convert mechanical motion into electrical energy. Piezoelectric materials, such as barium titanate and lead zirconate titanate (PZT), induce electrical voltage in response to the mechanical strain (e.g. vibrations). Prior results have shown [3, 6] that TMEGs perform best when vibration frequency is in the range of 1.0 Hz-10 Hz and gap between hot and cold side is 1-3 mm. This information reveals a fundamental difference between the spring-mass systems used in TMEG versus the spring-mass system used in usual vibrational energy harvesters. Vibration energy harvesters normally operate at much higher frequency up to hundreds of Hz [7]; therefore, the spring-mass system designed for vibration energy harvesting cannot be directly used for thermal energy harvesting using TMEG.

In this study, we propose a novel spiral beam structure that generates higher stresses and output voltage as compared to the regular rectangular cantilever beam of similar dimensions for same magnitude of tip deflection. We have considered poly[(vinylidenefluoride-co-trifluoroethylene], P(VDF-TrFE) as piezoelectric layer since its provide more flexibility as compared to ceramic materials such as PZT and it has high piezoelectric coefficient among the polymeric systems.

2. Spiral design
Thermal-to-magnetic energy conversion depends on TM properties of the working materials. Various TM materials have been proposed in literature, but gadolinium remains the most widely used material in TMEGs [1, 2]. Therefore, in this study, we have used gadolinium as the working material. Magnetic-to-vibrational energy conversion depends upon the strength of the permanent magnet. We have used NdFeB, Grade N42, as permanent magnet (maximum residual flux density 13,200 Gauss and surface field: 5248 Gauss). Our focus was to maximize the vibration to strain and strain to electrical energy conversion. This has been achieved in two steps. First, we developed a novel spiral beam design that produces larger stress as compared to the usual rectangular cantilever beams. Secondly, in order to obtain large strain to electrical energy conversion, we optimized PVDF-TrFE performance through microstructural design.

Fig. 1 depicts the schematic of the proposed spiral design. The spiral structure increases the effective length of the cantilever beam, leading to larger deflection under similar loading conditions. In addition, spiral structure experiences both torsional as well as bending moments. Lastly, because of the tapering, the stresses are better distributed in spiral beam than in the rectangular beam. Fig. 2(a) shows a rectangular cantilever beam of dimension: 2.8 mm x 0.45 mm x 0.1 mm while Fig. 2(b) shows the spiral cantilever beam.

Figure 1. The architecture of the proposed spiral cantilever beam for TMEG.

Figure 2. Performance comparison of a rectangular cantilever beam versus spiral cantilever beam, when oscillation frequency is 1 Hz and tip deflection is 0.25 mm. (a) Geometry of the rectangular cantilever, having same length, width, and thickness as spiral cantilever beam. (b) Geometry of the spiral cantilever, having titanium as the base material and PVDF as the piezoelectric material. (c) Stress contour on the top surface of the base material in the rectangular beam. (d) Stress contour on the top surface of the base material in the spiral beam.

Figure 3. Voltage output versus tip deflection across load resistance of RL=10 MΩ and oscillation frequency of 1 Hz.

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the rectangular beam is almost same as the length of the spiral beam. Width of the rectangular beam is average of the spiral beam’s width at the two extreme ends. Thickness of both the beams is equal. Both the structures contain PVDF layer of thickness 20 μm. The properties of PVDF in modeling were taken to be $d_{31}=13.58$ pC/N and $d_{33}=33.8$ pC/N (available in COMSOL material library). We have considered stainless steel (SST) as the base material. Fig. 2(c)-(d) depict the stress contour on top surface of the base material for these two structures. The results were obtained numerically using commercial code, COMSOL multi-physics. Simulations were run for the tip deflection of 0.25 mm. It can be noted that the maximum von-Mises stress in the spiral structure is about 1.8 times higher than that of the rectangular beam. In addition, stresses can be seen to be more uniformly distributed in the spiral beam in comparison to that in the rectangular beam. Fig. 3 shows the output voltage of the spiral beam and rectangular beam at various tip deflection across load resistance of $R_L=10$ MΩ and oscillation frequency of $f=1$ Hz. As expected, voltage output of the spiral structure can be seen to be higher than that of the rectangular structure.

3. Fabrication

3.1. Arrays of spiral cantilever beams

In order to fabricate arrays of spiral cantilever beams, laser cutting was performed on a stainless steel (SST) sheet of dimension: 25 mm x 25 mm x 100 μm. The advantages of laser cutting over photolithography include ease of fabrication, low contamination and superior dimensional accuracy. Fig. 4 shows the topology of the spiral arrays obtained on 25 mm x 25 mm sheet.

3.2. Synthesis of the piezoelectric polymer

P(VDF-TrFE) powder (100 mg) was mixed with 1 ml of MEK:DMSO (2:1) co-solvent and the solution was stirred at 60°C for 7 hours. This resulted in a transparent P(VDF-TrFE) solution. In order to make a metal-piezoelectric-metal (M-P-M) structure, Al bottom electrode (thickness ~ 80 nm) was deposited on stainless steel substrate and subsequently, P(VDF-TrFE) solution was drop-casted on it. The films were dried at 70°C for 30 minutes, allowing slow evaporation of the solvent. In order to enhance crystallinity of the films, following conditions were experimented: (a) Annealing only: At 140°C for 1 hour followed by ice quenching [8] [$T_a$ (100°C) < annealing temperature < melting point ($T_m=150°C$)], (b) Annealing and poling simultaneously: Poling at 1 MV/cm at 140°C/1 hour and (c) Annealing followed by poling: Annealing at 140°C/1 hour followed by ice quenching then poling at 1 MV/cm. Crystallinity of the films were examined by X-ray diffraction technique. XRD patterns of PVDF-TrFE films are shown in Fig. 5 (a). The characteristic diffraction peaks (110) and (200) at 20 ~20° confirm the β phase of the films. Crystallinity of the films are greater when poling and annealing both have been performed. Similarly, it is evident from the SEM images that the size of needle-like grains are increased when poling has been done either after or simultaneously with annealing (Fig. 5(b-d)). Both XRD and SEM data suggest the beneficial role of post drying process i.e., annealing and poling.
of the polymer films. The P–E hysteresis loops of various P(VDF-TrFE) films are shown in Fig. 6. The remanent polarization (Pr) values increased from 4 to 9 μC/cm² in dried only and poled with annealing devices respectively. The polarization trends also confirm that higher crystallinity of the β phase should exhibit a higher Pr. Both type of poled devices show similar Pr and coercive field as suggested by XRD and SEM study. Among the three configurations, in this work, we choose to use the polymer films annealed at 140°C/1 hour followed by poling.

3.3 Fabricating the energy harvesting structure with P(VDF-TrFE)

The process of fabricating the final structure with P(VDF-TrFE) is shown in Fig. 7(a). In order to fabricate M-P-M device structure with P(VDF-TrFE) films, P(VDF-TrFE) was drop casted on spiral shaped SST substrates (as shown in Fig. 7(b)) followed by annealing and poling of the polymer films. In order to complete the M-P-M structure, we selected Al as top electrode. At first, Al top electrode (80 nm) was deposited by sputtering (Fig. 7(c)). A PVDF cantilever beam was fabricated by exposing laser from the backside of the substrate. The substrate, therefore, acted as a mask and the laser power was maintained such that it ablated P(VDF-TrFE)/Al layer but did not etch SS. As shown in the Figure 7(d), the P(VDF-TrFE) film was engraved by the laser successfully and we obtained a precise spiral shaped P(VDF-TrFE)/Al cantilever.

4. Experimentation

Fig. 8 shows the set-up used to measure the vibrational and electrical characteristics of the spiral structure. As shown in the figure, a magnetic shaft was placed on the shaker, allowing it to vibrate at various frequencies. A tiny round piece (diameter ~1 mm) of gadolinium (Gd) was attached on top of the spiral beam. By exposing to vibration, the magnetic shaft moved back and forth, causing oscillation in the spiral beam, analogous to the motion of the beam in TMEG. The vibration of the beam caused a piezoelectric potential. A laser beam was incident on the spiral to monitor its displacement and velocity. Fig. 9(a) shows the displacement of the tip of the spiral beam when oscillation frequency was fixed at 1 Hz. It can be noted that displacement varies from 0.4 mm in the negative
direction to 1.5 mm in the positive direction. Fig. 9(b) shows the open circuit output voltage obtained from one spiral. The voltage can be seen to vary between -8 mV to 4 mV. Fig. 9(c)-(d) shows tip displacement and induced voltage at 3 Hz. Likewise, Fig. 9(e)-(f) shows tip displacement and induced voltage at 10 Hz. It can be noted that increasing frequency decreases tip deflection and increases the voltage output. A single spiral produces maximum voltage of about -10 mV at 3 Hz and -25 mV at 10 Hz.

5. Conclusions
Spiral beam experiences about two times higher stresses than the rectangular beam for the same amount of tip deflection. Consequently, the voltage output from the PVDF layer deposited on a stainless steel substrate was found to be higher for spiral beam than the rectangular beam. Experiments were conducted using vibrometer to replicate the oscillation of a 2.5 mm x 2.5 mm spiral beam inside a TMEG. It was found that output voltage varies between -8 mV to 4 mV at 1 Hz. The peak voltage output increases to -10 mV at 3 Hz and -25 mV at 10 Hz.

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