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Modeling and Simulation for PVDF-based Pyroelectric Energy Harvester

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Abstract

Energy harvesting technology allows the capturing of unused ambient energy such as solar, wind, thermal, strain and kinetic, energy of gas and liquid flows which is then converted into another form of usable energy. This paper focuses on the thermal-electrical energy harvesting based on pyroelectric effect. Pyroelectric materials generate a voltage, when subjected temperature variation. The pyroelectric polyvinylidene fluoride (PVDF) films were fabricated and characterized for pyroelectric and dielectric parameters. Using the foregoing parameters, the energy-harvesting capacity has been theoretically explored by capturing thermal energy available in the environment of Huntsville (pavement), Saudi Arabia (ambient) and MARS (ambient). The predicted maximum cumulative voltage by the end of a 300 hours cycle is approximately 0.13, 0.7 and 7.7 volts for Huntsville and Saudi Arabia and MARS, respectively for the PVDF based 10 cm^2 pyro-elements. The results indicate that the electrical energy harvesting via pyroelectricity holds promise for powering autonomous low-duty electric devices. Furthermore, the mathematical modeling and numerical simulations can be helpful in designing of pyroelectric micro-power generators.

Key words: Energy Harvester; Pyroelectric micro-power generator; Polyvinylidene fluoride (PVDF)

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INTRODUCTION

Energy harvesting, also referred to as energy scavenging or energy extraction allows the capturing of unused ambient energy such as vibration, strain, light, temperature variations, gaseous and liquid flows, thereby converting into usable electrical energy. Energy harvesting is a perfect match for low-power portable microelectronics and other wireless devices which otherwise depend on a battery power. It can provide sustained, cost-effective and environmental friendlier solutions for a variety of low-power applications. In recent past, these unconventional methods for waste energy harvesting and scavenging have been explored to provide sustained power to micro- and nano-devices (Priya and Inman, 2009; Roundy *et al.,* 2004; Beeby and White 2010). The efforts have been made to recover electric power from mechanical vibrations (Priya and Inman, 2009; Roundy *et al.,* 2004; Beeby and White 2010; Kim *et al.,* 2009), light (Wenham *et al.,* 2009), spatial and temporal temperature variations (Xie *et al.,* 2009; Buchanan and Huang 1999). The conversion of thermal energy has gained more attention in the recent years. Thermal energy is available almost everywhere in various forms; thermoelectric and pyroelectric are the universal techniques used for thermal energy harvesting. Pyroelectric energy conversion offers a novel and direct solution to convert waste heat into electricity; contrary to the thermoelectric generator, pyroelectric materials do not need a temperature gradient, but temperature fluctuations, thus the application targets are quite different.

Pyroelectricity is the ability of a certain class of materials to generate an electric charge when heated or cooled (Batra *et al.,* 2008). The temperature variations slightly modify the position of the atoms within the crystal structure such that the polarization changes. The change in polarization creates a voltage across the material, thus can be used as a thermal-electric converter. The pyroelectric materials basically, convert most of electromagnetic radiations spectrum (ultraviolet, infrared, microwave, X-rays, terahertz) energy into electrical energy. Thus, pyroelectric elements are mainly used in uncooled wide-band infrared detectors included in numerous scientific and medical instruments.

In the recent past, researchers have started exploring the pyroelectrics and piezoelectrics as possible energy harvesters on both theoretical and experimental arenas (Batra *et al.,* 2012; Batra *et al.,* 2011; Sebald *et al.,* 2008; Cuadrasa *et al.,* 2010; Khodayari *et al.,* 2009; Zhu *et al.,* 2009; Navid *et al.,* 2009; Buchanan and Huang 1999). Most of the innovative research deals with harvesting from vibrations while a very few deal with harvesting via pyroelectricity. The performance of pyroelectric materials depends strongly on their thermophysical and electrical properties. There are only a few high performance pyroelectrics known so far suitable for infrared detecting and imaging devices**,** both in single- and poly-crystalline and composite forms: triglycine sulfate (TGS) family, lithium tantalate (LT), barium strontium titanate (BST), polyvinylidene fluoride (PVDF) and its co-polymers, modified lead zirconate tantalate (PZT), poly (vinylidene fluoride-trifluoroethylene) (P(VDF-TrFE)):PZT and others (Batra *et al.,* 2008) investigated energy harvesting from high temperature increase (45ºC to 140ºC in ~10 seconds: 15ºC/s heating rate), i.e., pyroelectric effect using PZT sample via simple modeling and found that measured and predicted results showed good agreement with peak power density of 0.23 micro-W/cm. It is worth mentioning that such a heating rate (15ºC/s) sources are generally not available. Khodayari *et al.* (2009) investigated nonlinear energy harvesting from relaxor single crystals. Navid *et al.* (2010) worked on purified and porous poly (vinylidene fluoride-trifluoroethylene) (P(VDF-TrFE)) in order to improve the figure-of-merit for energy harvesting ($F_E = p^2/\varepsilon'$). For the commercial, purified, and porous films, F_E was 7.93, 10.17 and 5.24 J/m^3/K^2, respectively. Wen and Chung (2003) investigated the pyroelectric behavior of cement-based materials and displayed that the steel/carbon-nanofibers increase the dielectric properties of cement composites. Several researchers including authors of this paper have investigated pyroelectric, piezoelectric, and other physical properties of polymer-composites (Guggilla *et al.,2009*). In 2009, Batra *et al.* investigated pyroelectric polymer composites: silver nano-particles embedded in P(VDF-TrFE):LT and indicated an enhancement in pyroelectric performance as compared with virgin P(VDF-TrFE):LT composites. The PVDF polymer films, to the best of author's knowledge, have not been investigated for energy harvesting via thermal energy available in the environment. Further, it is worthwhile to investigate PVDF for energy harvesting applications considering that it has many unique properties such as lightweight, first-rate mechanical strength, formability and robustness. It can also withstand exposure to harsh thermal and chemical conditions, and is unaffected by long-term exposure to ultraviolet radiations. Thus, it was thought useful to investigate PVDF films via modeling to predict its performance in energy harvesting. Its use in electric generators can ensure sustained and uninterrupted power supply to wireless micro-sensors, pavement-management-system hardware, and other engineering applications; thereby providing a contribution to energy conservation.

In the present paper, the electrical and pyroelectric properties of PVDF films fabricated by solution casting technique have been investigated. An appropriate analytical model utilizing foregoing parameters was employed to predict cumulative voltage and electrical energy generated and stored in a capacitor over extended period. The available and extrapolated temperature data for Saudi Arabia, Huntsville, Alabama and planet MARS are incorporated as heat-energy source. Apart from previously stated properties of PVDF, it is also known for its operational versatility in both hot and very cold climatic conditions as well viz., hot and ~~very~~ cold climate of Saudi Arabia and MARS respectively. It is worth mentioning, besides other important properties of the PVDF film mentioned above, it has been chosen because of its operational versatility in both hot and very cold climatic conditions i.e. hot and very cold climate of Saudi Arabia and MARS respectively.

1. EXPERIMENT

1.1 Materials Selection

A brief description of the characteristics of pyroelectric materials is worth presenting for lucidity:

All crystalline materials are categorized into one of the possible 32 different classes, i.e., points groups divided by using the symmetry elements: (i) center of symmetry, (ii) axes of rotation, (iii) mirror planes, and (iv) several combinations of them. The 32 point groups are subdivisions of seven basic crystal systems that are, in order of ascending symmetry, triclinic, monoclinic, orthorhombic, tetragonal, rhombohedral (trigonal), hexagonal and cubic. Eleven of these forms are centrosymmetric. Of the remaining 21 non-centrosymmetric groups, 20 are piezoelectrics, meaning that these materials produce an electric surface charge in response to applied mechanical stress. Of the 20 piezoelectric crystal classes, 10 crystals have a permanent electric dipole, and equilibrium of the electrostatic potential caused by this dipole is distorted by mechanical stress (piezoelectricity) or temperature change (pyroelectricity). Certain pyroelectrics can be further divided into ferroelectric materials. The ferroelectric group is a subgroup of the spontaneously polarized pyroelectric crystals. On one hand, the polarization of ferroelectric is similar to the polarization of pyroelectric. However, there is a difference between the two polarizations in that the ferroelectric polarization is reversible by an external applied electric field. Therefore, materials that can be defined as ferroelectrics must have two characteristics: (1) the presence of spontaneous polarization and (2) reversibility of the polarization under an electric field. A ferroelectric material is therefore both pyroelectric and piezoelectric, and these materials are termed as *smart materials*. There are also organic ferroelectric as well as pyroelectric materials available, such as, Poly vinylidene fluoride ((CH_2-CF_2)n; PVDF) and its co-polymer with trifluoroethylene P(VDF-TrFE) (70/30). PVDF and the P(VDF-TrFE) copolymer consists of a crystalline and an amorphous fraction. The PVDF shows significant pyroelectric and piezoelectric behavior in the temperature range from -40 ºC to +100 ºC.

1.2 Fabrication of PVDF Films

The first step in the preparation of PVDF solution (Pmix) was to dissolve a suitable amount of PVDF in methyl-ethyl-ketone (MEK) at 60 ºC (Batra *et al.,* 2008). The obtained PMix solution was kept in a suitable glass container for the solvent to evaporate over night. The films were then annealed for 2-3 hours in the air, at 110 ºC for the present case. A full-face silver electrode was deposited on the film (front and back faces); then the film was cut into 5 mm x 5 mm for testing. The electrode samples were poled at 60 ^{0}C using 5 kV/cm for 2 hours. After the poling process, the samples were short circuited and annealed at 50 ^{0}C for 2 hours.

1.3 Pyroelectric Coefficient (*p*) and Dielectric Constant (ε') Measurements

The parameters required for energy harvesting modeling included the dielectric constant (ε') and pyroelectric coefficient (p), which were calculated. A real part (ε') of the dielectric constant was determined as:

$$\varepsilon' = \frac{C_p d}{\varepsilon_0 A}, \tag{1}$$

where C_p is the parallel capacitance of the sample at signal frequency of 1 kHz, A is the electrode area (identical areas for the opposite electrodes were used in each sample), d is the thickness of the sample, $\varepsilon_0 = 8.854\times10^{-12}$ F/m is the permittivity of vacuum. To record the relative pyroelectric current $I_{p,}$ the direct method of measurement is used (Batra *et al.,* 2008). The pyroelectric current I_p was measured at various temperatures at a constant heating rate, and the pyroelectric coefficient (p) was calculated using the relationship:

$$p = \left(\frac{I_p}{A}\right) / \left(\frac{dT}{dt}\right), \tag{2}$$

where dT/dt is the rate of change of temperature, which was kept constant throughout the measurement. The change in pyroelectric coefficient indicates the change in dipole orientation inside the material; higher the coefficient, the better the material is for converting temperature change into electrical charge. The additional charge generated via heating or cooling within a temperature change, *dT,* can be calculated as:

$$dQ = dI_P dt = pA\frac{dT}{dt}dt = pAdT \tag{3}$$

1.4 Energy Harvesting Capacity of Materials Investigated Through Modeling and Numerical Simulation

The pyroelectric electric generator is modeled as a current source with a capacitor and a resistor in parallel (Batra *et al.* 2008). The current is generated within the pyroelectric element with the change in temperature. Figure 1 shows the circuit of pyroelectric element. Eq. (2) indicates that the pyroelectric current is directly proportional to the rate of change of temperature. However, one problem with this behavior is that the current will flow in opposite direction when the rate changes from positive to negative or from negative to positive. In other words, a heating followed by cooling or cooling followed by heating will produce charge accumulation in different direction. However, to charge an external capacitor, it is essential that the capacitor be charged continuously. To mitigate this problem, a full bridge diode rectifier circuit, as shown in Figure 2, can be used. The pyroelectric source is connected to an external capacitor (C_E) and an external resistor (R_E). There are two pairs of diodes; one pair is used for each direction of charge flow. Diodes (D_1-D_2) are used when charge is flowing in one direction and diodes (D_3-D_4) are used when the charges flow in the other direction. At each time only the forward biased diodes work, the other two pairs blocks current flow under reverse biased condition. As it can be seen, in both cases, the external capacitor (C_E) is charged via charge flows in one direction and that causes the voltage to increase across the external storage capacitor.

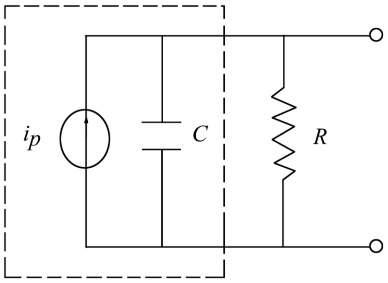


Figure 1
Pyroelctric Crcuit Diagram i_p is the generated current, C and R are the capacitance and the resistance of pyroelectric cell, respectively

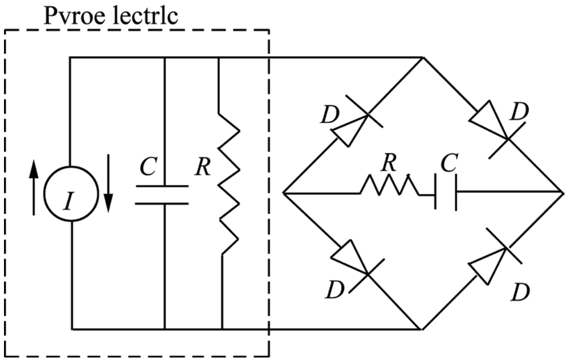


Figure 2
Pyroelectric Cell Current Generator with Full-wave Bridge Rectifier Circuit for Charge Storage in C_E Using Diodes D_1-D_2 and D_3-D_4

The charge flow in the two-capacitor system can be modeled as follows (Cuadrasa *et al.*, 2010): When the new charge is accumulated, it is distributed in both capacitors and the charge balance equation can be written as:

$$\Delta Q_n = Q_{E,n} - Q_{E,n-1} + Q_{P,n} \pm Q_{P,n-1} \tag{4}$$

$$\begin{aligned} Q_{P,n} &= V_n C_P \\ Q_{P,n-1} &= V_{n-1} C_P \\ Q_{E,n} &= V_n C_E \\ Q_{E,n-1} &= V_{n-1} C_E \end{aligned} \tag{5}$$

Where C_p and C_E are pyroelectric cell capacitance and external charging capacitance, respectively, V_n and $V_{n\text{-}1}$ are voltage at temperature data points n and n-1, respectively, Q_p and Q_E are charge accumulated in the pyroelectric cell and the external capacitance, respectively, and ΔQ_n is the additional charge generated at the n^{th} data point (from heating or cooling). The ± sign in front of the right hand side term indicates that current generated in the pyroelectric cell can be in the opposite direction if the sign of the rate of change of temperature changes from $(n\text{-}1)^{\text{th}}$ datum point to n^{th} datum point.

Substitution of Eq. (5) into Eq. (4) results the following recurrence equation, from which the voltage across the external capacitance can be calculated at a given temperature datum point:

$$V_n = \frac{\Delta Q}{C_P + C_E} + \left(\frac{C_E \pm C_P}{C_E + C_P}\right) V_{n-1} = \frac{pA\Delta T}{C_P + C_E} + \left(\frac{C_E \pm C_P}{C_E + C_P}\right) V_{n-1} \tag{6}$$

Once the voltage is determined, the energy stored at n^{th} datum point can be calculated from the following equation:

$$E_n = 0.5 C_E V_n^2 \tag{7}$$

Eqs. (6) and (7) have been used to simulate the voltage and energy produced, respectively, from a measured or available temperature profile of the specific interrogative environment.

2. RESULTS AND DISCUSSION

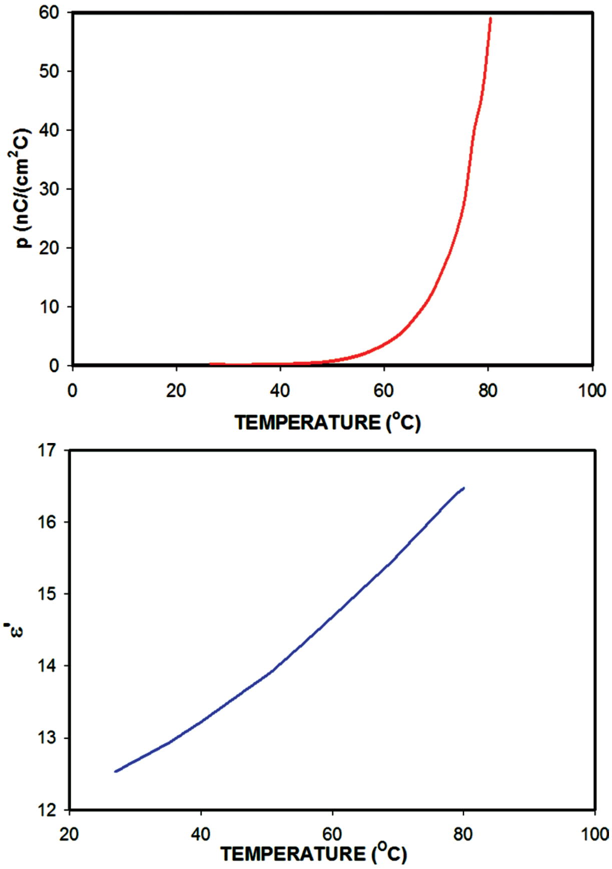


Figure 3
(a) The Dependence of Dielectric Constant (ε') and Pyroelectric Coefficient (p) on Temperature of PVDF Film From 25 to 80 ºC; (b) The Variation of Dielectric Constant (ε') and Pyroelectric Coefficient (p) with Temperature of Pyroelectric PVDF Films

The simulation of voltage generated has been conducted for three different thermal climate conditions i.e. temperature variation over extended period of time: (a) Huntsville (Alabama, USA; May-Oct., Figure 4(a)) (b) Saudi Arabia (Figure 5(a)) and (c) Mars (Figure 6(a)) respectively using foregoing pyroelectric and dielectric properties of PVDF films. The atmospheric temperature variations of planet Mars and Saudi Arabia were extended to 300 hours from available 24 hours data.

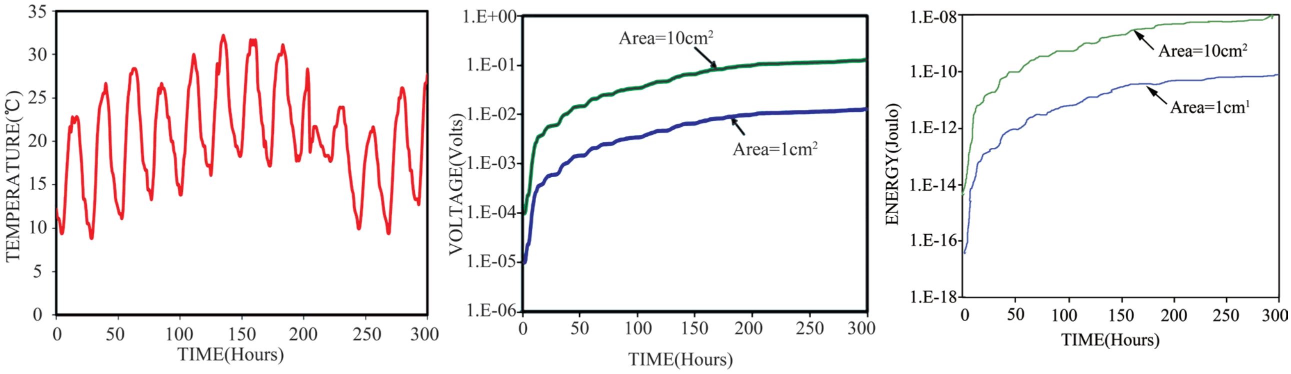
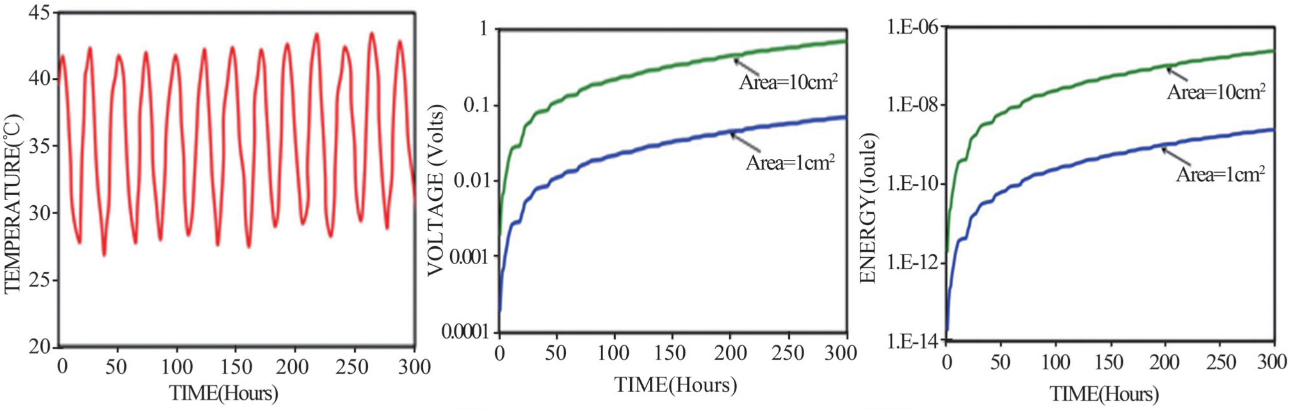
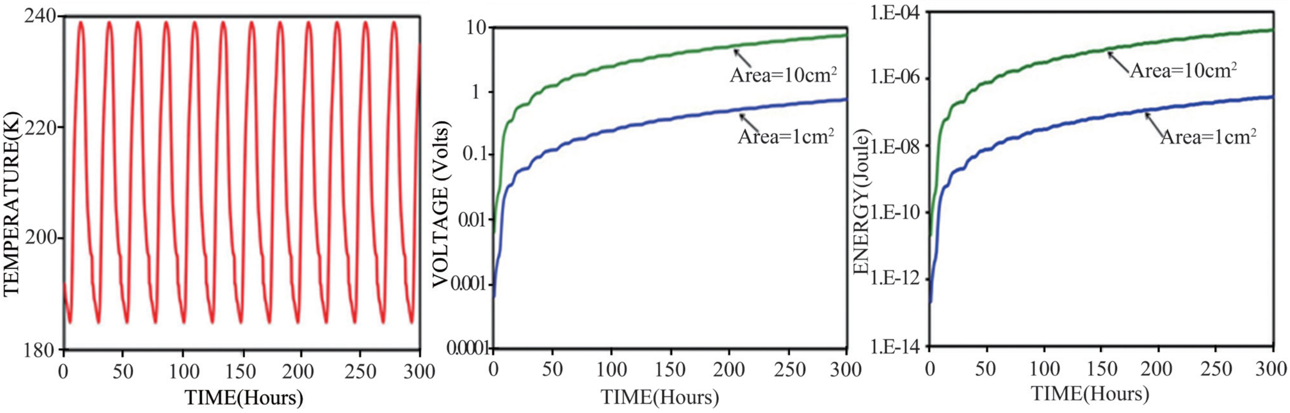


Figure 4
Plot of (a) Pavement Temperature at Huntsville (Alabama, USA) and Respective (b) Generated Voltage and (c) Energy



(a) (b) (c)

Figure 5
Plot of (a) Environment Temperature at Saudi Arabia and Respective (b) Generated Voltage and (c) Energy



(a) (b) (c)

Figure 6
Plot of (a) Environment Temperature at Planet MARS and Respective (b) Generated Voltage and (c) Energy

It is worth mentioning that for storing energy from temperature change/fluctuations, the values of C_P and C_E should be optimized for highest energy storage. Furthermore, the external resistor, R_E, and the external capacitor, C_E, can be adjusted to obtain fast charging. The simulated voltage generated was calculated by assuming area of 1 cm^2 and 10 cm^2 of the pyroelectric cell with 0.1 cm thickness. The external storage capacitor was assumed 1.0 μF. From the p-T and ε'-T graphs (Figure 3), the actual functional relation was obtained by curve fitting and was utilized in modeling. The capacitance of the pyroelectric element was determined using Eq. (1). The predicated cumulative (accumulated) voltage and energy stored in a 1.0 μF capacitor via modeling and simulation for 1 cm^2 and 10 cm^2 pyro-elements are presented in Figure 4 (b, c) to Figure 6 (b, c) for the Huntsville, Saudi Arabia and MARS, respectively.

The predicted maximum voltage and energy at the end of 300-hour cycle for 1 cm2 and 10 cm2 for PVDF material at three different locations are given in the table 1. These predicted performance parameters are largest for MARS , 0.77 volts and 0.29 μJ, respectively.

Table 1
The Predicted Results (Voltage and Energy) Obtained Numerically for Three Locations

Location	Area = 1 cm^2		Area = 10 cm^2	
	Voltage (volts)	Energy (J)	Voltage (volts)	Energy (J)
Huntsville	0.013	$8.34\text{x}10^{-11}$	0.13	$8.34\text{x}10^{-9}$
Saudi Arabia	0.07	$2.94\text{x}10^{-9}$	0.7	$2.45\text{x}10^{-7}$
MARS	0.77	$2.95\text{x}10^{-7}$	7.7	$2.95\text{x}10^{-5}$

CONCLUSION

The potential for energy harvesting through pyroelectric effect has been demonstrated numerically for PVDF-based energy harvester. In this study, PVDF thick-films were fabricated via cost-effective technique and characterized for dielectric and pyroelectric properties. The material parameters (p, *ε'*) determined have been used to perform numerical simulation with *actual* available temperature data for Huntsville (pavement), MARS (ambient) and Saudi Arabia (ambient). The harvested voltage and energy at MARS is the largest than other two locations selected. It is realized that with cyclic heating and cooling of PVDF harvester as per available thermal environment conditions, the temperature gradients are smaller but over time, the total harvested voltage and energy accumulate to be larger. The larger area pyroelectric elements give higher voltages. One posibility to enhance energy generation is to use pyroelectric materials with significantly higher pyroelectric coefficients. Another one is to maximize the area of the element with optimized electrical circuit parameters of its components. Other properties of the selected material such as physical, mechanical and chemical have to be considered for their proper funtionality in the chosen environment as well. Thus, the suitability of the materials will also be based on availability, life, weathering and cost-analysis. Therefore, only the field applications of the pyroelectric material will determine if the predicted harvested energy can be realized in practice. It will be also interesting and important to investigate electric energy generated via combined pyroelectric and piezoelectric effects found in the same candidate material. Then, hybrid and multi-module energy harvester could be designed with enhanced charge-storage rate in the capacitor. In conclusion, results for energy harvester based on PVDF film show that the harvested energy can be compatible with use in an autonomous sensor module operating in low-duty-cycle switched-supply mode.

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Dr. A. K. Batra gave the concept, design of the research, and analyzed the results. Graduate students Ashwith K. Chilvery and Mychal Thomas carried out the experiments (fabrication and characterization of PVDF films). Dr. Alak Bandyopadhyay did the modeling and simulation work including writing the computer program needed for the numerical modeling.

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