Efficient Thermoelectric Transformation of Daily Thermal Fluctuations into Electricity

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**Abstract.** We present an enhanced micro-energy harvester design that couples a thermoelectric module to a heat storage unit formed by a Phase Change Material embedded within a metallic foam. The effect of the thermal resistance between the thermoelectric material and the ambient is investigated through an effective heat transfer coefficient. A case study is analyzed to transform daily thermal fluctuations into electricity during a full day on ground conditions in a Southern Hemisphere typical winter day, using hexadecane as PCM and aluminium as metallic foam. For base PCM as a heat storage unit, the micro-harvester generates 0.01 J after a full day of operation. However, the metallic foam multiplies the electric energy production: from 0.23 J for $\epsilon = 0.95$ to 0.49 J for $\epsilon = 0.85$. Importantly, the relative boost in electric energy production is robust across a wide range of thermal resistance loads.

1. Introduction

The transformation of thermal gradients of temperature into electricity, through the Seebeck effect, is a promising technology to power autonomous monitoring sensors. Low consumption electronic sensors can track the evolution of environmental variables, monitor industrial processes, or measure health parameters. Applications in non-accessible locations or under extreme environmental conditions require operational autonomy because of the difficulty or impossibility of periodically recharge batteries in these situations.

Thermoelectric Generators (TEG) are solid-state devices that employ the Seebeck effect to transform into electricity temperature gradients between their layers. They usually operate with high-temperature gradients to reach efficiency. This requirement restricts their use to applications where high gradients are available. This limitation can be overcome using an external heat storage unit to transforms time-temperature fluctuations into spatial temperature gradients.

The usage of Phase Change Materials (PCM) as heat storage units is particularly convenient due to their very high thermal density. The latent heat released (stored) during melting (solidification) at almost isothermal conditions is much higher than the sensible heat released during cooling (heating) changing the temperature of the material [1–3].

Experiments on TEG coupled to a PCM as a heat storage unit show a meaningful increase of the micro-energy harvesting capacity of the TEG alone. Thus, Agbossou et al.[4] using an organic PCM as a thermal storage unit showed that it is possible to use the daily ambient temperature fluctuations to generate small amounts of electricity. Later, in a follow-up of this work, Zhang et al.[5] used the same
work unit filled with hydrate salt as PCM to harvest solar energy, showing how the harvesting of the daily irradiation is greatly improved with the addition of the PCM. In particular, they report 0.8 mW per work unit. In a recent experiment, Tuoi et al. [6] showed a maximum output power of 190 μW in a real ambient environment (temperature range from 12°C to 24°C) using a TEG of Seebeck coefficient 15 mV/K coupled to Polyglycol E600. More sophisticated configurations of PCM have been used to optimize the energy output. Thus experimental results in an environment with a temperature range from 0°C to 40°C during tree days show that the average output power of a double-PCM-based thermoelectric energy-harvesting device outperforms that of the single-PCM device by 35.8% [7]. The combination of TEG with PCM has also been investigated in other applications involving the harvesting of solar radiation using capric acid [8] or in hybrid photovoltaic where PCM in the form of NaOHKO [9] have been used to enhance the efficiency of the photovoltaic modules.

Despite the improvement in the efficiency of the transformation of thermal fluctuations into electricity brought by the PCM, it is frequent to include heat sink units over the TEG to diminish the thermal resistance between the TEG unit and the environment. This is the case of wearable devices [10], where the body heat is used to generate electricity in the range of microWatts, and the resistive effect of ambient air decreases the electric output strongly if a proper heat sink is not included.

Another particularly relevant and challenging scenario is the harvesting of daily thermal fluctuations due to the night and day cycle. The possibility of using daily thermal fluctuations to power low consumption sensors offers a vast range of applications due to the ubiquitous presence and accessibility to them. In previous work, we have shown how enhancing the heat transfer rate in the heat storage unit embedding PCMs in metallic foam boosts the efficiency in the energy harvesting capacity several times [11]. However, the heat transfer between the ambient and the TEG must be considered when meaningful thermal resistance exists between them. A double challenge appears in the presence of mild or strong thermal resistance: (i) low thermal gradients and (ii) delayed thermal response between the TEG plates and the ambient. To overcome the second difficulty, sophisticated heat sinks are designed to approach the ideal of no thermal resistance. This work addresses their effect using an effective heat transfer coefficient that allows to scan a full range of ambient and realistic thermal loads.

The purpose of this work is to extend the model discussed in Ref. [11] to include appropriate boundary conditions that allow to investigate the effect of the thermal resistance between the micro-harvester and environment on the realistic harvesting of ambient thermal fluctuations. The model uses two sets of partial differential equations to account for the heat transfer in the heat storage and TEG units. The model is very versatile, and the simulations show how the efficiency of the micro-harvester can be significantly improved by using metallic foams within the thermal storage unit, and how the boost in performance is robust across a wide range of difficult thermal resistance loads.

The equations governing the TEG, and these of the PCM embedded in metallic foams used to model the heat storage unit, are outlined together with their thermal coupling in the Section 2. The geometry of the TEG and heat storage unit is also described in this Section. The results from simulating a case corresponding to the energy harvesting in a winter day of the Southern Hemisphere and different thermal resistances are given in Section 3. Finally, Section 4 gives the conclusions of the work.

2. Model equations of the thermoelectric module and heat storage unit

2.1. Evolution equation of a Phase Change Material in a metallic foam

The heat equation of a Phase Change Material within a porous metallic foam written in terms of the temperature reads, as shown by Beckermann et al.,[12], as:

$$\frac{\partial T}{\partial t} = \nabla \left( \kappa_{\text{eff}} \nabla T \right) - \frac{\partial f_i}{\partial t}$$

(1)

here \( L \) denotes the solid/liquid latent heat of the PCM, \( \kappa_{\text{eff}} \) the conductivity of the foam, \( \varepsilon \) is the porosity, \( \tilde{\rho}c = f_I \rho_c c_I + (1-f_I) \rho_p c_p + (1-\varepsilon) \rho_m c_m \) the weighted thermal capacity of the foam; \( c_p, c_I, c_m \) the specific heats of the solid PCM, liquid PCM, and metallic foam, respectively; \( \rho, \rho_m \) the density of
the PCM and metallic foam, and $f_i$ the volume fraction of melted PCM per unit volume of PCM. The liquid fraction field $f_i$ is determined by the temperature field: $f_i = 0$, for $T \leq T_s$, $f_i = 1$ for $T \geq T_i$, and $\frac{T - T_s}{T_i - T_s}$ in the mushy region $T_s < T < T_i$.

The thermal conductivity of metallic foams is usually very different from that of the fluid around them and makes their modeling particularly challenging. However, it is necessary for a realistic determination of the conductivity for their accurate modeling. The usual procedure is to lump the porous matrix and fluid contributions into an effective conductivity $\kappa_{\text{eff}}$ [13–16].

This work uses a model developed by Yang et al. [14], validated using empirical data of several combinations of metallic foam/fluid at high porosities. The effective conductivity is modeled as

$$\kappa_{\text{eff}} = \frac{4\lambda(1-\delta)}{(1-\delta)\rho c_s e - 6\lambda e \ln[(1-e)/(1-\delta)]} \cdot \frac{1-e}{2(1-e)+\lambda e-(1-e)^2(1-\delta)} + \frac{\kappa_{\text{pcm}} e}{\kappa_m}$$

(2)

where $\lambda$, $\delta$, and $e$ define the geometry of the shape of the porous of the metallic foam, $\kappa_{\text{pcm}} = \kappa_{\text{fl}} + \kappa_s(1 - f_i)$ the conductivity of the PCM weighted by the fraction of the liquid ($\kappa_{\text{fl}}$) and solid ($\kappa_s$) phases. We use the parameters corresponding to the validation of Yang et al. [14] in metallic foams: $e=0.3$, $\lambda = 1.5$ and $\delta = 0.5$.

2.2 Governing equations of the Thermoelectric Generator (TEG)

Pairs of semiconductors joined by metallic junctions form the thermoelectric modules. When subjected to a difference of temperature, develop a difference of potential as a result of the Seebeck effect. A single thermoelectric module generates a voltage $V_T = \alpha(T_{HJ} - T_{CJ}) = \alpha \Delta T_{\text{eff}}$; where $\alpha$ is the Seebeck coefficient of the module, whose value depends on the number of n-type and p-type pairs, and $\Delta T_{\text{eff}} = T_{HJ} - T_{CJ}$ refers to the variation between the temperature at the hot junction and the cold junctions. Layers of ceramic plates electrically insulating protect the semiconductors physically and allow the conduction of heat. Thus a temperature $T_H$ at the hot ceramic plate, and $T_C$ at the cold plate generate a difference of temperature across the whole device $\Delta T = T_H - T_C$, related to $\Delta T_{\text{eff}}$ through the relation [17,18]: $\Delta T_{\text{eff}} = \frac{K}{K+2K_i+\frac{2\rho_T\rho_L}{R_i}+R_L} \Delta T$, where $R_i$ denotes the resistance of the thermoelectric module, $R_L$ the external load of the circuit, $K$ the thermal conductivity of the protective plates, $K_i$ the conductivity of the thermoelectric module, and $T_m = (T_H + T_C)/2$ a mean temperature.

The evolving distribution of temperature in the thermoelectric module is calculated through the heat equation

$$\rho_{\text{teg}} c_{\text{teg}} \frac{\partial T}{\partial t} = \kappa_{\text{teg}} \nabla T$$

(3)

where $\rho_{\text{teg}}$ is the effective density, $c_{\text{teg}}$ is specific heat, and $\kappa_{\text{teg}}$ the conductivity. This model has been validated using the empirical data of temperature measured in the hot and cold side reported by Samson et al. [20] and mimicking their results for the voltage curves. The value of the coefficients is provided in Ref. [11]. The physical properties of the PCM used in this work, hexadecane, are provided in Ref. [21]. Finally, the value of the electric and thermal properties of the thermoelectric module used in this work, the model TEG1 $9.1 - 9.9 - 0.8/200$ manufactured by Eureka and based on Bi$_2$O$_3$ are provided by the manufacturer [19].
2.3 Boundary conditions and geometry
The TEG unit is represented as a rectangle with a horizontal dimension of side 1 cm and thickness 0.1 cm. The PCM unit is superposed to the TEG and has a horizontal dimension of 1 cm and a height of 20 cm. The TEG and PCM units couple physically and thermally on the cold side of the thermoelectric module, as shown in Figure 1.

The hot side (bottom) of the thermoelectric module is exposed to the ambient temperature. The top side of the heat storage unit and lateral sides of the TEG/PCM harvester are adiabatic. For simplicity, the initial temperature of the whole micro-harvester is the same for simplicity.

2.3.1 TEG/PCM boundary condition. The temperature at the TEG/PCM boundary must be calculated by solving the heat equations (1) and (3). It is calculated equaling the flux of heat leaving the TEG to the flux entering into the PCM: \( \kappa_{\text{TEG}} T_y = \kappa_{\text{PCM}} T_y \), leading to the following value at the TEG/PCM boundary:

\[
T_i = \frac{\kappa_{\text{TEG}} \Delta y_{\text{TEG}} + \kappa_{\text{PCM}} \Delta y_{\text{PCM}}}{\frac{\kappa_{\text{TEG}}}{\Delta y_{\text{TEG}}} + \frac{\kappa_{\text{PCM}}}{\Delta y_{\text{PCM}}}}
\]  

where \( T_i \) is the temperature of the boundary at the position of the cell \( i \), \( T_{\text{LPCM}} \) is the temperature at the centroid of the nearest cell to position \( i \) at the TEG (PCM) domain. Then, Eqs. 1 and 3 can be solved to compute the difference of temperature \( \Delta T = T_H - \langle T_i \rangle \), where \( T_H \) is the environmental temperature, and the spatial average \( T_C = \langle T_i \rangle \) is the temperature at the cold side of the TEG.

2.3.2 TEG/Air boundary condition We use a temperature profile, \( T_{\text{air}} \) corresponding to a sunny winter day in Brazil measured in a flat solar plane (Figure 7 of Ref. [22].) The profile starts at 12:00 am, the temperature increases up to \( \sim 14 \) h later and decreases up to \( \sim 16 \) h. The thermal resistance between the hot side of the TEG and the circulant air introduces a delay between \( T_{\text{air}} \) and \( T_H \). Usually, this effect is diminished using heat sinks. Their design depends not only on the TEG but also on the particular ambient conditions the device is intended to be used. Because of that, several values of the convective heat transfer coefficient \( h_a \) are employed to model different thermal resistances. This coefficient is incorporated into a Robin boundary condition between the hot side of the TEG (temperature \( T_H \)) and the ambient temperature (temperature \( T_{\text{air}} \)): \( -K \frac{\partial T_y}{\partial y}|_{y=0} = h_a(T_{\text{air}} - T)|_{y=0} \), and \( T_H = \langle T \rangle |_{y=0} \). Thus this boundary condition at \( y = 0 \) takes into account: (i) the external temperature profile and (ii) the thermal resistance between the air and hot side of the TEG. Notice that the thermal resistance is the inverse of the heat transfer coefficient \( R_{th} = \frac{1}{h_a A} \) where \( A \) is the area of the hot side of the TEG.
Figure 2. (color online) (a) Electric energy accumulated along the time at different porosities, (b) Instantaneous voltage along the time.

3. Results

The heat reservoir used is large enough to have a liquid/solid phase change occurring in the PCM during the whole harvesting period. If smaller volumes of PCM are used, the PCM is fully melted or solidified during some parts of the harvesting cycle, and the efficiency of the TEG/PCM device is reduced.

To evaluate the impact of the metallic foams on the energy harvesting capacity, we first simulate the base PCM and compare its performance with the results after the introduction of metallic foams at different porosities. Figure 2(a) shows the electric energy accumulated during the whole harvesting period for different porosity values $\varepsilon$. After a full day of operation, the harvester has generated 9.99 mJ in the absence of metallic foam ($\varepsilon = 1$). However, this amount is highly increased in the presence of the metallic within the PCM. Thus, the harvester generates 0.23 J for $\varepsilon = 0.95$, which is twenty-three times higher than the amount of energy generated in the absence of metallic foam, and further decreasing the porosity the harvester generates 0.37 J for $\varepsilon = 0.9$ and 0.49 J for $\varepsilon = 0.85$. Therefore, the PCM increased conductivity due to the metallic foam increases more than one order of magnitude the available electric energy for the same ambient conditions and TEG module.

Figure 2(b) shows the evolution of the instantaneous voltage as a function of the time for the porosity values discussed above. There is a striking difference in the generated voltage between the base PCM and that generated introducing the metallic foam. For the latter, there are well-defined peaks during the phase of decreasing $T_{air}$ (negative) and increasing $T_{air}$ (positive). In the absence of metallic foam, the maximum voltage value is 5.6 mV and the minimum -0.5 mV. These values are strongly modified when the heat storage unit becomes more efficient, transferring heat faster from the cold side of the TEG to the heat storage unit by including the metallic foam. At $\varepsilon = 0.95$, the maximum peak of voltage is found during the PCM warming phase at 32 mV, and the minimum value at -15 mV. For the lowest porosity at $\varepsilon = 0.85$, these values are extended to 53 mV for the highest and -22 mV to the lowest. Thus decreasing the porosity increases the magnitude of the voltage at the peaks, but differences across different porosities are not as significant compared to pure PCM. These values show that melting and solidification are not equivalent as per electric energy production purposes. It is melting and not solidification the phase change stage of the PCM that produces the highest electric energy. The results for the voltage explain the figure Figure 2(a). In the cumulative energy curve, the greatest production of energy occurs after 6000 s, which is the ambient warming stage of $T_{air}$, where the highest voltage peaks occur.
Figure 3. (color online) Total accumulated energy as a function of the porosity at different values of the convective heat transfer coefficient.

For ideal heat sink conditions, the porous foam boosts enormously the efficiency of the TEG/PCM device in transforming thermal fluctuations into electricity. For a small volume fraction of metallic foam at $\varepsilon = 0.95$, the electric energy harvested is augmented 2221%, and for the highest volume fraction of metallic foam at $\varepsilon = 0.85$, it is raised 4807% with respect to a heat storage unit formed by pure PCM. While more metallic foams lead to a higher electric output, decreasing the porosity leads progressively to smaller electricity gains. In addition to that, notice that the porosity of the metallic foam cannot be decreased continuously without changing the model outlined in Section 2.1; since then, that model loses validity.

The results discussed so far correspond to an ideal heat sink $h_a = \infty$, where there is no thermal resistance between the hot side of the TEG and the ambient. We now consider the effect of non-ideal heat transfer in the performance of the micro-harvester. The effect of the thermal resistance is studied through a convective heat transfer coefficient with values corresponding to four different scenarios: (i) very high thermal resistance with $h_a = 10 \text{ Wm}^{-2} \text{K}^{-1}$ typical of quiescent surrounding air, (ii) high thermal resistance with $h_a = 100 \text{ Wm}^{-2} \text{K}^{-1}$ typical of forced convection, and (iii) $h_a = 300 \text{ Wm}^{-2} \text{K}^{-1}$ and $h_a = 1000 \text{ Wm}^{-2} \text{K}^{-1}$, which correspond to cases where heat sinks are included with different levels of effectiveness.

Figure 3 summarizes the total accumulated energy for different porosities at the set of thermal resistances discussed previously. For an ideal heat sink, the harvested electric energy increases monotonously when the porosity diminishes, and there is a reduction of improvements in the energy harvested at lower $\varepsilon$. At fixed porosity, the harvested electric energy increases with the heat transfer coefficient $h_a$; and, as expected, higher values of the convective heat transfer coefficient approach more to the ideal heat sink at $h_a = \infty$. The curves show that at least $h_a = 100 \text{ Wm}^{-2} \text{K}^{-1}$ is required to have a usable electric output to power low consumption electronic devices. As an example, the energy accumulated during a day with a heat storage unit of porosity $\varepsilon = 0.85$ can power a thermal wireless sensor with consumption of about 1mW during 83s for $h_a = 100 \text{ Wm}^{-2} \text{K}^{-1}$, 161s for $h_a = 300 \text{ Wm}^{-2} \text{K}^{-1}$, or 309s for $h_a = 1000 \text{ Wm}^{-2} \text{K}^{-1}$.

Importantly, when the thermal resistance is included, the curves exhibit similar behavior: increased energy production at lower porosities accompanied with a more downward slope of the curves. These results prove that the presence of the thermal resistance does not negate the substantial increase in efficiency of TEG/PCM micro-harvesters with PCM embedded in a metallic foam, even in the presence of adverse thermal resistance, and points to PCM embedded in metallic foams as a robust design to boost the performance of current TEG/PCM micro-harvesters.

4. Conclusions
We have presented the model of a micro-energy harvester formed by a thermoelectric device coupled to
a heat storage unit. This unit is filled by a Phase Change Material embedded in a metallic foam. In addition, the thermal resistance between the TEG and the ambient has been included in the model. The model has been applied to simulate the transformation of environmental thermal fluctuations occurring naturally during the night and day cycle into electricity. The thermal load corresponds to a typical winter day in the Southern Hemisphere (Brazil). The harvesting time is 24 h, and the PCM used is hexadecane because its phase change temperature is within the fluctuation range of the temperature load. The TEG module is a unit manufactured by Eureca [19] with a Seebeck coefficient of 27 mV/K.

The porous metallic foam increases the conductivity and allows a more effective evacuation of heat from the cold side of the TEG to the heat storage unit, leading to an increased $\Delta T$ between the hot and cold sides of the TEG. When the porosity $\varepsilon$ decreases from 1 to 0.95, the harvester increases the conversion into electric energy from 9.9 mJ to 230 mJ, respectively. This is more than one order of magnitude and is a consequence of the increased thermal conductivity of the heat storage unit. Increasing the fraction of metallic foam leads to a diminishing return on electric energy due to the reduction of PCM mass for the same volume of the heat storage unit.

The realistic operation of thermal micro-harvesters often requires the coupling of a heat sink to the hot side of the TEG. The cause is the thermal resistance between the TEG plate exposed to the ambient (the hot side) and the ambient. This reduces the amplitude of the thermal fluctuations at the hot side and the efficiency of the harvester. This work studies the performance under different thermal resistances, very strong, mild, and low. We show that for very high thermal resistance $h_a = 10 \, W \, m^{-2}K^{-1}$ the electric output of the micro-harvester is tiny and useless in practical applications. However, under ambient conditions that reduce the thermal resistance, such as moderate wing speed, the electric energy obtained for porosities lower than one is about tens to one-hundredth millijoules. For milder ($h_a = 300 \, W \, m^{-2}K^{-1}$) and low thermal resistance ($h_a = 1000 \, W \, m^{-2}K^{-1}$) conditions that can happen by high forced convection or the introduction of an appropriate heat sink, the performance is boosted to hundreds of millijoules. This amount of energy is about half to one third of that of an ideal heat sink; however, it is enough to power a range of low consumption sensors. These results show that micro-energy harvesters with a thermal storage unit enhanced with a metallic foam can virtually power a wide range of low consumption electronics, even in situations of low thermal gradients with mild thermal resistance.

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