Combined Pyroelectric, Piezoelectric and Shape Memory Effects for Thermal Energy Harvesting

D Zakharov1,2, B Gusarov1,2, E Gusarova3, B Viala3, O Cugat1,2, J Delamare1,2 and L Gimeno1,2

1G2Elab, Univ. Grenoble Alpes, F38000 Grenoble, France
2CNRS, Univ. Grenoble Alpes, F38000 Grenoble, France
3CEA, LETI, MINATEC Campus, F38000 Grenoble, France

dmitry.zakharov@g2elab.grenoble-inp.fr

Abstract. This work proposes an enhanced method for thermal energy harvesting exploiting combined pyroelectric, piezoelectric and shape memory (SME) effects, and presents its experimental validation. A material which is pyroelectric is also piezoelectric. If it is combined with a material with SME, which generates large strain and stress in a rather narrow temperature range, the resulting composite material would generate voltage from temperature variations using two different energy conversion principles at once: (1) pyroelectric effect, (2) piezoelectric effect driven by SME. A Macro Fiber Composite piezoelectric was shown here to exhibit significant pyroelectric effect (~4 V/°C). When combining it with a SME Ti-Ni-Cu alloy into a laminated structure, this effect increased by 50%. This increase may be an order of magnitude higher for an optimized system. Such composites open an opportunity to harvest thermal energy from natural sources, since this method can increase the rather low efficiency of current pyroelectric materials especially for small temperature variations.

1. Introduction

Besides macro-power systems such as solar cells, wind and watermills, unconventional small-scale power systems are emerging from labs. They aim to bring energy autonomy to ultra-low-power (ULP) electronics. This gives rise to substantial research activities in the fields of micro or nano-energy harvesting and ULP devices. As a result, devices are being optimized to require less and less energy, down to picojoules for some applications [1], while harvesting systems are now able to generate energies up to the millijoule range [2]. Micro- and nano- harvesting systems are starting to offer a real alternative over battery-powered solutions with virtually inexhaustible sources, no maintenance and little adverse environmental effects.

Considering thermal sources which are widely available in our environment, energy can be directly converted into electricity by means of thermoelectricity (Seebeck effect) or pyroelectricity. Thermoelectric and pyroelectric power generators are already in common use. However, for acceptable efficiency, applications require significant spatial- and time-dependent temperature variations respectively. This in turn requires optimized cold source management systems. The cold source usually consists in a radiator whose size and shape can become problematic at small scales.
Another strong limitation stems from the low voltage or current delivered by these generators, which require complex and power-consuming buck-boost converters.

An alternative scheme is to indirectly convert heat into electricity through mechanical transformations using smart composite materials. Such composite requires two materials being mechanically coupled. This principle is discussed in detail in the next section.

2. Principle

Recently, we proposed and studied an original hybrid laminated composite material for harvesting quasi-static temperature variations [3]. It consisted of Macro Fiber Composite (MFC) piezoelectric and Ti-Ni-Cu shape memory alloy (SMA). During temperature variations, large thermally induced strain generated by the SMA layer is transmitted to the piezoelectric layer, which in turn generates a voltage. In this way thermally induced strain is converted into useful voltage with neither complex electronics nor cold source management system (no radiator).

In this previous work, pyroelectric effect was not considered for MFC, relying on literature data [4]; however, here we give first experimental evidence that pyroelectricity is indeed significant in MFC. As a consequence, the SMA/MFC composite material can generate voltage from temperature variations using two different energy conversion principles at once: (1) pyroelectric effect, and (2) piezoelectric effect driven by shape memory effect (SME). The principle is illustrated in figure 1. Since all pyroelectrics are also piezoelectrics, this approach can be applied to enhance the electric response of any pyroelectric material in a certain temperature range, where the thermoelastic straining of the SMA is pre-determined to take place. When designing such a functional material, arrangements should be made to ensure that both effects will induce voltage of the same sign, otherwise they risk canceling each other.

This approach is different from that using the difference of thermal expansion coefficients of the pyroelectric and its substrate to drive piezoelectricity [5]: since SME generates much larger strains in a narrow temperature ranges. This is especially advantageous for harvesting small temperature variations.

![Figure 1. Principle of proposed enhancement of pyroelectric material performance. 1 – pyro/piezo-electric layer, 2 – SMA layer with SME pre-determined at the temperature range of interest. When temperature changes by ΔT, (a) pyroelectric material alone generates voltage ΔV_{pyro} due to pyroeffect, (b) hybrid composite generates voltage ΔV_{pyro} due to pyroeffect plus ΔV_{piezo} due to piezoelectric effect driven by SME.](image)
3. Results and discussion

3.1. Pyroelectric effect for MFC

Figure 2 shows absolute values of voltage generated by MFC alone when dipping in hot and cold water, measured by electrostatic non-contact voltmeter. The use of electrostatic voltmeter allows observing time-dependent direct voltage generation with no losses [6]. In this experiment, the MFC was firstly moved from the air (room temperature) into the hot water for about a minute (curve 1). After registering the curve but before taking the sample out, the generated voltage was discharged into a resistor, thereby bringing the MFC back to the uncharged state. Then it was quickly taken out from the hot water and put into the cold water (curve 2, the first slope between 0 and ~2 s corresponds to the travel in air before immersion in cold water). As observed on the plot, for both cases the voltage firstly increased due to pyroelectricity and then decreased due to the intrinsic charge leakage. Leakage at heating was significantly higher (the decreasing time $t_{1/2}$ from maximum to half-maximum was 3 s at heating versus 30 s at cooling). The leakage is known to increase with temperature [7].

![Figure 2. Absolute electric response of MFC alone when heated (1) and cooled (2) by dipping in hot and cold water (opposite voltage signs). Voltage firstly increases due to pyroelectricity, and then decreases due to intrinsic charge leakage. Leakage is faster at high temperatures.](image)

The peak voltage generated by MFC alone was measured at various temperatures of hot water. This dependence was linear and characterized by a remarkable high pyroelectric voltage coefficient $\rho_V \approx 4 \, \text{V/°C}$ (figure 3, red filled squares). In fact, MFC has been used mainly as an actuator up to now and its pyroelectric properties were not studied before. Our work gives evidence of significant pyroelectric effect for MFC in the working conditions described above. This result is rather expected, since MFC contains PZT (PZT5A1 type) [8], which is known to have pyroelectric properties [9]. The pyroelectric voltage coefficient $\rho_V$ can be evaluated knowing its pyroelectric charge coefficient $\rho_Q$, relative dielectric permittivity $\varepsilon_r$ and thickness $h$ using the following expression [10]:

$$\rho_V = \frac{\rho_Q \varepsilon_r}{\varepsilon_0} \cdot h,$$

where $\varepsilon_0$ is the vacuum permittivity ($8.85 \times 10^{-12} \, \text{Fm}^{-1}$). Using the following values: $\rho_Q = 2.38 \times 10^{-4} \, \text{Cm}^{2} \text{K}^{-1}$ [9], $\varepsilon_r = 1800$ [11], $h = 127 \, \mu\text{m}$ [4], one obtains $\rho_V = 1.9 \, \text{V/°C}$. The measured value is of the same order of magnitude which is consistent with the theoretical calculation.

![Figure 3. Peak voltage generated by MFC alone and by Ti-Ni-Cu/MFC composite, when heated to various temperatures. In the region ~30-40 °C the composite shows an increase of “pyro”-electric voltage coefficient due to thermoelastic straining of Ti-Ni-Cu SMA, and then resumes the “pyro” slope.](image)
3.2. **Ti-Ni-Cu/MFC composite**

The fabrication details of our Ti-Ni-Cu/MFC composite were reported in [3]. Its electric response is also plotted on figure 3 (filled blue triangles). The pyroelectric voltage coefficient $\rho_V$ is the same as that of MFC alone below ~30 °C. But in the region ~30-40 °C it increases by ~50% (6 V/°C) due to the thermoelastic straining of Ti-Ni-Cu SMA. Thereby, above ~40 °C, after the transformation in the SMA has been completed, the output voltage of the composite stays higher than that of MFC alone, since the piezoelectric voltage contributes in addition to the pyroelectric one. In fact, this increase was expected to be much higher since the SMA was pre-strained to about 1-3%. Part of the strain is believed to be lost at the interface (glue), which is critical for the performance of such functional composites. Also, the sizes of the SMA ribbon and the MFC used in this work were not perfectly adapted: the SMA layer covered only 15% of the MFC layer. As a consequence, a part of PZT fibers were probably not experiencing the deformation.

3.3. **Sign of the effects**

It is important here to deal with the question of the sign of the different effects. When the MFC was subjected to heating, the observed voltage was positive. As it was explained in [3], the Ti-Ni-Cu ribbon has been pre-deformed to shorten at heating. Considering the Ti-Ni-Cu/MFC bilayer, we assume that it bends and fibers become tensile. Thus since PZT piezoelectric voltage coefficient $g_{33}$ is positive [11], the generated voltage is positive. For such type of composites mechanical engineering (planar or flexural deformation) must be considered with respect to the sign of piezoelectric coefficients.

3.4. **Optimization**

These first experiments were aimed at proving the proposed concept of enhanced thermal energy harvester, and the system was not optimized. Optimization of the composite can be realized by taking an SMA element of the same area as the MFC in order to provide homogeneous deformation of all the PZT fibers. The thickness of the SMA element and its preset strain should be optimized in order to apply adequate strain and stress to the MFC. The optimized glue connection should allow transferring the mechanical work of the SMA with minimal losses. All these arrangements should allow us to obtain thermally-induced strain in MFC layer close to 0.1% and corresponding contribution of piezoelectric effect of more than 300 V [12] in a narrow temperature range ($\Delta T \sim 10-20$ °C for Ti-Ni-Cu SMA) resulting in significant enhancement of the thermoelectric-like response.

4. **Conclusion**

The proposed method of combining pyroelectric material with a shape memory material provides an enhanced electric response compared to MFC pyroelectricity alone. This opens an opportunity to harvest thermal energy from natural sources, since the new method can increase the rather low efficiency of current pyroelectric materials, especially for small temperature variations. Since the exploited physical effects do not deteriorate at microscale, the proposed concept is suitable for MEMS.

**Acknowledgements**

This work was supported by the French National Research Agency (ANR) under the Carnot Institute Program and by the Nanosciences Foundation of Grenoble under RTRA program. The research leading to these results has received funding from the European Community’s Seventh Framework Programme (FP7/2007-2013) under grant agreement NANOFUNCTION n°257375.

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