Stretchable Thermoelectronics

Integration of thermoelectricity to stretchable electronics

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Abstract

Thermoelectricity is a phenomenon in which coupling between thermal and electrical effects occurs, making the direct transformation of energy from one nature to another in a reversible way possible. Devices capable of making use of it can work as sensors, electric generators or heat pumps, providing a wide rank of applications.

This study focuses on the understanding of the phenomenon along with, moving towards stretchable electronics, new crafting methods and materials in order to create a stretchable thermoelectric device that may enhance the field of application from that of conventional, rigid thermoelectric devices.

Stretchability was achieved by using bulk bismuth telluride semiconductor pellets interconnected by galinstan and immersed in PDMS, reaching values on the generated electromotive force up to 60% compared to raw pellets.
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1 INTRODUCTION

1.1 Background

Nowadays we cannot think of a modern life without all facilities technology offers. From the time we wake up till the end of the day and even during sleep time we depend on technology, a technology powered by electricity. It is a fact that our comfort relies on electrical power, and so is the growth of population and the continuous increasing demand of electric power.

It is only natural then in these times to aim for alternative sources of energy and improvement on the efficiency of current processes.

Thermoelectric generators not only provide an alternative electricity source but they also are fed with heat waste, meaning an improvement on efficiency for other processes, dealing with both above mentioned aims within one shot.

As a rough impression in numbers, let us mention a nuclear power plant like Forsmark, situated on the east coast of Uppland, Sweden. It provides an electrical power of 23 TWh per year, implying a heat loss of around 46 TWh (considering an efficiency of 33% [1]). Even if the thermoelectric generators suffer from extreme low efficiency (around 2-3% [2]), its use in Forsmark would imply an additional generation of 0.92-1.38 TWh of electrical energy.

Moreover, a thermoelectric device can work in reverse, pumping heat if fed by electricity, raising the temperature on one of its faces and cooling down the other. The main application of such performance is its use as a refrigerator. While they lack efficiency, they have the advantage over conventional compressor technologies of not having mobile parts and quick response.

In this era electronics also move towards stretchability and conformability, leaving behind the rigidity by which they used to be characterized. Means to achieve so are quickly being developed over the last decade, such as the use of extremely thin layers of brittle materials to ensure bendability, the use of rigid islands embedded in stretchable polymers or the entire use of stretchable materials.

The combination of both thermoelectric phenomenon and stretchable electronic technologies should provide conformable thermoelectric devices that will enhance the field of application beyond that of conventional, rigid models.

Picture 1. A stretchable thermoelectric device fabricated with Wacker PDMS adapting to a curved surface

Picture 2. Image of stretchable thermoelectric devices fabricated with different materials
1.2 Introduction to the phenomenon

Thermoelectricity is a phenomenon that causes the apparition of an electric current when a heat flux goes through a material or, symmetrically, a heat flux is forced if a current is applied to it.

This implies a coupling between thermal and electrical phenomena, making possible direct transformation of energy from one nature to another in a reversible way with the advantage of not requiring middle steps or mobile parts like in other technologies like turbines or compressors.

Taking into advantage this reversible phenomenon a thermoelectric device can be used to harvest thermal energy to provide electric power or, in reverse, by applying a current heat can be pumped, resulting in the cooling of one surface and the heating of the other.

Thermoelectricity can be divided into three small effects, named after the researchers that first observed them [3]:

1.2.1 The Seebeck effect

In 1821 Thomas Johann Seebeck found that a circuit made from two dissimilar metals with junctions at different temperatures would deflect a compass magnet. Seebeck initially believed this was due to magnetism induced by the temperature difference and thought it might be related to the Earth's magnetic field. However, it was quickly realized that a "Thermoelectric Force" induced an electrical current, which by Ampere's law deflected the magnet. More specifically, the temperature difference produces an electric potential (voltage), which can drive an electric current in a closed circuit. Today, this is known as the Seebeck effect.

The voltage produced is proportional to the temperature difference between the two junctions. The proportionality constant ($S$ or $\alpha$) is known as the Seebeck coefficient, and often referred to as "thermopower" even though it is more related to potential than power.

The effect occurs inside the very material as we will see in the theory chapter, not being necessary two different materials to generate an electromotive force. On the other hand, it is impossible to measure it without the use of at least two dissimilar materials, since if the same are used, one electromotive force would terminate the other, resulting in a null effect. Hence, the coefficient must be measured along with another material and thus related to it.

1.2.2 The Peltier effect

In 1834, a French watchmaker and part time physicist, Jean Charles Athanase Peltier found that an electrical current would produce heating or cooling at the junction of two dissimilar metals. In 1838 Lenz showed that depending on the direction of current flow, heat could be either removed from a junction to freeze water into ice, or by reversing the current, heat can be generated to melt ice. The heat absorbed or created at the junction is proportional to the electrical current. The proportionality constant is known as the Peltier coefficient.
1.2.3 The Thomson effect

Twenty years later, William Thomson (later Lord Kelvin) issued a comprehensive explanation of the Seebeck and Peltier Effects and described their relationship (known as the Kelvin Relations). The Seebeck and Peltier coefficients are related through thermodynamics. The Peltier coefficient is simply the Seebeck coefficient times absolute temperature. This thermodynamic derivation leads Thomson to predict a third thermoelectric effect, now known as the Thomson effect. In the Thomson effect, heat is absorbed or produced when current flows in a material with a temperature gradient. The heat is proportional to both the electric current and the temperature gradient.

Along with these three thermo-coupling effects, Fourier heat transfer and Joule energy loss also take part.

Good thermoelectric materials should possess large Seebeck coefficients ($\alpha$) to maximize the electromotive force, high electrical conductivity ($\sigma$) to minimize Joule heating due to electrical resistance and low thermal conductivity ($k$) to minimize Fourier transfer. The quality of the thermoelectric performance of the material is commonly referred as the figure of merit $zT = \frac{\alpha^2 T}{k}$; where $T$ is temperature.

1.3 Applications

Thermoelectricity offers several applications depending on how we approach the above mentioned effects.

**High precision thermometers**

By taking advantage of the Seebeck effect the temperatures can be measured (Fig. 2).

More in detail, an electromotive force appears in the circuit due to and proportional to the difference of temperature of the junctions of material A and B. Thus, controlling one of the temperatures and measuring the difference of potential in an open circuit makes possible to know the temperature of the other junction.

Thermoelectric thermometers show high accuracy and wide range of working temperatures.

Moreover, the amount of matter that needs to be adapted to the temperature of the object that is to be measured is minimal and their thermal capacity is low. Thus, the temperature of the object is not modified and the response of the thermometer is almost immediate, allowing its use for measuring changing temperatures or as fast-response thermal sensors.

Measurement of heat fluxes is also possible by means of the same principle. A difference of temperature through a known material can easily be obtained reading the generated voltage due to the Seebeck effect on both sides and, with it, indirectly the heat flux through it.
Thermoelectric generators and heat pumps

When using these approaches, five phenomena will be responsible for the final effect.

Since a difference of temperature will exist, there will be a heat transfer due to the Fourier effect and an electromotive force due to the Seebeck effect.

When the circuit is closed, electrical current will appear producing Joule loss of power and a heat absorption/release due to the Peltier effect.

And finally, due to both difference of temperature and electrical current, there will again appear a heat absorption/release due to Thomson effect. (Some consider the distinction between Peltier and Thomson effect to be artificial. See section 2.2.1).

According to this, we have difference of temperature and electrical current as variables to control these five phenomena, which will contribute to the final effect, turning out into a harvest of heat energy and supply of electric power or into a pump of heat (Fig. 3).

Basically, if a difference of T is forced on the sides of the thermocouple some of the heat flux through it will be transformed into electrical work.

On the other hand, if current is applied to the thermocouple, electrical work will be transformed into heat flux, cooling down one side and heating up the other.

The use of this technology as a cooler has its limitations due to its low efficiency and so its applications as heat pump need to meet specific conditions; such as coolers for the army, where size prevails over power consumption, or such as in this very research, where two thermoelectric chips were used to accurately fix a constant difference of temperature on the sides of the samples.

As thermoelectric generators they humble themselves to the same limitation in efficiency (around 2-3% [2]), but one must take into account that the feed of these devices is already a waste in the first instance. So even if the heat energy transformed into electric work is relatively low, it is always a recovery and plus, the cases in which heat is wasted are very numerous and so it is the amount, making the potential recovery of heat huge. The field of application lies into every process that releases heat; covering a wide range, from industrial to daily processes, such as the machinery on a factory, a car, a computer, human skin or even space crafts, where the extreme cold provides an ideal heat sink.

Another approach to the future applications of the generators is, instead of aiming for the amount of electric energy produced, the focus on the endless character of this source in contrast to a battery and its fast response. If low power is required thermoelectric generators might be the ideal, never-ending power source. This relates to auto-fed monitors of variables and wireless sensors-transmitters of signals, with applications such as patches for machines or even human beings.
2 THEORY

A thermoelectric device consists of P and N type semiconductors connected electrically in series and thermally in parallel. The minimum unit is formed by a P-N pair.

Doped semiconductors are the materials with highest thermoelectric performance [4] due to their uneven amount of carriers, and it is precisely the ability of the carriers to store heat energy what thermoelectricity takes into advantage.

When used as a thermogenerator, a heat source and a heat sink must be applied to each side, creating a difference of T along the elements, which will then induce an electromotive force and thus a current will go through if the circuit is closed.

In reverse, when used as a cooler, a current is applied through it and a heat flux then appears from one side to the other, heating up one side and cooling down the other.

![Fig. 3. Schematic illustration of a thermocouple working as a power generator and as a heat pump [4]](image)

There are many phenomena taking place in this process and different ways to approach them. In this project we chose to address them by the Classical Irreversible Thermodynamics (CIT), which might not be the easiest but provides a complete understanding.

The following theory will be built and supported by the local equilibrium hypothesis [5], which states:

“The local and instantaneous relations between thermodynamic quantities in a system out of equilibrium are the same as for a uniform system in equilibrium.”

or

“In every system in disequilibrium but close to equilibrium it can be assumed the existence of thermodynamic equilibrium in all its points, although the equilibrium conditions may vary from one point to another.”

Let us analyze what occurs inside the semiconductor.
2.1 Generated entropy: Phenomena Coupling

The generated entropy at certain point in a continuous system considering electrical and thermal exchange phenomena is:

\[ TdS = \delta Q = du - \Phi de \]  \hspace{1cm} 2.1

where \( T \) is temperature, \( S \) is entropy, \( Q \) is heat energy, \( u \) is internal energy, \( \Phi \) is the electrical potential and \( e \) is the unit of electrical charge. Regarding the variation in time when the state is close to equilibrium (the intensive variables \( T \) and \( \Phi \) are constant in time):

\[ T \frac{dS}{dt} = \frac{du}{dt} - \Phi \frac{de}{dt} \] \hspace{1cm} 2.2

The net entropy evolution at that local volume must be equal to zero or positive:

\[ \frac{dS}{dt} + \nabla \cdot \vec{J}_s = \gamma \geq 0 \] \hspace{1cm} 2.3

where \( \vec{J}_s \) is the entropy flux and \( \gamma \) the entropy sources in case they exist.

Adding the conservation of internal energy and electrical charge:

\[ \frac{du}{dt} + \nabla \cdot \vec{J}_u = 0 \] \hspace{1cm} 2.4

\[ \frac{de}{dt} + \nabla \cdot \vec{J}_e = 0 \] \hspace{1cm} 2.5

where \( \vec{J}_u \) and \( \vec{J}_e \) are the internal energy and electrical charge flux respectively.

Including these equations in equation 2.2:

\[ \frac{dS}{dt} = -\frac{1}{T} \nabla \cdot \vec{J}_u + \frac{\Phi}{T} \nabla \cdot \vec{J}_e \] \hspace{1cm} 2.6

Taking advantage of the nabla operator properties we can write:

\[ \frac{1}{T} \nabla \cdot \vec{J}_u = \nabla \left( \frac{1}{T} \frac{du}{dt} \right) - \vec{J}_u \cdot \nabla \left( \frac{1}{T} \right) \] \hspace{1cm} 2.7

\[ \frac{\Phi}{T} \nabla \cdot \vec{J}_e = \nabla \left( \frac{\Phi}{T} \frac{de}{dt} \right) - \vec{J}_e \cdot \nabla \left( \frac{\Phi}{T} \right) \] \hspace{1cm} 2.8

Subtracting them and using equation 2.6:

\[ \frac{dS}{dt} = -\frac{1}{T} \nabla \cdot \vec{J}_u + \frac{\Phi}{T} \nabla \cdot \vec{J}_e = -\nabla \left( \frac{1}{T} \frac{du}{dt} - \frac{\Phi}{T} \frac{de}{dt} \right) + \vec{J}_u \cdot \nabla \left( \frac{1}{T} \right) - \vec{J}_e \cdot \nabla \left( \frac{\Phi}{T} \right) \] \hspace{1cm} 2.9

\[ \frac{dS}{dt} + \nabla \left( \frac{1}{T} \frac{du}{dt} - \frac{\Phi}{T} \frac{de}{dt} \right) = \vec{J}_u \cdot \nabla \left( \frac{1}{T} \right) - \vec{J}_e \cdot \nabla \left( \frac{\Phi}{T} \right) \] \hspace{1cm} 2.10
Comparing it with 2.3:

\[ \mathbf{j}_s = \frac{1}{T} (\mathbf{j}_u - \mathbf{\varphi} \mathbf{j}_e) \quad 2.11 \]

\[ \gamma = \mathbf{j}_u \cdot \nabla \left( \frac{1}{T} \right) - \mathbf{j}_e \cdot \nabla \left( \frac{\mathbf{\varphi}}{T} \right) \geq 0 \quad 2.12 \]

We also know:

\[ \mathbf{j}_Q = \mathbf{j}_u - \mathbf{\varphi} \mathbf{j}_e \quad \mathbf{j}_u = \mathbf{j}_Q + \mathbf{\varphi} \mathbf{j}_e \quad 2.13 \]

So we obtain:

\[ \gamma = (\mathbf{j}_Q + \mathbf{\varphi} \mathbf{j}_e) \cdot \nabla \left( \frac{1}{T} \right) - \mathbf{j}_e \cdot \nabla \left( \frac{\mathbf{\varphi}}{T} \right) \geq 0 \quad 2.14 \]

\[ \gamma = \mathbf{j}_Q \cdot \nabla \left( \frac{1}{T} \right) + \mathbf{\varphi} \mathbf{j}_e \cdot \nabla \left( \frac{1}{T} \right) - \mathbf{j}_e \nabla \mathbf{\varphi} - \mathbf{\varphi} \mathbf{j}_e \cdot \nabla \left( \frac{1}{T} \right) \geq 0 \quad 2.15 \]

\[ \gamma = - \frac{\nabla T}{T^2} \mathbf{j}_Q - \frac{\nabla \mathbf{\varphi}}{T} \mathbf{j}_e \geq 0 \quad 2.16 \]

The importance of this last equation is evident for the condition \( \gamma \geq 0 \) refers to both processes, thermal and electrical, simultaneously.

Consequently, it implies a coupling between them allowing one to diminish the entropy as long as the other compensates it (one of them can evolve towards opposite direction of the one it would naturally do if it occurred individually). This coupling phenomenon is called thermoelectricity.

We can see in 2.16 what are called affinities or general forces \( \nabla T \), \( \nabla \mathbf{\varphi} \) and fluxes \( \mathbf{j}_Q \), \( \mathbf{j}_e \). Since they are coupled, each force affects both flows and for a state close to equilibrium the relation can be considered linear:

\[ \mathbf{j}_K = \sum_j \left( \frac{\partial \mathbf{j}_k}{\partial \mathbf{j}_j} \right)_0 \mathbf{j}_j = \sum_j L_{jk} \mathbf{j}_j \quad 2.17 \]

where \( L_{jk} \) are known as phenomenological coefficients. Thus, we can express heat and electric fluxes:

\[ \mathbf{j}_Q = L_{11} \frac{\nabla T}{T^2} + L_{12} \frac{\nabla \mathbf{\varphi}}{T} \quad 2.18 \]

\[ \mathbf{j}_e = L_{21} \frac{\nabla T}{T^2} + L_{22} \frac{\nabla \mathbf{\varphi}}{T} \]

These two equations describe the thermoelectric behavior of any material. Let us find the coefficients:

- If we consider a situation in which \( \nabla T = 0 \), we have \( \mathbf{j}_e = L_{22} \frac{\nabla \mathbf{\varphi}}{T} \); and also according to Ohm’s law \( \mathbf{j}_e = - \frac{\nabla \mathbf{\varphi}}{\rho} \) (where \( \rho \) is the electrical resistivity of the material):
If we now consider an open system where $\vec{J}_e = 0$, we find $0 = L_{21} \frac{\vec{V}T}{T} + L_{22} \frac{\vec{V}\phi}{T}$.

$$\vec{V}\phi_{\text{max}} = -\frac{L_{21}}{T L_{22}} \vec{V}T = -\alpha \vec{V}T$$

The term $\frac{\vec{V}\phi_{\text{max}}}{\vec{V}T} = -\frac{L_{21}}{T L_{22}} = -\alpha$ represents the Seebeck coefficient, the electromotive force generated by a difference of temperature.

Taking into account Onsager’s reciprocity theorem:

$$L_{21} = L_{12} = -\frac{\alpha * T^2}{\rho}$$

Regarding the heat flux at the same situation and considering Fourier’s law $\vec{J}_Q = -k \vec{V}T$ (where $k$ is the thermal conductivity of the material):

$$\vec{J}_Q = L_{11} \frac{\vec{V}T}{T^2} \frac{\alpha T}{\rho} \vec{V}\phi_{\text{max}} = \left(\frac{L_{11}}{T^2} + \frac{\alpha^2 T}{\rho}\right) \vec{V}T = -k \vec{V}T$$

$$L_{11} = -\left(k + \frac{\alpha^2 T}{\rho}\right) T^2$$

With all coefficients we finally obtain the two equations that govern over thermoelectricity:

$$\vec{J}_Q = -\left(k + \frac{\alpha^2 T}{\rho}\right) \vec{V}T - \frac{\alpha T}{\rho} \vec{V}\phi$$

$$\vec{J}_e = -\frac{\alpha}{\rho} \vec{V}T - \frac{1}{\rho} \vec{V}\phi$$

In a matrix form:

$$\begin{bmatrix} \vec{J}_Q \\ \vec{J}_e \end{bmatrix} = \begin{bmatrix} -k_E & -\alpha T \sigma \\ -\alpha \sigma & -\sigma \end{bmatrix} \begin{bmatrix} \vec{V}T \\ \vec{V}\phi \end{bmatrix}$$

where $k_E$ includes not only thermal conductivity but also convectivity, and $\sigma$ is the electrical conductivity.

The equation for the electric flux can be written:

$$\vec{V}\phi = -\alpha \vec{V}T - \vec{J}_e \rho$$

which represents the load line of a point in which there is an electromotive force $\varepsilon = -\alpha \vec{V}T$.

And introducing this equation into the first one we rewrite the heat flux:

$$\vec{J}_Q = -\left(k + \frac{\alpha^2 T}{\rho}\right) \vec{V}T - \frac{\alpha T}{\rho} \left(-\alpha \vec{V}T - \vec{J}_e \rho\right)$$

$$\vec{J}_Q = -k \vec{V}T + \alpha T \vec{J}_e$$
A P-type semiconductor produces a positive electromotive force in the same direction as the heat flows (following $-\nabla T$ direction), thus presenting a positive Seebeck coefficient. Exactly the opposite happens with a N-type semiconductor, presenting a negative Seebeck coefficient.

### 2.2 Energy balance

Considering the heat energy sources are big enough compared to $\overrightarrow{j_Q}$ so that $\nabla T$ is maintained in time, the system would be in a stationary mode, implying:

\[
\frac{du}{dt} = 0 \quad \nabla \cdot \overrightarrow{j_u} = 0 \tag{2.2.1}
\]
\[
\frac{de}{dt} = 0 \quad \nabla \cdot \overrightarrow{j_e} = 0 \tag{2.2.2}
\]

Using the divergence on $\overrightarrow{j_Q}$ to study the energy balance:

\[
\overrightarrow{j_Q} = \overrightarrow{j_u} - \phi \overrightarrow{j_e} \tag{2.2.3}
\]

\[
\nabla \cdot \overrightarrow{j_Q} = \nabla \cdot \overrightarrow{j_u} - \nabla (\phi \overrightarrow{j_e}) = \nabla \cdot \overrightarrow{j_u} - (\nabla \phi \overrightarrow{j_e} + \phi \nabla \cdot \overrightarrow{j_e}) \tag{2.2.4}
\]

\[
\nabla \cdot \overrightarrow{j_e} = -\nabla \phi \overrightarrow{j_e} \tag{2.2.5}
\]

Since the variation of inner energy is null, this balance of energy shows that the difference in the heat energy is transformed into potential energy or, in other words, into supplied energy to the load.

\[
\nabla \phi \overrightarrow{j_e} = -\alpha \nabla T \overrightarrow{j_e} - \overrightarrow{j_e} \rho \tag{2.2.6}
\]

*Supplied energy = Total work – Inner work loss*

By integration we can reach to the power equation on the whole semiconductor:

\[
\int \nabla \phi \overrightarrow{j_e} dV = \int (-\alpha \nabla T \overrightarrow{j_e} - \overrightarrow{j_e} \rho) dV \tag{2.2.7}
\]

\[
\iiint \overrightarrow{\nabla} \phi \overrightarrow{j_e} dAdx = \iiint (-\alpha \nabla T \overrightarrow{j_e} - \overrightarrow{j_e} \rho) dAdx \tag{2.2.8}
\]

\[
I \Delta \phi = -I \int a dT - I^2 R \tag{2.2.9}
\]

\[
\hat{I} \Delta \phi = -\hat{I} \hat{a} \Delta T - \hat{I}^2 \hat{R} \tag{2.2.10}
\]

where $\bar{\alpha}$ is the average $\alpha$ between the 2 temperatures:

\[
\bar{\alpha} = \frac{1}{\Delta T} \int \alpha dT \tag{2.2.11}
\]

The supplied power is then a function of state, not dependent on the distribution of $T$ inside the sample.
Integrating the heat flux over the pellet area:

\[ \int \vec{Q} \, dA = \int (-k \vec{V}T + \alpha T \vec{f}_e) \, dA \]

\[ \vec{Q} = -k \alpha \vec{V}T + \alpha T \vec{f} \]

2.2.1 Heat flux, closer look

Making a zoom into the divergence [6] of the heat flux and remembering \( \vec{V} \cdot \vec{J}_e = 0 \):

\[ \vec{V} \cdot \vec{J}_e = \vec{V}[-k \vec{V}T + \alpha T \vec{f}_e] \]

\[ \vec{V} \cdot \vec{J}_e = -\vec{V}[k \vec{V}T] + \vec{V} \alpha T \vec{f}_e + \alpha \vec{V}T \vec{f}_e + \alpha T \vec{V} \vec{f}_e \]

\[ \vec{V} \cdot \vec{J}_e = -\vec{V}[k \vec{V}T] + \vec{V} \alpha T \vec{f}_e + \alpha \vec{V}T \vec{f}_e \]

- Heat flux due to a non-linear distribution of T and to the variation of thermal conductivity with T:

\[ \vec{V}[k \vec{V}T] = \vec{V}k \vec{V}T + k \nabla^2 T = \frac{dk}{dT} (\nabla T)^2 + k \nabla^2 T \]

- Electrical work production and dissipation, Seebeck + Joule effect:

\[ \alpha \vec{V}T \vec{f}_e = -[\vec{V} \phi + \vec{f}_e \rho] \vec{J}_e \]

- Peltier-Thomson term:

\[ \vec{V} \alpha T \vec{f}_e = \vec{V} \left( \frac{\Pi}{T} \right) \vec{J}_e = T \vec{J}_e \left( \frac{\vec{V} \Pi}{T^2} - \frac{\vec{V} T}{T^2} \right) \]

\[ \vec{J}_e \left( \vec{V} \Pi - \alpha \vec{V} T \right) \]

When the process of electrical conduction occurs isothermal, the Peltier-Thomson term becomes \( J_e \vec{V} \Pi \) (where \( \Pi = \alpha T \) is the Peltier coefficient) and it is known as pure Peltier effect. It is pronounced when there is a change of material (implying a notable change of \( \Pi \)) and the effect is a release/absorption of heat in the junction.

When it is non-isothermal, we can write:

\[ \vec{J}_e \left( \frac{d\Pi}{dT} - \alpha \right) \vec{V} T = \vec{J}_e \tau \vec{V} T \]

where \( \tau \) is the Thomson coefficient. For better understanding, since we have \( \vec{V} T \) we can think of it as a series of Peltier effects due to the fact that the coefficient is not constant with the temperature. For this reason, some authors consider the distinction between Peltier and Thomson effect artificial; being Peltier effect a particular case of Thomson effect or, in reverse, being Thomson effect a succession of Peltier effects along the material.
The Peltier-Thomson term can also be written:

$$\nabla \alpha T \mathbf{j}_e = \left( \frac{d\alpha}{dT} \nabla T \right) T \mathbf{j}_e$$

with the advantage that for small temperature differences we can take $\frac{d\alpha}{dT}$ as a constant.

All together:

$$\nabla \cdot \mathbf{j}_Q = -\nabla \cdot \nabla \phi_{te} - \nabla \phi_{te} - \mathbf{j}_e^2 \rho + \frac{d\alpha}{dT} T \nabla T \mathbf{j}_e$$

The interpretation of this equation as the balance of energy states that the difference of heat flux is due to a non-linear distribution of $T$, to a variation of the thermal conductivity with the $T$, to a transformation into electrical work, to a loss due to the Joule effect and to a gain/loss due to the Peltier-Thomson effect.

Remembering that we are analyzing a stationary mode, and making use of equations 2.13 and 2.2.1.10:

$$\nabla \cdot \mathbf{j}_Q = -\nabla \phi_{te} = -\nabla [k \nabla T] - \nabla \phi_{te} - \mathbf{j}_e^2 \rho + \frac{d\alpha}{dT} T \nabla T \mathbf{j}_e$$

$$-\nabla [k \nabla T] - \mathbf{j}_e^2 \rho + \frac{d\alpha}{dT} T \nabla T \mathbf{j}_e = 0$$

$$\nabla [k \nabla T] = -\mathbf{j}_e^2 \rho + \frac{d\alpha}{dT} T \nabla T \mathbf{j}_e$$

Integrating with regard to the volume of the pellet:

$$\int \nabla [k \nabla T] \, dV = \int \left( -\mathbf{j}_e^2 \rho + \frac{d\alpha}{dT} T \nabla T \mathbf{j}_e \right) \, dV$$

$$Ak \nabla T = -\frac{l^2}{A} \rho x + \frac{d\alpha T^2}{dT} \frac{1}{2} + C$$

What is physically happening can be deduced from this last equation.

When there is no current, the $T$ descends linearly from the hot end to the cold end ($T_H$ to $T_C$). Once a current appears, so do Joule and Thomson release of heat, increasing the temperature of every point (according to the heat capacitance of the material) until a new equilibrium is reached, in which all released heat flows away (due to Fourier transfer and the modified $\nabla T$) from the element at the same ratio that it is appearing.

We can conclude that in a closed circuit the $T$ along the semiconductor follows a non-linear distribution and so will the heat flux do since there are heat sinks/sources. Further integration of this equation leads to the distribution of $T$ along the semiconductor and to the possibility of applying the boundary conditions ($T(0) = T_H$; $T(l) = T_C$) to find the constants of integration. With it precise information about the heat flux at every point would be achieved, which can provide accuracy for the calculations on the efficiency and, in case of the use as a cooler, for the rate of pumped heat.

Numerical methods are to be used to achieve complex results. We will suggest and follow a different, simplified path that will provide accurate results.
2.2.1.1 Particular considerations for the device

Until here theory has been developed. From this point on we will make some simplifications of the theory for the case of study of the device.

While the Seebeck coefficient is strongly T-dependent (Fig. 15), the electrical resistivity and thermal conductivity are not [7]. For this reason they will be considered as a constant along the pellet even if a gradient of T exists.

The generated voltage and power is defined in equations 2.27 and 2.2.10 respectively. For the heat flux let us analyze 2.2.1.15:

Separating the heat transfer into the different effects, at the hot and cold end we find the following fluxes:

<table>
<thead>
<tr>
<th>Effect</th>
<th>Hot</th>
<th>Cold</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fourier</td>
<td>$Q_F = -kA \frac{\Delta T}{l}$</td>
<td></td>
</tr>
<tr>
<td>Joule</td>
<td>$\frac{1}{2} I^2 R$</td>
<td>$+\frac{1}{2} I^2 R$</td>
</tr>
<tr>
<td>Thomson</td>
<td>$-rl \int T , d\alpha$</td>
<td>$+(1-r)l \int T , d\alpha$</td>
</tr>
<tr>
<td>Carriers</td>
<td>$+rH_T H_H I$</td>
<td>$-rC_T C_C I$</td>
</tr>
</tbody>
</table>

with $r$ being the ratio of the amount of energy released by the Thomson effect that escapes through the hot side.

Simplified model for calculations

The carriers have the capacity to hold heat energy to an amount of $Q_P = \alpha T I$, which suffers a variation meanwhile they move through the semiconductor (From point A to B):

$$dQ_P = (T \, d\alpha + \alpha dT)I$$

Variation of carrier heat = Release by Thomson effect + Transformation to work
According to table 1, the heat through the hot and cold end:

\[
\tilde{q}_H = -kA \frac{\Delta T}{l} - \frac{1}{2} I^2 R - rl \int T \, da + \alpha_H T_H \tilde{I} \tag{2.3.1}
\]
\[
\tilde{q}_C = -kA \frac{\Delta T}{l} + \frac{1}{2} I^2 R + (1 - r)l \int T \, da + \alpha_C T_C \tilde{I} \tag{2.3.2}
\]

The new graph (Fig. 6) is generated by the unfairly dividing the Thomson heat and adding it up to the to the carriers capacity (Fig. 5), which turns into an error that slightly affects the calculations on the heat fluxes. However, it does not affect the power and the easiness gained outweighs the loss of accuracy for this present study.

\[
-r l \int T \, da + \alpha_H T_H \tilde{I} \approx \bar{a} T_H \tilde{I}
\]
\[
(1 - r) l \int T \, da + \alpha_C T_C \tilde{I} \approx \bar{a} T_C \tilde{I}
\]

The heat flux then becomes:

\[
\tilde{q}_H = -kA \frac{\Delta T}{l} - \frac{1}{2} I^2 R + \bar{a} T_H \tilde{I} \tag{2.3.3}
\]
\[
\tilde{q}_C = -kA \frac{\Delta T}{l} + \frac{1}{2} I^2 R + \bar{a} T_C \tilde{I} \tag{2.3.4}
\]

It is remarkable the simplicity that these equations present with respect to the previous ones since only the average Seebeck coefficient appears representing both Thomson release/absorption and the carriers capacity.
2.3 Working conditions

To construct the TEG, semiconductors must be connected electrically in series to add up their individual voltages and thermally in parallel to take maximum leverage on the difference of temperature.

![Fig. 7. Thermoelectric device formed by single type semiconductor](image)

To reduce thermal Fourier transfer P-type and N-type pellets are used so that the electrodes (superconductors thermally and electrically) are positioned in isothermal planes.

![Fig. 8. Sketch of stretchable thermoelectric devices and its materials](image)

With regard to the connections between semiconductors, there is a relevant factor to take into account: the electrodes are modeled as superconductors, their net balance of carriers is close to be null leading to a Seebeck coefficient very proximate to zero.

This turns out into a release/absorption of heat in the junction electrode-semiconductor, known as the Peltier effect.

Let us illustrate it with a particular case. Focusing on the P-type semiconductor pellet and its junctions when we subject it to a difference of T and the circuit is closed:

At the hot end, the heat flux:

\[
\dot{Q}_{H-E} = -kA\nabla T
\]

2.4.1

At the end of the pellet:

\[
\dot{Q}_{H-P} = -kA\nabla T + \alpha_H T_H \dot{I}
\]

2.4.2
Subtracting them:

$$\dot{Q}_{H-P} - \dot{Q}_{H-E} = \alpha_H T_H I$$  \hspace{1cm} 2.4.3

Right in the hot junction and current streamwise, the heat flux increases its value $\alpha_H T_H I$, which turns into an absorption of heat energy from the surroundings.

At the cold end, the heat flux:

At the end of the pellet:

$$\dot{Q}_{C-P} = -kA\overline{\nabla}T + \alpha_C T_C I$$  \hspace{1cm} 2.4.4

In the electrode, since it is a superconductor the value of $\alpha \approx 0$:

$$\dot{Q}_{C-E} = -kA\overline{\nabla}T$$  \hspace{1cm} 2.4.5

And the difference:

$$\dot{Q}_{C-E} - \dot{Q}_{C-P} = -\alpha_C T_C I$$  \hspace{1cm} 2.4.6

Right in the cold junction the heat flux decreases its value $|\alpha_C T_C I|$, which turns into a release of heat energy to the surroundings.

If it is working as a thermoelectric generator, it transports heat from the hot end to the cold one. It is important to note that the amount of absorbed heat in the hot end is higher than that released in the cold one, being the difference the transformation into work and the release by the Thomson effect.

If we reverse the current by applying a superior voltage than the electromotive force of the Seebeck effect, it works as a heat pump, transporting heat from the cold end to the hot one.

Again, the heat absorbed in the cold end is lower than that released in the hot one, so the carrier completes its missing heat energy from the supplied electrical power and from the surroundings by the Thomson effect.

The heat pump will reach to an end if the heat is not dissipated from the faces due to a growing Fourier and Seebeck effect.
2.3.1 Characterization of the device

Heat flux per pellet due to Fourier transfer, open circuit.

We can divide the structure in three layers:

two cover layers of polydimethylsiloxane (PDMS) (thickness \(l\); area A) and the bismuth telluride (BiTe) semiconductor pellet in the middle (thickness \(l_p\); area A). Galinstan electrodes are not taken into account since its thickness is 100 µm and its thermal conductivity is enormous [7] compared to the other materials. Exemplifying on a P-type pellet:

Q through the structure:

\[
\dot{Q} = - \frac{(T_c - T_h)}{\frac{l}{kA} + \frac{l_p}{k_{pA}} + \frac{l}{kA}}
\]

Introducing the values of chapter 3.Materials and methods:

\[
\dot{Q} = -\Delta T * 2,65 \text{ mW/K}
\]

Q through first layer of PDMS:

\[
\dot{Q} = -\frac{kA}{l}(T_1 - T_h)
\]

Q through Pellet:

\[
\dot{Q} = -\frac{k_{pA}}{l_p}(T_2 - T_1)
\]

Q through second layer of PDMS:

\[
\dot{Q} = -\frac{kA}{l}(T_c - T_2)
\]

Since there is no source or swell the fluxes must be similar:

\[
-\frac{k_{pA}}{l_p}(T_2 - T_1) = -\frac{(T_c - T_h)}{\frac{l}{kA} + \frac{l_p}{k_{pA}} + \frac{l}{kA}}
\]

\[
\Delta T_p = \Delta T - \frac{kl_p}{2lk_p + kl_p} = \Delta T * 0,32
\]

So the pellet inside the PDMS cover suffers \(\Delta T_p = \Delta T * 0,32\). We can see the high insulating properties that the PDMS shows, reducing \(\Delta T\) in such amount regardless of being a rather thin layer.

Once the circuit is closed, the heat flux through the pellet is modified due to the Joule loss, Thomson effect and the contribution of the carriers.
Electrical resistance

One thermocouple

\[ R_t = \frac{\rho_p l_p}{A_p} + \frac{\rho_n l_n}{A_n} + 2 \frac{\rho_g l_g}{A_g} + 4b = R_p + R_n + 2R_g + 4b \]

n-thermocouples device

\[ R_D = a + nR_t \]

where \( a \) is a basal resistance due to the contact galinstan-copper in the electrodes that connect to the load; \( R_p, R_n, R_g \) the resistances of P-type pellets, N-type pellets and galinstan electrodes respectively; \( b \) is the contact resistance between galinstan-BiTe.

Thermal conductivity

The spaces between semiconductors are not included since they are pure PDMS and its thermal conductivity is around 10 times lower than that of BiTe.

One thermocouple

\[ K_t = \left[ \frac{l_p}{k_p A_p} + 2 \frac{l_{PDMS}}{k_{PDMS} A_p} \right]^{-1} + \left[ \frac{l_n}{k_n A_n} + 2 \frac{l_{PDMS}}{k_{PDMS} A_n} \right]^{-1} \]

\[ K_t = \left[ k_p^{-1} + 2K_{PDMS-p}^{-1} \right]^{-1} + \left[ k_n^{-1} + 2K_{PDMS-n}^{-1} \right]^{-1} \]

n-thermocouples device

\[ K_D = nK_t \]

Figure of merit

\[ Z = \frac{n^2 \bar{a}^2}{KR} \]

The figure of merit represents the thermoelectric quality of the materials and it is to be increased to improve the performance of such devices. Good thermoelectric materials should possess large Seebeck coefficients to maximize the electromotive force, high electrical conductivity to minimize Joule heating and low thermal conductivity to minimize Fourier transfer.

However, not only is the materials nature relevant but also their geometries [8].

Taking a closer look to the product \( KR \) without considering neither the cover of PDMS nor the contact resistances:

\[ KR = n^2 \frac{k_p}{\sigma_p} \left( 1 + \frac{1}{xk_{pn}} + x\sigma_{pn} + \frac{\sigma_{pn}}{k_{pn}} \right) \]

where \( \sigma_{pn} = \frac{\sigma_p}{\sigma_n}, k_{pn} = \frac{k_p}{k_n}, x = \frac{A_p}{A_n} \frac{l_n}{l_p} \)

The geometrical factor \( x \) can play an important role in the figure of merit of the device. The value that maximizes \( KR \):

\[ x_{min-KR} = \frac{1}{\sqrt{\sigma_{pn}k_{pn}}} \quad KR_{min} = n^2 \frac{k_p}{\sigma_p} \left( 1 + \frac{\sigma_{pn}}{k_{pn}} \right) \]
2.4 Practical equations for thermoelectric generator and heat pump mode

In this section we present the equations in a non-vectorial mode for a more intuitive understanding.

All following variables refer to absolute values and to a single thermocouple \((\bar{\alpha}_t = \bar{\alpha}_p + \bar{\alpha}_n)\).

- **Thermoelectric generator mode**

![Diagram](Image)

**Total heat flux**

- Total heat incoming through the hot side:
  \[
  \dot{Q}_H = K_t \Delta T - \frac{1}{2} I^2 R_t + \bar{\alpha}_t T_H I \quad 2.5.1
  \]

- Total heat released through the cold side:
  \[
  \dot{Q}_C = K_t \Delta T + \frac{1}{2} I^2 R_t + \bar{\alpha}_t T_C I \quad 2.5.2
  \]

**Load line**

\[
\Delta \phi = \bar{\alpha}_t \Delta T - IR_t \quad 2.5.3
\]

**Supplied power**

\[
P_{ef} = I \Delta \phi = \bar{\alpha}_t T I - I^2 R_t \quad 2.5.4
\]

The maximum supplied power corresponds to a load of the same value of the inner resistance \(R = R_t\):

\[
P_{\text{max}} = \frac{E I}{2} = \frac{E^2}{4R_t} = \frac{(\bar{\alpha}_t \Delta T)^2}{4R_t} \quad 2.5.5
\]

where \(E\) is the electromotive force generated by the difference of temperature.
Efficiency

The efficiency is the relation between the supplied power to the total heat income:

\[
\eta = \frac{\text{Supplied Power}}{\text{Heat energy income}} = \frac{I\bar{a}_t\Delta T - I^2R_t}{K_t\Delta T - \frac{1}{2}I^2R_t + \bar{a}_tT_HI}
\]  

2.5.6

We will refer the efficiency to the maximum possible, which according to Carnot:

\[
\eta_{\text{max}} = \frac{T_H - T_C}{T_H} = \frac{\Delta T}{T_H}
\]  

2.5.7

Then the relative efficiency is:

\[
\eta_r = \frac{\eta}{\eta_{\text{max}}} = \frac{I\bar{a}_t\Delta T - I^2R_t}{K_t\Delta T - \frac{1}{2}I^2R_t + \bar{a}_tT_HI} * \frac{T_H}{\Delta T}
\]  

2.5.8

- **Heat pump mode**

![Fig. 11. Heat fluxes directions in heat pump mode](image)

Transported heat flux

Total heat absorbed through the cold side:

\[
\dot{Q}_c = -K_t\Delta T - \frac{1}{2}I^2R_t + \bar{a}_tT_CI
\]  

2.5.9

Total heat released to the hot side:

\[
\dot{Q}_H = -K_t\Delta T + \frac{1}{2}I^2R_t + \bar{a}_tT_HI
\]  

2.5.10

Consumed power

\[
P = \bar{a}_t\Delta T I + I^2R_t
\]  

2.5.11
Equilibrium $\Delta T$

When the heat absorbed through the cold side turns null it means that the carriers are moving the same amount of heat that it is arriving due to the Fourier transfer and half Joule release. At that moment the device cannot keep increasing $\Delta T$, is has reached the equilibrium.

$$\dot{Q}_c = -K_t \Delta T - \frac{1}{2} I^2 R_t + \bar{a}_T T_c I = 0 \quad 2.5.12$$

$$\Delta T = \left( -\frac{1}{2} I^2 R_t + \bar{a}_T T_c I \right) \frac{1}{K_t} \quad 2.5.13$$

Optimum I

Since the Joule effect grows proportional to the square of the current, there is a point in which further increase of the intensity turns into a decrease of heat transport.

$$\frac{d\dot{Q}_c}{dI} = -R_t + \bar{a}_T T_c = 0 \quad 2.5.14$$

$$I_{op} = \frac{\bar{a}_T T_c}{R_t} \quad 2.5.15$$

$I_{optimum}$ is the current that maximizes the heat transport and so the reached $\Delta T$ by this current will be maximum for the device.

$$\Delta T_{max} = \left[ -\frac{1}{2} \left( \frac{\bar{a}_T T_c}{R_t} \right)^2 R_t + \left( \frac{\bar{a}_T T_c}{R_t} \right)^2 \right] \frac{1}{K_t} = \frac{1}{2} \frac{(\bar{a}_T T_c)^2}{R_t K_t} \quad 2.5.16$$

![Fig. 12. Difference of $T$ achieved depending on the applied current](image)

Efficiency

The efficiency is the heat pumped from the cold side in relation to the supplied power:

$$\eta = \frac{\text{Pumped heat}}{\text{Supplied Power}} = \frac{-K_t \Delta T - \frac{1}{2} I^2 R_t + \bar{a}_T T_c I}{\bar{a}_T \Delta T I + I^2 R_t} \quad 2.5.17$$
3 MATERIALS AND METHODS

3.1 Device fabrication

The aim of this project is to research on alternative materials and methods to fabricate not only a flexible thermoelectric generator but also stretchable, achieving great shape conformability and thus optimum contact for non-flat surfaces.

For this purpose, semiconductor BiTe pellets will be embedded into a PDMS matrix and connected via galinstan electrodes, which is a liquid alloy at temperatures over -19 °C. This will turn into rigid islands floating into elastic polymer interconnected by liquid electrodes. The device will be a compound of rigid parts but stretchability will be still achieved focusing all strain into the polymer section, whose Young’s modulus is low.

The design of the structure requires parallel positioning of the semiconductor pellets with regard to the thermal flux, and series positioning regarding the electromotive force.

![Sketch of stretchable thermoelectric device with 4 thermocouples. BiTe pellets are 2.8x2.8 mm² in width and 1 mm height. The galinstan electrodes are 2.8x6.6 mm² and 0.1 in height, covering two pellets and leaving 1 mm of separation in between them. All elements are embedded in a matrix of PDMS with a thickness of 1.30 mm (it covers the BiTe pellets and galinstan with a 0.15 mm layer on each side).](image)

Materials:

- Plastic film
- Wacker PDMS
- Galinstan
- Hot plate and oven
- Sharp blade
- BiTe pellets, P-type and N-type
- Copper foil
- Spray pistol for galinstan
- Precision roller
- Microscope glasses
Method:

Wacker PDMS pre-polymer was mixed with its curing agent in proportion 9:1 and properly stirred until homogeneity was achieved. The mix was subdued to a vacuum for 20 minutes and rested on a freezer at -18°C until a free bubble state was reached.

Some PDMS was poured onto a thin, clean plastic film and extended to a 150 µm thick layer with the precision roller.

Leaving the film at room temperature 6 minutes led the PDMS to a half-cured state, then a mask with the electrode design was placed on top and galinstan was sprayed, creating a pattern with the dimensions 2.8x6.6x0.1 mm³. After removing the mask, P-N bismuth telluride pellets and the two cupper electrodes were carefully placed on the resulting pattern of liquid electrodes.

The pellets and the copper electrodes had been previously sprayed with galinstan (Method 2) to ensure proper contact to the electrodes. An undesired contact resistance appears if this step is skipped (Method 1; Fig. 23).

Then the whole structure was surrounded by a wall of the same height as the pellets (in this case using microscope glasses) creating a pool around them. PDMS was poured carefully, allowing it to move by superficial tension rather than by gravity so that it smoothly filled up all space in between the pellets but avoided their top faces.

Once a flat PDMS-Pellet surface was achieved, the whole structure was half cured at room temperature for 2 hours. The complementary electrode mask was placed on top and galinstan was spayed. After removing the mask, fresh PDMS was poured on top and laminated with the roller to a 150 µm thick layer again.

The sample was then placed into the oven for another 2 hours at 75 °C.

Finally, the device was cut and extracted from the pool.

Device improvements

Devices with a variation on the outer layers were also crafted in order to improve the thermal conductivity of PDMS by mixing it in a 1:4 w/w ratio with galinstan (it maintains its electrical insulator properties).

Devices were also crafted using Ecoflex PDMS instead of Wacker PDMS to increase the stretchability (Young’s modulus = 55 kPa).
Table 2. Reference properties of the components of the stretchable thermoelectric device

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical formula</td>
<td>(C$_2$H$_6$OSi)$_n$</td>
<td>Bi$_2$Te$_3$</td>
<td>Ga(68.5%) In(21.5%) Sn(10%)</td>
</tr>
<tr>
<td>Density</td>
<td>0.97 g/cm$^3$</td>
<td>7.64 g/cm$^3$</td>
<td>6.44 g/cm$^3$</td>
</tr>
<tr>
<td>Young's modulus</td>
<td>360-870 kPa</td>
<td>50 GPa</td>
<td>-</td>
</tr>
<tr>
<td>Poisson ratio</td>
<td>0.5</td>
<td>0.3</td>
<td>-</td>
</tr>
<tr>
<td>Tensile or fracture strength</td>
<td>2.24 MPa</td>
<td>20-40 MPa</td>
<td>-</td>
</tr>
<tr>
<td>Melting point</td>
<td>-</td>
<td>586 °C</td>
<td>-19 °C</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>0.15 W/m K</td>
<td>1.20 W/m K</td>
<td>16.50 W/m K</td>
</tr>
<tr>
<td>Electrical conductivity</td>
<td>2.50x10$^{-14}$ S/m</td>
<td>1.10x10$^5$ S/m</td>
<td>3.46x10$^6$ S/m</td>
</tr>
<tr>
<td>Biocompatibility</td>
<td>Nonirritating to skin, no adverse effect on rabbits and mice, only mild inflammatory reaction when implanted</td>
<td>May emit toxic fumes when heated to decomposition May react slowly with water to evolve toxic gases</td>
<td>Non-toxicity Non-reactivity</td>
</tr>
<tr>
<td>Other</td>
<td>Highly hydrophobic, contact angle 90-120°</td>
<td>Seebeck Coefficient</td>
<td>Seebeck Coefficient</td>
</tr>
</tbody>
</table>

100-287 μV/K ~0 μV/K

Fig 14. Chemical structure of PDMS
3.2 Measurement Setup

In order to measure the performance of the thermoelectric generators a set-up was built in. The aim of the setup is to fix a temperature in each face of the sample and read its performance.

It was monitored from a LabView software that used a PID control system, analyzing the temperature readings on different points of the setup and applying current to Peltier elements in concordance to them until the desired temperatures were achieved with a tolerance of ±0.05 °C.

The setup consists of:

Data acquisition device DAQ

This device has the capacity to gather information through its 20 channels, which can be set for temperature or voltage measurement. In case of temperature 6 channels were used to perform the readings on different points along the setting by k-type thermocouples, 3 of them in the cold side and 3 in the hot side. More specifically, in each side, 2 of them were in between the cupper block and the Peltier element, whose readings were considered to be approximately the temperature on the sample surface due to the high thermal conductivity of cupper, and the other one to the other face of the Peltier element. The function of this last one is to secure the Peltier element preventing excess of difference of temperature through it, which could be harmful. Another two channels consisting of copper wires were used to measure voltage on the devices.

TEG special conditioning device

Formed by two cupper blocks in charge of gripping the sample and fixing the temperature on its faces, a Peltier element on each block to heats it up or to cools it down, and two heat exchangers that facilitate heat dissipation enabling the Peltier elements to reach higher difference of temperatures.

Sourcemeter

This device not only can measure voltage and current but also offers the possibility of acting as a potentiometer. It was used to sweep the performance of the sample, from short-circuit to open-circuit state, obtaining readings on several points of the load line while maintained the sample at a constant difference of temperature.

Direct current supplier

These were in charge of supplying power to the thermoelectric heaters/coolers.
4 RESULTS

4.1 Pellets

Seebeck coefficient

Measurements of the Seebeck coefficient were taken in 12 pellets of each type (table 4) by setting $(10±0.1) \degree C$ difference on the faces at $25 \degree C$ average temperature and measuring the electromotive force in an open circuit.

\[
\Delta \phi = - \int a dT - IR
\]

\[
\Delta \phi = -\bar{a} \Delta T - IR
\]

\[
\bar{a} = -\frac{\Delta \phi_{\text{max}}}{\Delta T}
\]

Example of reading by DAQ on a N-type pellet:

Table 3. Example of data reading by the DAQ

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1.98E-03</td>
<td>30.00</td>
<td>20.03</td>
<td>9.97</td>
<td>-157.41</td>
<td></td>
</tr>
<tr>
<td>1.98E-03</td>
<td>29.99</td>
<td>20.02</td>
<td>9.97</td>
<td>-157.53</td>
<td></td>
</tr>
<tr>
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<td>29.99</td>
<td>20.01</td>
<td>9.98</td>
<td>-157.38</td>
<td></td>
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<tr>
<td>1.98E-03</td>
<td>30.00</td>
<td>20.02</td>
<td>9.98</td>
<td>-157.35</td>
<td></td>
</tr>
<tr>
<td>1.98E-03</td>
<td>30.00</td>
<td>20.01</td>
<td>9.99</td>
<td>-156.96</td>
<td></td>
</tr>
</tbody>
</table>

Table 4. Seebeck coefficient measurements on BiTe pellets at $25 \degree C$

<table>
<thead>
<tr>
<th>Pellet</th>
<th>Average α (µV/K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>P</td>
</tr>
<tr>
<td>1</td>
<td>-157.33</td>
</tr>
<tr>
<td>2</td>
<td>-144.59</td>
</tr>
<tr>
<td>3</td>
<td>-152.67</td>
</tr>
<tr>
<td>4</td>
<td>-154.23</td>
</tr>
<tr>
<td>5</td>
<td>-147.75</td>
</tr>
<tr>
<td>6</td>
<td>-134.94</td>
</tr>
<tr>
<td>7</td>
<td>-149.74</td>
</tr>
<tr>
<td>8</td>
<td>-142.15</td>
</tr>
<tr>
<td>9</td>
<td>-149.29</td>
</tr>
<tr>
<td>10</td>
<td>-154.24</td>
</tr>
<tr>
<td>11</td>
<td>-137.32</td>
</tr>
<tr>
<td>12</td>
<td>-151.98</td>
</tr>
</tbody>
</table>

Mean (µ) | -148 | 139 |
Standard Deviation (σ) | 7 | 9 |
The total amount of pellets was 200 units, so when choosing them randomly to craft the device and assuming the Seebeck coefficient follows a normal distribution, the variation within a 95% interval of confidence was:

\[ \bar{\alpha} = \mu \pm 1.96 \frac{\sigma}{\sqrt{12}} \left( \sqrt{1 - \frac{12}{200}} \right) \]

\[ \bar{\alpha}_p = 139 \pm 1.96 \frac{9}{\sqrt{12}} \left( \sqrt{1 - \frac{12}{200}} \right) = (139 \pm 5) \mu V/K \]

\[ \bar{\alpha}_n = -148 \pm 1.96 \frac{7}{\sqrt{12}} \left( \sqrt{1 - \frac{12}{200}} \right) = -(148 \pm 4) \mu V/K \]

\[ \bar{\alpha}_{Device} = n(287 \pm 9) \mu V/K \]

Characterization of the Seebeck coefficient was also made along T[20-100] °C. The means to get the approximation to such curve were reading the average coefficient at \( \Delta T = 5 \) °C in steps of 5 °C on the average T. Once the points for each average T were taken, the results showed that the variation indeed can be approximated by a degree one square fit curve for the interval T[20-100] °C with a regression factor of \( R^2 = 99\% \).

Example reading (N-type had the sign changed):

![Graph showing the variation of Seebeck coefficient with temperature](image)

**Fig. 15.** Variation of Seebeck coefficient with T
More thorough measurements were taken on the same population of pellets:

Fig. 16. Temperature dependence of Seebeck coefficient of P-type (A) and N-type (B) BiTe semiconductors [9]
4.2 Device Measurements

Load lines were measured at 5, 10, 15, and 20 °C of difference in between the faces of the devices with the sourcemeter acting as a voltmeter and as a direct current source varying its resistance (R) from 0 to \( \infty \) Ω. Supplied power was extracted from the data and was plotted against the relation \( R/R_o \) (external load resistance/inner resistance). Open circuit voltages (\( V_0 \)) were also extracted and plotted against the difference of T.

**Load line (Eq. 2.5.3)**  
\[ \Delta \phi = IR = \bar{\alpha} t \Delta T - IR_o \]

**Supplied Power (Eq. 2.5.4)**  
\[ P_{ef} = I^2 R = \bar{\alpha} t \Delta T I - I^2 R_o \]

In the regression equations of the load lines, the x coefficient represents and the constant the open-circuit voltage. Where the line crosses the X axis, the short-circuit current (I_{sc}) can be read. The maximum supplied power corresponds, as predicted in theory, to a load of the same value of the inner resistance \( R = R_o \).

4.2.1 PDMS

![Graphs of load lines and supplied power](image-url)
In Fig. 17, $V_0$ is shown as the constant of the regression lines. The resistance is the x coefficient, it is proportional to the number of thermocouples, although a basal resistance is present due to the contact to the copper electrodes (further explanation is presented in the discussion). The maximum supplied power corresponds to $R/R_0=1$.

In Fig. 18 it is perceptible how $V_0$ is linearly proportional to the temperature difference and also to the number of thermocouples.
4.2.2 Load line dependence on Average T

![Graph](image)

Fig. 19. Evaluation of the performance of an 8-pair device at different average temperatures.

The open-circuit voltage slightly decreased as Fig. 19 shows and the resistance increased when the average T was raised. These two factors imply a reduction in the supplied power.

4.2.3 Comparison to initial fabrication method

![Graph](image)

Fig. 20. Comparison between fabrication methods on a 16-pairs device at 25ºC average T, ΔT 10ºC.

Fig. 20 shows both methods of fabrication. In method 1 the semiconductor pellets and copper electrodes were placed on top of the galinstan electrodes. In method 2 galinstan was previously sprayed on the surface contact of the pellets and copper electrodes and then placed on top. The inner resistance was reduced by a factor ten, implying ten times higher short-circuit current and maximum supplied power.
4.2.4 Improvement of thermal conductivity of the outer layers by using composite PDMS

In Fig. 21 it is shown how the improvement on the thermal conductivity of the composite led to an increase of the open-circuit voltage up to 1.6 times and of the supplied power up to 2.5 times.
Fig. 2. Comparison of open circuit voltage versus temperature difference of a 1-pair device fabricated entirely with PDMS to a 1-pair device with composite PDMS in the outer layers.

Fig. 22 shows the difference in the electromotive force of the devices due to the improvement of the thermal conductivity, which is 1.6 times.

4.2.5 Evaluation of Ro (inner resistance) at 25°C.

In the regression equation of Fig. 23, the x coefficient is the resistance of each thermocouple and the constant is the basal resistance due to the contact to the copper electrodes. A study of R(n) shows a high basal resistance of α = 0.34 Ω. The reason lies in an undesired contact resistance to the copper electrodes due to deficient wetting and oxide formation.
5 DISCUSSION

The use of PDMS as substrate for the packaging of the semiconductors entails several advantages such as:

- Deformability and stretchability of the sample, making a fact the conformability to non planar surfaces.
- Transparency, facilitating the observation of the inner structures visually or under microscope.
- Biocompatibility.
- Simple and inexpensive production.
- Possibility of bonding layers to each other if a multilayer device is desired/needed.

On the other hand, as predicted in theory, even with only a thin layer (150 µm) of PDMS as a cover, the voltage obtained is around one third of the one expected if the heat sources/sinks were in direct contact to the semiconductors. Small variations on the cover thickness led to notable variation on the performance of the devices, being of need high accuracy on the crafting process.

Also, the adhesion of PDMS-BiTe is deficient, resulting in detachment when low strain affects the bond. Galinstan can then flow through the generated gap covering part of the lateral face of the pellet and thus shortening its effective length, implying a reduction on the electromotive force.

Devices crafted following the suggested method with Wacker PDMS can afford substantial bending before inner leakage of galinstan, but not stretching. Stretchability was achieved using Ecoflex PDMS, whose Young’s modulus is several times lower than that of Wacker PDMS and whose adhesion to BiTe was enough to sustain the stress caused by stretching the substrate up to 50%.

Wacker and Ecoflex PDMS devices generated an open circuit voltage of around 37% compared to the maximum possible value of the pellets (if they were uncovered) and thus, 14% of their potential power.

If higher power per area is desired, such cover is not to be reduced to prevent apparition of breaches and outwards leakage of galinstan. Instead, composite PDMS layer (PDMS-Galinstan 1:4 w/w), same thickness, was shown to offer higher thermal conductivity leading to an open circuit voltage 1.6 times higher than PDMS, reaching values of 60% compared to the maximum possible value of the pellets and thus, 36% of their potential power. It also entails a loss of the transparency and biocompatibility is still to be studied.

With regard to the galinstan electrodes used for the connections between semiconductors, the main feature is its liquid state at temperatures above -19 °C, providing superb conformation to its container even if deformation takes place in it. It also offers high thermal and electrical conductivity, making it the ideal choice for stretchable electronics.
When using liquid alloys as electrodes, the wetting to the different elements should be taken into account. A deficient wetting will lead to an improper connection, which will turn into an undesired, notable increase of the resistance. Unfortunately, this is the case between galinstan and BiTe, as it is shown in the comparison between two different crafting methods in Fig. 20. Nevertheless, this hindrance was addressed by spraying the galinstan on the pellets instead of on the PDMS, achieving a generous reduction on the final resistance of around ten times, and thus a great increase of the maximum supplied power of the same proportion.

BiTe semiconductors were chosen due to the fact that bismuth telluride offers the highest figure of merit among the different semiconductors for temperatures in between (250-600) K.

With regard to the dependence of the Seebeck coefficient to the temperature, it can be considered linear for the studied rank of temperatures as shown in Fig. 15 with a constant, quite homogeneous slope from 25 ºC to 100 ºC.

Regarding these results, it was expected for the devices to show higher power for superior average temperatures of work due to an increase on the open circuit voltage. This was not occurring (Fig. 19). Contradicting the expectations, the open circuit voltage of the device dropped with the increase of the average temperature. This is most likely due to an expansion of the Wacker PDMS cover which would imply a reduction on the difference of T suffered by the semiconductors. When composite PDMS and Ecoflex PDMS were used as outer layers, the open circuit voltage slightly grew with the average temperature.

An increase of the resistance appears with the higher average temperatures due to a raise on the value of the resistivity of the materials and possibly to a variation on the quality of the junctions of the different materials.

A study of R(n) shows a high basal resistance of $a = 0.34 \, \Omega$. The reason lies in an undesired contact resistance to the copper electrodes due to deficient wetting and oxide formation.

Simple calculations on the theoretical resistances of BiTe pellets and galinstan pattern without taking the contact resistances into account show 6.50 mΩ and 7.84 mΩ per thermocouple pair respectively; 15.34 mΩ in total.

Bringing back the suggested formula to estimate the resistance in 2.4.1 and comparing with the measurements makes it obvious that not only is the contact to galinstan-copper deficient but also to BiTe.

$$R_D = a + n(R_p + R_n + 2R_g + 4b)$$
$$R_D = 0.42\Omega = (0.34 + 15.34 \times 10^{-3} + 4b)\Omega$$
$$b = 16.17 \text{ m}\Omega \text{ per Galinstan-BiTe contact.}$$

The electrical resistance of the device is still far from its potential (Fig. 24), being the suppression of the contact resistances necessary as much as possible. Was the galinstan-BiTe contact resistance eliminated, the resistance in a thermocouple would be decreased around five times, meaning five times more generated power per thermocouple.

The suppression of the galinstan-copper contact resistance would also mean an improvement in the supplied power which would be more relevant for devices with reduced number of thermocouples.
As an example, in the 1-pair device, the resistance would be decreased \( \frac{0.42}{15.34 \times 10^{-3}} \approx 27 \) times; in the 16-pairs device \( \frac{1.75}{15.34 \times 10^{-3}} \approx 7 \) times, presenting 27 times and 7 times higher generated power, respectively.

Fig. 24. Estimation on the increment of power if the contact resistances are suppressed (power increase against number of thermocouples). The factor of increment is calculated by dividing the resistance line of Fig. 23, which includes contact resistances, by the theoretical resistance of the thermocouples without contact resistances.
6 CONCLUSION

In the present work a thorough theory about thermoelectricity is developed along with a suggestion for simplified calculations for both thermoelectric generators and heat pumps.

We successfully created stretchable thermoelectric devices that, while showing lower power than commercial ceramic ones, offer the possibility to adapt to non-planar surfaces, achieving a proper contact and thus offering a wider range of applications.

Furthermore, if applied to human skin, no high power drainage is desired since it would turn out to an unpleasant feeling for the user. In this scenario stretchable thermoelectronics may play an important role as sensors and small sources of endless power.

If thermal conductivity of the outer layers is to be increased to raise the output of power, composite PDMS packaging can be used, reaching up to 60% of the potential electromotive force. While being close to ceramic devices, they present the advantage of stretchability and shape conformance, although biocompatibility is still to be studied.

Stretchability up to 50% of the effective length of the PDMS matrix was reached without leakage. For its further development, improvement in the adhesion PDMS-BiTe must be achieved.

A factor five reduction in the resistance per thermocouple is estimated to be possible, entailing five times higher generated power. Alas, electrical resistance of the device is still far from its potential and therefore future efforts should be done in suppressing the contact resistances.

Combination of the suppression of the contact resistances and an increase in the thermal conductivity of the outer layers can theoretically lead to an increase of the generated power per thermocouple up to 15 times (five and three times respectively).
7 ACKNOWLEDGEMENTS

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I also thank my tutor from Spain, Dr. Gonzalo Tévar, for he represents the essence of a true engineer for me.

8 REFERENCES

## GLOSSARY

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<thead>
<tr>
<th>Symbol</th>
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<tbody>
<tr>
<td>$\alpha$</td>
<td>Seebeck coefficient</td>
</tr>
<tr>
<td>$\bar{\alpha}$</td>
<td>Average Seebeck coefficient with regard to T</td>
</tr>
<tr>
<td>$e$</td>
<td>Unit of electrical charge</td>
</tr>
<tr>
<td>$\phi$</td>
<td>Electrical potential</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>Entropy sources</td>
</tr>
<tr>
<td>$J_e$</td>
<td>Electrical charge flux; current density</td>
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<td>Heat flux</td>
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<tr>
<td>$J_u$</td>
<td>Internal energy flux</td>
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<td>$k$</td>
<td>Thermal conductivity</td>
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PDMS | Polydimethylsiloxane |
BiTe | Bismuth telluride |