TAMPEREEN TEKNILLINEN YLIOPISTO
TAMPERE UNIVERSITY OF TECHNOLOGY

EHSAN SADEGHIAN RAEI

PRINTABLE ORGANIC THERMOELECTRIC ENERGY HARVESTING DEVICES FOR APPLICATIONS IN WEARABLE BIOMEDICAL DEVICES

Master of Science thesis

Examiners:
Prof. Paul Berger
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ABSTRACT

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Thermal energy as an alternative renewable source of electricity can be used in a wide range of applications. Over the past decade, thermoelectric (TE) devices have emerged as potential candidates to convert thermal energy to electrical power. Due to the advantages of using organic TE materials over conventional TE generators, including light weight, low thermal conductivity, cost effectiveness, flexibility, and processability, they have become the subject of universal research in recent years.

Poly (3,4-ethylenedioxythiophene):poly(styrenesulfonate)(PEDOT:PSS) is a promising candidate among other polymers to be used in TE modules due to its unique characteristics. Therefore, the focus on this thesis was to design and develop a thermoelectric energy harvesting module using only PEDOT: PSS as the active component. In addition, in order to test the performance of the module, a test setup was designed and developed particularly for the purpose of this work.

The performance of the TE device was evaluated by examining an induced voltage resulting from establishing a temperature difference across the two sides of the modules. It was observed that by increasing the temperature difference across the module, the generated voltage will also increase linearly reaching a maximum value of 280 μV for a 40 °C temperature difference.

The TE device developed in this work can be used as a power source in a wide range of applications from electronic devices to power supplies for distributed sensor networks in the Internet of Things. However, the main application is wearable medical devices in which the electricity is generated by thermoelectric conversion of body heat.

PREFACE

This master thesis was done in the Organic Electronics research group at the Department of Electronics and Communications Engineering at Tampere University of Technology (TUT) during the years 2015-2016.

I wish to thank my supervisor Prof. Paul Berger for the guidance of my work and his insightful ideas and comments. I really appreciate him having provided me with the opportunity to complete my thesis under his supervision. I would like to thank my examiner Prof. Donald Lupo for giving me the opportunity to work in his research group and also for his valuable feedbacks and encouragement during the work.

This work is dedicated to my family, especially my mother Farideh and my sister Haideh for their endless kindness and continuous support. Finally, I thank Marzieh for her love and support.

Tampere, June 2016

Ehsan Sadeghian Raei

CONTENTS

LIST OF SYMBOLS AND ABBREVIATIONS

Al	Aluminum
Bi_2Te_3	Bismuth telluride
IC	Integrated circuit
PbS	Lead (II) sulfide
PbTe	Lead telluride
PbSe	Lead selenide
PEDOT	(Poly) 3,4-ethylenedioxythiophene
PET	Polyethylene terephthalate
PF	Power Factor
PSS	Polystyrenesulfonate
Sb_2Te_3	Antimony telluride
SiGe	Silicon-germanium
T	Absolute Temperature
TE	Thermoelectric
TEC	Thermoelectric cooler
TEG	Thermoelectric generator
TUT	Tampere University of Technology
ZnSb	Zinc antimonide
ZT	Dimensionless figure of merit

1. INTRODUCTION

There are a variety of serious challenges which threaten the future of human kind, such as global warming, air pollution, clean energy, etc. These issues grow constantly, mainly due to the human society's dependency on non-renewable, ecologically destructive fuels. Currently, fossil fuels, such as natural gas, petroleum and coal are the main energy resources, especially in developing countries. In order to keep the development of human civilization sustainable, replacing conventional energy resources with clean and renewable alternative resources is inevitable [1]. To this end, a universal effort has started by both scientific and industrial communities for harvesting energy from our living environment, such as light energy, mechanical vibration, radio waves, and temperature gradients [2].

Over the past few years, a dramatic growth in personal electronic devices and wearable technologies has been observed across the globe. Presently, these devices play a key role in communication, healthcare, and well-being monitoring. Currently, most of these devices use primary or rechargeable batteries as their source of electrical energy. Although the power needed to supply these devices are relatively low, the increasing number of such devices demands a huge amount of the batteries each including toxic metals. This has raised major concerns regarding the recycling and replacement of batteries and environmental pollution associated with them. Therefore, replacing traditional power supplies with other clean and more environmentally friendly energy resources is not only highly desired, but required [3]. In addition, there is a rapid technological trend in developing the Internet of Things. Many scientists and research communities are working firmly to produce flexible and printable devices that are able to communicate with each other wirelessly without needing batteries or any other external energy sources. These emerging technologies also confirm the acute need of developing devices to use green energy resources.

In this context, organic thermoelectric materials have attracted much interest from both industrial and scientific communities across the globe. When it comes to green energy conversion, organic thermoelectric materials are potent candidates due to their compatibility with the environment, flexibility, and their great potential from the economical point of view [4]. These materials have a good potential to be used in different ranges of applications including industrial applications, healthcare, sports, and wearable biomedical devices. In recent years, there has been a growing demand for wearable medical devices, capable of monitoring vital signs, such as Electrocardiogram, body temperature, blood pressure and pulse rate, etc. Organic thermoelectric materials can be perfectly utilized in such devices by converting the temperature difference between the skin and the surrounding environment to the electrical power needed for the devices.

The First objective of this thesis was to design and develop a reliable test setup which can be used for testing different thermoelectric modules by maintaining a constant temperature difference across the two sides of the modules. The Secondary aim of this thesis is to fabricate an energy harvesting device made of organic thermoelectric materials and testing it with the assembled test setup. In this work, the expectation is to induce a measurable electrical voltage across the thermoelectric module which can be used as a green energy source for wearable biomedical devices.

This thesis includes 5 main chapters. Chapter 2 comprises the literature review and theoretical background of thermoelectric phenomenon and its principles, as well as an introduction to the organic thermoelectric materials. Fabrication methods and descriptions of materials and components used in this work are explained in Chapter 3. Chapter 4 reviews the performance of devices under test (DUT) prototypes and also presents a discussion regarding the results obtained in this study. Finally, chapter 5 sums up the main results of the thesis.

2. THEORETICAL BACKGROUND OF THE THERMOELECTRIC EFFECT

Conducting research in the area of organic thermoelectric materials requires a deep understanding of the thermoelectric phenomenon in general. To this end, this chapter presents an introduction to thermoelectricity and related principles. Theoretical background and characterization of thermoelectric coolers and thermoelectric generators are also explained in this chapter. Finally, most common candidate thermoelectric materials and their features are introduced.

2.1 Thermoelectricity

Over the past decades, there have been continuous attempts for the development of thermoelectric materials which are able to generate green power through direct conversion of natural heat to electricity. In recent years, due to the shrinking supply of fossil fuels and their related environmental problems, universal efforts are becoming more urgent to replace the traditional energy sources with alternative green energy sources.

The fundamental principles for thermoelectric energy harvesting using a temperature gradient were discovered around 180 years ago. However, most of the research in the field of organic thermoelectric materials has been developed since the 1990s. Over the last two decades, a rapid growth in the development of organic thermoelectric materials has been observed in research communities. In the following section, a brief overview on thermoelectricity, from the primary findings of Seebeck to recent research trends in organic thermoelectric materials is provided [5].

2.1.1 History of Thermoelectricity

The history of thermoelectricity began with the initial studies on the thermoelectric effect by academic scientists in Europe.

Thomas Seebeck

In 1821, Thomas Johann Seebeck, German-Estonian physicist, discovered that a circuit made from two different metals would deflect a compass magnet if their junctions were at different temperatures. At first, Seebeck reckoned this incident was related to the magnetic field of the Earth. However, after more investigation, he realized that there is a thermoelectric force which induces an electrical current. Therefore, he concluded that the temperature difference generates an electric potential which induces an electric current in the circuit. This phenomenon is known as the Seebeck Effect, which can be used in producing thermoelectric power generators [6]. The primitive device developed by Seebeck is illustrated in Figure 1.

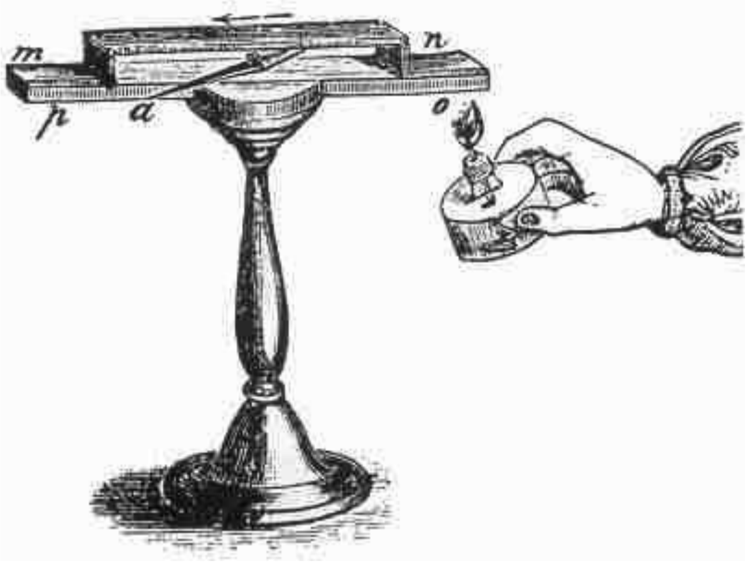


Figure 1.Device used by Seebeck to observe the thermoelectric effect [6]

Seebeck investigated the thermoelectric properties of different materials, minerals and alloys including zinc antimonide (ZnSb), lead (II) sulfide (PbS), and cobalt arsenide ($CoAs_2$). He also provided a qualitative ordering of their related Seebeck effect [6].

It is generally believed by scientific communities that the first practical application of the Seebeck effect was developed by Georg Ohm in 1826. Ohm studied the relationship between an applied potential through a conductor and resulted current using a thermocouple to produce the voltage [7].

Charles Peltier

In 1834, Charles Peltier, a French watchmaker and physicist, discovered that passing an electric current across the junctions of two different metals would produce heating or cooling at the junctions. The heat produced or absorbed at the junction is proportional to the applied electrical current. This phenomenon is known as Peltier Effect. In 1838, Heinrich Lenz, a Russian scientist, discovered that by changing the direction of electrical current, the heat can be either produced to melt ice at the junction, or can be removed from a junction to turn water into ice [6].

Lord Kelvin

In 1854, William Thomson (Lord Kelvin), an Irish mathematical physicist, learned the interrelationship between Seebeck effect and Peltier effect. He claimed that the Peltier coefficient is proportional to the Seebeck coefficient times absolute temperature. This thermodynamic basis helped Lord Kelvin to describe the third thermoelectric effect, presently known as the Thomson effect. He announced that any thermoelectric material could be utilized to either pump heat by applying a current or generate electrical power by inducing a temperature gradient. Thus, the heat is proportional to the temperature gradient and the electric current [6] [8].

In 1909, Edmund Altenkirch used the constant property model to derive the maximum efficiency of a thermoelectric generator for the first time. In addition, he used the model in 1911 in order to optimize the design and performance of a thermoelectric cooler [9]. Altenkirch's findings later developed into an important concept called Figure of Merit [6].

Thermoelectric Applications

From 1920 to 1970, research on thermoelectricity was continuously conducted in different technologies including power generators and cooling devices. In 1949, Abram Fedorovich Ioffe, Russian/Soviet physicist, developed the modern theory of semiconductor physics to explain thermoelectric energy conversion. Ioffe and his colleagues actively pursued studies in thermoelectric materials which resulted in the development of the first commercial thermoelectric cooling devices and generators [6]. Figure 2 illustrates one of the first commercial thermoelectric generator applications in an oil burning lamp which was able to supply a radio.

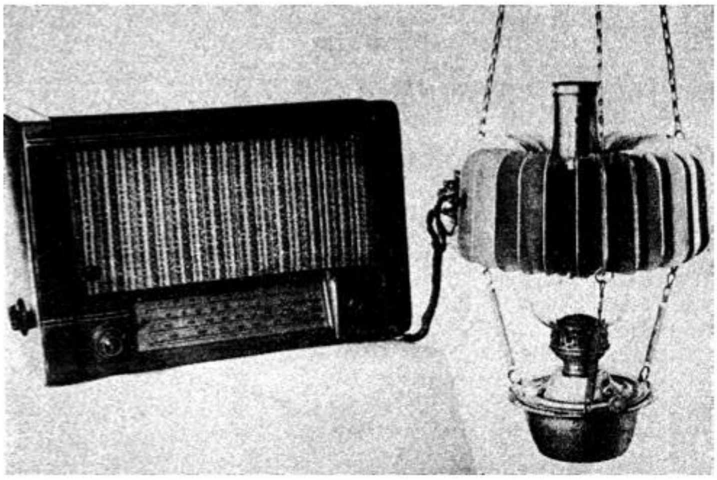


Figure 2.Oil burning lamp powering a radio containing ZnSb and constantan built in Soviet Union beginning in 1948 [10].

Throughout the 1950s, Abram Ioffe made further breakthroughs in the area of thermoelectric materials. He was able to develop many low-temperature materials, such as PbTe, PbSe, Sb_2Te_2, Bi_2Te_2, , etc. Devices made by Ioffe still suffered from low efficiency; however, they had the benefits of miniaturization. His new inventions were suitable for military applications. Nonetheless, due to their toxicity and high prices, they were not attractive for large-scale commercialization [5].

The increasing demand for remote, autonomous sources of power indicates the suitability of thermoelectric power generation in some niche applications. In 1977, NASA developed the first thermoelectric generator for space exploration missions. MHW-RTG3 was a radioisotope thermoelectric generator which was able to provide power by converting the heat from a source of decaying radioactive material into electricity using thermoelectric couples. Figure 3 shows a cutaway view of MHW-RTG3.This technology have been used for years by NASA in different deep space missions, outside the influence of the sun’s illumination, mostly beyond the Asteroid Belt, such as Apollo, Pioneer, Viking, Voyager, and Galileo [6].

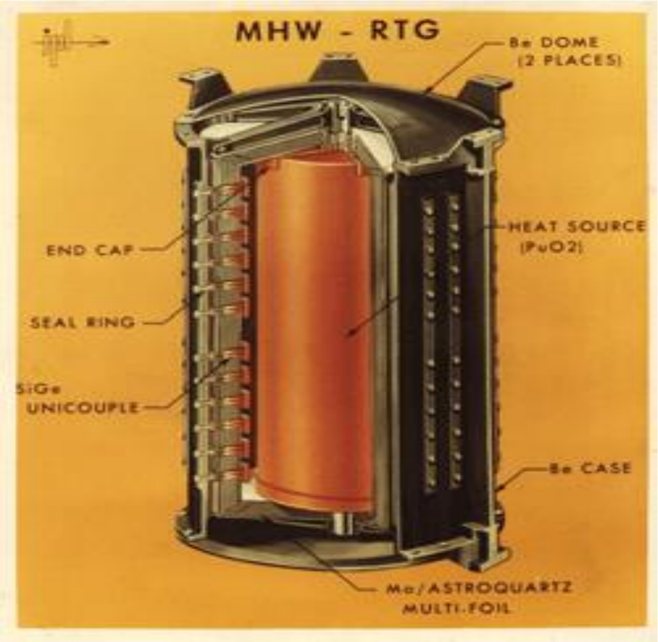


Figure 3.MHW-RTG3, a Silicon Germanium (SiGe) thermoelectric generator manufactured by NASA [6].

The universal trend to replace conventional sources of energy with alternative, green energy resources has restored interest in commercial applications [11]. In recent years, novel applications have emerged triggered by new developments in the field of organic thermoelectric materials.

2.1.2 Thermoelectric Effect

Thermoelectricity describes the direct conversion of a temperature difference into an electrical energy which is used in thermoelectric generators (TEG) or a reverse process which is used in Peltier devices (thermoelectric coolers, TEC). The thermoelectric effect is based on three different effects, named after the scientists who discovered them [12].

- Seebeck effect

- Peltier effect (the reverse Seebeck effect)

- Thomson effect

Seebeck Effect

A discussion of thermoelectric effect usually begins with the Seebeck effect since it is one of the most important phenomena in the field. According to the Seebeck phenomenon, when two ends of a wire have unequal temperatures, the electrons on the hot site possess more kinetic energy than the electrons on the side with lower temperature. The thermally driven diffusion drives the electrons from the hot side towards the cold side. Therefore, the electrical potential on the cold side is relatively more negative than that of the hot side. Due to the potential difference of the cold and the hot sides, a thermoelectric voltage is established between them [13]. The potential difference is called Seebeck coefficient and can be described by equation (1):

$$\mathrm{S} = \frac{\mathrm{dV}}{\mathrm{dT}} \qquad (1)$$

Where S is the Seebeck coefficient, dV is the potential difference and the temperature gradient is presented with dT.

Peltier Effect

Based on the Peltier effect, if an electrical current is passed through a junction of two dissimilar conductors, heat will be either absorbed or rejected at the junction, depending on the direction of the electrical current [14].The Peltier and Seebeck effects are related to each other as it can be seen in the definition of the Peltier coefficient:

$$\Pi = TS \qquad (2)$$

Where Π is the Peltier coefficient, S is the Seebeck coefficient and T is the absolute temperature in kelvin.

Kelvin Relations

In 1854, Kelvin claimed that the 3 thermoelectric effects are actually different expressions of one effect [6]. He described their interrelationship by defining Eqn. 3 for the Kelvin coefficient:

$$\mathrm{K} \equiv \frac{d\Pi}{dT} - S \qquad (3)$$

With the Thomson coefficient K, the Peltier coefficient Π, the absolute temperature T and the Seebeck coefficient S.

In addition, Lord Kelvin also discovered the following equations to explain the behavior of thermoelectric (TE) materials [13]:

$$\vec{\imath} = \sigma\left(\vec{E} - S\vec{\nabla}T\right) \qquad (4)$$

$$\vec{q} = ST\vec{\imath} - \lambda\vec{\nabla}T \qquad (5)$$

Where $\vec{\imath}$ is the electric current density, $\vec{q}$ presents the heat current, σ is the electrical conductivity, $\vec{E}$ is the electric field , thermal conductivity λ, temperature gradient $\vec{\nabla}$T and S is the Seebeck coefficient.

Thermoelectric Performance

In order to evaluate the performance of a thermoelectric material, a dimensionless figure of merit (ZT) is usually used [14]. This is defined as:

$$ZT = \frac{S^2\sigma}{\lambda}T \qquad (6)$$

The ZT usually plays a key role in the determination of a material potential to be used in thermoelectric applications. Equation (6) is commonly used for material evaluation since it considers all of the primary factors in thermoelectricity, including thermal and electrical conductivities, as well as Seebeck coefficient. Based on the equation (6), an optimal TE material should have a high Seebeck coefficient (S), a high electrical conductivity (σ), and a low thermal conductivity (λ). However, evaluating the efficiency of a TE material is not that simple due to the complicated nature of thermoelectric properties. In general, having a high electrical conductivity will result in a high thermal conductivity and a low Seebeck coefficient. Consequently, if achieving a maximum efficiency is the target, providing a correct balance between these factors is inevitable [5].

When the information of thermal conductivity (λ) is not available, it is possible to apply the concept of Power Factor (PF) in evaluation of TE materials [5]. This leads to a simplified equation:

$$PF = S^2\sigma \tag{7}$$

Equation (7) is able to determine the capability of a thermoelectric material to generate electrical power; however, it cannot provide any information on the efficiency of the material [5].

In general, the theoretical efficiency of a heat engine, such as a TEG element, can be measured by the Carnot efficiency [13]:

$$\eta_{carnot} = \frac{T_h - T_c}{T_h} = 1 - \frac{T_c}{T_h} \tag{8}$$

In which η represents the Carnot efficiency, T_h is the temperature in the hot side, and T_c is the temperature at the cold side. In order to evaluate the performance of a TE device in the power generation mode, equation (9) can be used [13]:

$$\eta = \frac{T_h - T_c}{T_h} \frac{\sqrt{1+ZT}-1}{\sqrt{1+ZT}+\frac{T_c}{T_h}} \tag{9}$$

Where η yields the efficiency, T_h and T_c are the temperatures on the hot side and the cold side, respectively. As it can be seen from equation (9), the TE device efficiency is directly related to the figure of merit (ZT).

2.1.3 Thermoelectric Devices

In recent years, portable devices and wearable technologies have attracted a huge interest in both scientific communities and industry. With the advent of such new technologies, the problems of conventional power generation strategies are more highlighted. Therefore, severe efforts on replacing the traditional strategies with novel, eco-friendly methods are ongoing. To this end, thermoelectric devices are among the best candidates to be used. Currently, a large number of modern TE refrigeration devices are made based on the Peltier effect. Similarly, the Seebeck effect is the basis for many power-generation modules [14].

In this section, the major characteristics and function of the most common thermoelectric modules, thermoelectric coolers and thermoelectric generators are explained in detail.

Thermoelectric Cooler

One of the most common applications of the thermoelectric effect comes from Peltier modules. These devices are usually used for thermoelectric heating and thermoelectric cooling. TEC elements possess many privileges. They have no moving parts and can be used in localized cooling or heating applications [14].

TEC elements are able to convert electrical energy into heat directly. A temperature gradient is established in a TE material when an electrical current is passed through it. The heat will be absorbed on the cold side and will be transferred to the hot side where it is rejected by a heat sink. This process provides the refrigeration ability in a TEC module [14].

A thermoelectric device usually comprises an array of n-type and p-type elements which are heavily doped with electrical charge carriers. The elements are organized in a way that they are thermally connected in parallel while electrically connected in series. On each side of the elements, two ceramic substrates are attached to the array [15].

Figure 4 illustrates a segment of a thermoelectric cooler including a pair of n-type and p-type elements usually referred to as a couple.

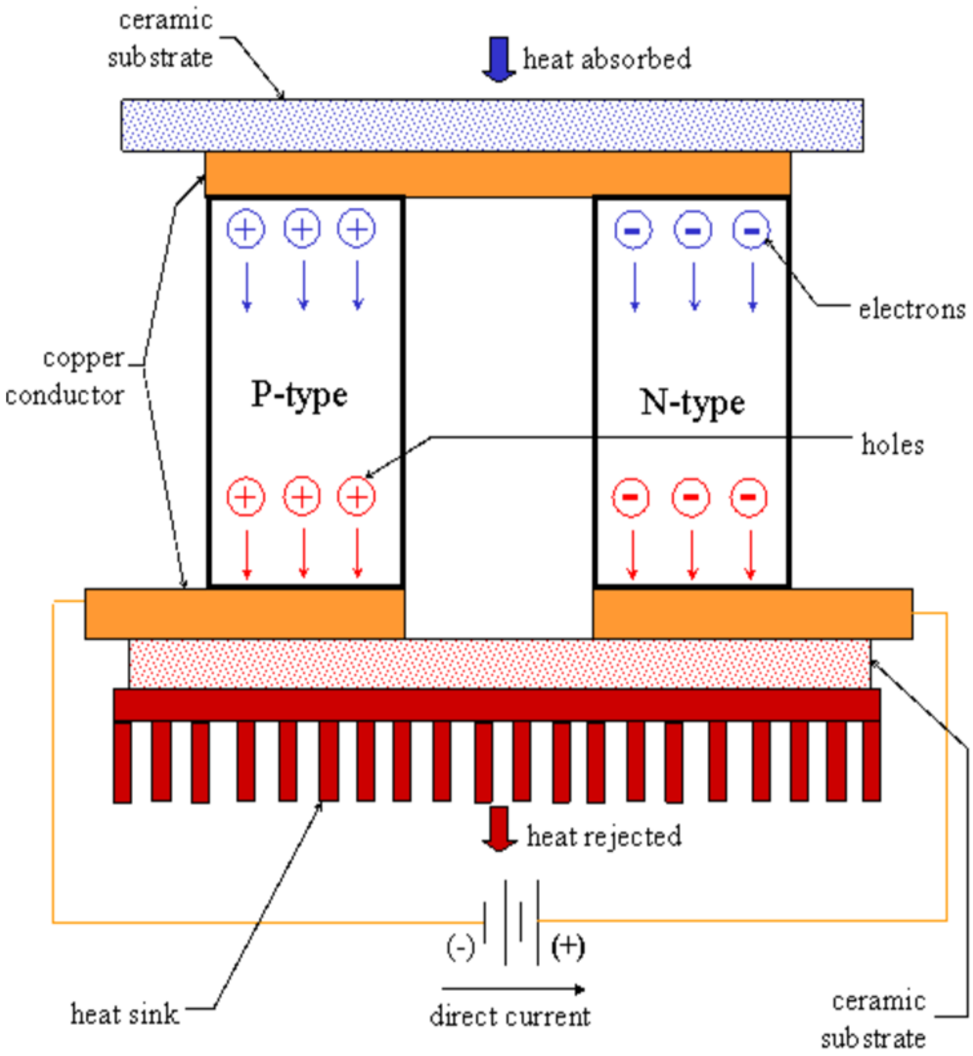


Figure 4.Schematic of a thermoelectric cooler [15].

In general, p-type semiconductors are doped with atoms that possess insufficient number of electrons to complete their atomic bonds. If an electrical current is applied, conduction electrons tend to complete the bonds. In this process, conduction electrons leave holes. Holes are basically atoms that possess positive charges in the crystal lattice. Electrons are then moving via the holes by jumping to the next hole available. Therefore, the holes are actually the electrical charge carriers in the material [15].

Generally, electron movement is easier in conductors (copper in this case) than in semiconductors. When electrons enter the conductor at the cold end from the p-type semiconductor, holes will be created in the semiconductor. This is mainly due to the fact that the electrons jump to the higher energy level to be matched with the energy level of the electrons in the copper conductor. Heat is absorbed on the cold side while providing the extra energy needed to make these holes. In parallel, the generated holes move down to the conductor on the hot side. Moreover, electrons from the hot side move towards the p-type semiconductor and fill the holes in which the extra energy is released as heat [15].

In contrast with the p-type semiconductors, the n-type semiconductors are doped with atoms that contain extra electrons to complete their atomic bonds. If an electrical current is applied, excessive electrons can readily move to the conduction band. Nevertheless, for n-type electrons to reach the energy level of incoming electrons from the cold side, more energy is needed which is obtained by the absorption of heat. The electrons again are able to move freely in the conductor when they leave the hot side of the n-type semiconductor. When electrons fall into a lower energy level, heat will be released in the process [15].

To sum it up, heat will always be absorbed from the cold side of the semiconductors and will be released at the hot side of the Peltier module as it can be seen from the Figure 4. The performance of a Peltier element is dependent on different factors, such as the properties of materials and the quantity of couples [15].

Thermoelectric Generator

Another popular application of the thermoelectric effect is in Thermoelectric Generators (TEG). TEG elements are able to convert temperature differences directly into the electrical power based on the Seebeck effect.

The architecture of thermoelectric generators is quite similar to the design of thermoelectric coolers but they are slightly different. In the TEC elements, the module is connected to an electrical current supply in order to provide a cold side and the hot side. However, TEG devices are usually connected to a load resistance in order to produce electrical power to drive a device [13]. A diagram of a thermoelectric generator containing p- and n-type materials is shown in Figure 5.

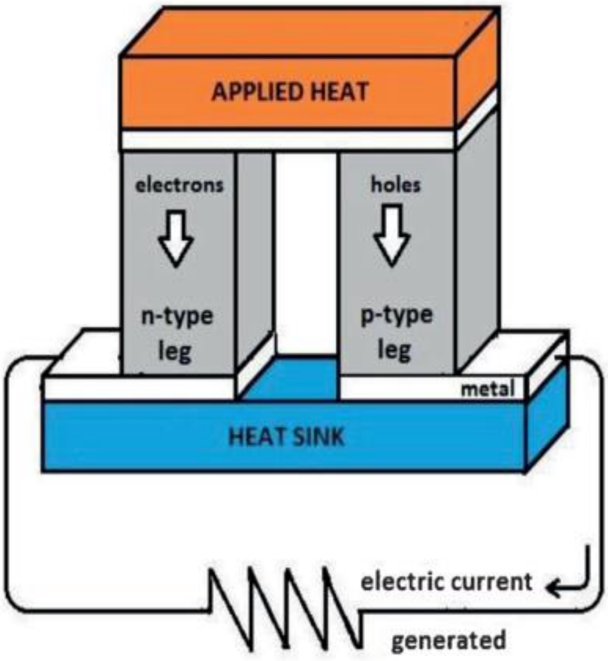


Figure 5.Diagram of a typical thermoelectric generator [5].

As it can be seen from the Figure 5, when heat is applied to one side of the module, a temperature gradient will form between the two sides of the device which leads to the generation of a thermoelectric voltage.

Thermoelectric generators are also accompanied with remarkable advantages. In the same way as TEC elements, TEG devices have no moving parts, which make them favorable candidates to work in rough environments for a long-time usage. In addition, since TEG devices do not require any fuels to operate, they are usually considered as one of the most environmentally friendly technologies available [13].

2.2 Thermoelectric Materials

Thermoelectric materials have recently attracted increasing attention in scientific communities. A considerable number of studies and reviews have been published on TE materials over the past few years [16] [17] [18].The major application of thermoelectric materials is in Peltier coolers and TEG elements for industrial and scientific purposes.

An optimum thermoelectric material should possess a high Seebeck coefficient to be used in TE devices. Furthermore, thermal conductivity should be minimized while electrical conductivity and the concentration of charge carriers are maximized.

In addition, from an environmental point of view, TE materials should be harmless and sustainable to be considered as a competitive source of energy [19].

In this section, an introduction to commonly used thermoelectric materials is presented. At the end of the section, a promising organic TE material, PEDOT: PSS used in this work is introduced in details.

2.2.1 Inorganic Thermoelectric Materials

The prominent requirement for a thermoelectric material to be considered a potent candidate in power generation applications is to have a relatively high ZT in the targeted temperature range. In existing devices, the best TE material has a ZT equal to 1. However, there is no reason for ZT=1 to be the upper limit. A wide range of ongoing research is focused on discovering novel TE materials that are able to increase the efficiency of TE devices through higher ZTs , especially in the lower temperature ranges below 250K [14].

Over the past three decades, there has been extensive investigation on alloys made of Bi_2Te_2 and SiGe to be used as thermoelectric materials in both the power generation and heating modes [20]. Therefore, it may seem that there is no more space for further improvement of these materials; nevertheless, recent promising results on TE materials nanostructures have given high hopes to scientists to conduct more research to discover new materials [14]. Figure 6 demonstrates the figure of merit (ZT) as function of temperature for some recently studied TE materials.

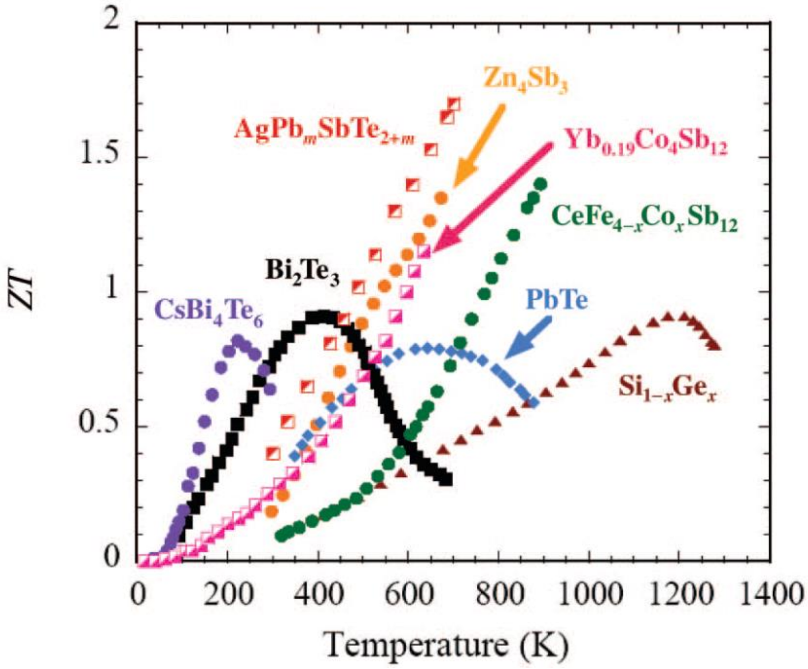


Figure 6.ZT as a function of temperature for some TE materials [14].

As can be seen from Figure 6, the dimensionless figure of merit (ZT) for bismuth telluride rises to the value of 1over the temperature up to 400K, and then it decreases to values less than 0.5 as the temperature increases.

By having a close look at Figure 6, it can be concluded that bismuth telluride (Bi_2Te_2) has shown the best performance at moderate temperatures (T<400) among the TE materials. This is the main reason that bismuth telluride is commonly used in the production of conventional thermoelectric generators and coolers to be used in moderate temperature applications [21].

There is no doubt that inorganic conductors and semiconductors are able to perform efficiently in thermoelectric devices. However, they are associated with some considerable drawbacks which limit their usage in many applications. Inorganic TE materials are usually made of rare elements and are usually characterized as brittle materials. In addition, from an economic point of view, the production cost is not justifiable in many applications. From an environmental point of view, inorganic TE materials usually consist of toxic substances which make them hard to recycle. Due to these problems associated with inorganic TE materials, organic thermoelectric materials have come to the fore front [22].

Organic semiconductor and semi-metal materials possess unique advantages when used as thermoelectric materials. Polymer-based TE materials are made of elements which are abundant in the nature. They are able to be adjusted to the favorable chemical and physical properties by performing simple modifications on their molecular structure [23]. Furthermore, they have an intrinsic lower thermal conductivity in comparison to most of the inorganic TE materials which makes them potent candidates in many thermoelectric applications.

In addition, polymer-based TE materials have the advantage of being processed as solutions. This property enables them to be produced in various ranges of advance processing methods, such as roll-to-roll (R2R) technology [24]. In spite of the above mentioned benefits, organic TE materials still suffer from modest electrical conductivity. However, the advantages will far outweigh the disadvantages.

2.2.2 Organic Thermoelectric Materials

Utilization of polymer-based semiconductor materials as the thermoelectric components is rather a new concept in the thermoelectric field. Over the last two decades, interest in organic thermoelectric materials and devices has grown rapidly within the scientific community [5].

In 1977, a significant breakthrough for doped polyacetylene was reported allowing conduction in conjugated system. At that time, there was no connection between polyacetylene and thermoelectricity; however, now conjugated polymers are regarded as potent candidates in plastic electronic applications [25].

In the late1980s, polyacetylene was widely investigated for optimization of its thermoelectric properties by tuning the concentration of its dopants. Since then, different polymer materials have been investigated for their thermoelectric properties [5]. However, most of the TE materials demonstrated modest values of ZT with a maximum ZT of 0.25 for PEDOT reported in 2011 [26].

As mentioned before, polymer-based materials have several properties that make them attractive to be used in TE applications. They are flexible, lightweight, cost-effective, and responsive to large area applications [27] [28]. Nevertheless, a relatively low ZT is still a major drawback for such a material.

In order to enhance the electrical conductivity of semiconductor polymers, doping them with a suitable quantity of doping agents is highly recommended. The doping can be p-type or n-type depending on the conduction properties of the polymers. The doping process could be implemented either chemically or electrochemically. Previous studies in the field of thermoelectric materials were mainly focused on improving TE efficiency by adding high levels of dopant materials. However, recent studies have proven that by increasing the doping quantity in some polymer material, the Seebeck coefficient may actually decrease [22]. The reason is that by increasing the amount of charge carriers in a polymer, the Fermi energy will be pushed into the conduction band. Therefore, there will be significantly more charges in the conduction band. In such a process, the movement energy of charge carriers will be declined and consequently, the Seebeck coefficient will be reduced as well [29]. Accordingly, maintaining a proper balance between these parameters is required when improving the electrical conductivity of polymer materials.

In order to enhance the electrical conductivity of polymer-based TE materials, various ranges of dopants have been used including iodine, methane sulfonic acid, Fe (III)chloride, hexafluorophosphate, arsenic pentachloride, camphor sulfonic acid, etc. As it mentioned above, the doping process can be done chemically, or electrochemically. The process is usually implemented by exposing a semiconductor polymer film to the dopant solutions or dopant vapors [22].

Over the past few years, there have been multiple studies on a wide range of polymer-based TE materials. According to experimental results, some of them have proven to be suitable to be used in TE applications, such as polythiophenes (PT) [30], polyacetylene [31], polyanilines [32], polypyrroles [33] . Figure 7 illustrates the chemical structure of some of the most promising polymeric TE materials [22].

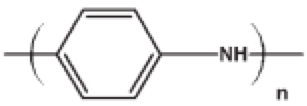
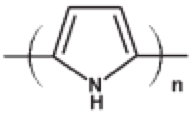
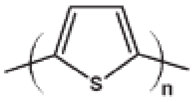
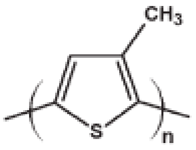
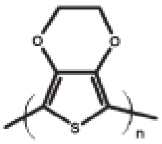
Name	Structure
Polyacetylene	
Polyaniline	
Polypyrrole	
Polythiophene	
Poly(3-methylthiophene)	
Poly(3,4-ethylenedioxythiophene) PEDOT	

Figure 7.Chemical structure of undoped polymer materials [22].

In general, polymer-based thermoelectric materials seem to be an attractive option for TE applications due to their better thermal conductivity and processability. However, their figure of merit is still a drawback and needs to be improved through further research. Among the above mentioned polymers, poly (3,4-ethylenedioxythiophene) (PEDOT) has attracted remarkable attentions in recent years. This polymer will be discussed in details in the following section.

2.2.3 PEDOT: PSS

Early research on organic thermoelectric materials mostly focused upon polymers, such as polythiophene, polyaniline, polypyrrole, etc. However, low electrical conductivity is the common, major drawback of these polymers [34]. In recent years, Poly (3,4-ethylenedioxythiophene):poly(styrenesulfonate)(PEDOT:PSS) has become one of the most promising thermoelectric polymers mainly because of its superior electrical conductivity [35].

Since the late 1990s, a remarkable number of studies have been conducted on Poly (3,4-ethylenedioxythiophene) (PEDOT). PEDOT has always been an interesting option for material scientists due to its distinguished features in addition to its outstanding stability in the environment. To date, PEDOT has shown the best thermoelectric performance among organic compounds when it is emulsified with polystyrenesulfonate (PSS) and tuned with proper oxidation level [5].

PEDOT is usually formed under chemical/electrochemical oxidation by the polymerization process of 3,4-ethylenedioxythiophene (EDOT). The processability of this polymer can be enhanced by performing the polymerization process using poly (styrenesulfonic acid) in order to provide a PEDOT: PSS emulsion [5].

Commercial PEDOT: PSS is available in the form of a blue, opaque suspension. This material can be easily processed by various methods to form a film on a flexible or rigid substrate. Different processing techniques can be applied for this purpose including screen printing, inkjet printing, slot die coating, doctor blading, spin casting, spray deposition, etc. The resulting thin films of PEDOT: PSS are usually smooth and transparent in the range of visible light [35].

PEDOT: PSS, as an organic thermoelectric material, is accompanied with several remarkable advantages and unique properties. The most distinguishing properties of PEDOT: PSS are its high electrical conductivity and its compatibility with different fabrication techniques. Optical transparency and physical and chemical stability are also considered as important merits for this material [35] [36]. In spite of the above mentioned advantages, PEDOT: PSS has some disadvantages, such as relatively low Seebeck coefficient, time-consuming process, and low control over the oxidation process [37].

In the past few years, considerable improvements in the thermoelectric performance of the PEDOT: PSS has been reached. Nevertheless, further research to enhance its Seebeck coefficient and electrical conductivity are needed. In order to improve the electrical conductivity of PEDOT: PSS films, doping with organic solvents is recommended [38] [39]. Furthermore, treating with some substances, such as inorganic acids, polar organic compounds or cosolvents can promote this application [35] [40].

Although prior investigations on thermoelectric properties of PEDOT: PSS films mainly focused on improving its electrical conductivity, its thermal conductivity has been also studied over the past few years. One successful approach is doping and de-doping of the polymer. This method plays a key role in charges carrier concentration and mobility, as well as oxidation level [35].

Further investigations on the thermoelectric properties of PEDOT: PSS resulted in a reduction in its thermal conductivity reaching a value of 0.42 $Wm^{-1}k^{-1}$. The electrical and thermal conductivities of some of the most common polymers are demonstrated in table 1.

Table 1. Thermoelectric properties of some conjugated polymers [5]

	PEDOT	Polyacetylene	Polyaniline
Dopant	PSS	Iodine	Camphorsulfonic acid
Electrical conductivity (Scm^{-1})	1000	38	268
Thermal conductivity ($Wm^{-1}k^{-1}$)	0.42	0.21	0.2

As can be seen in table 1, PEDOT doped with PSS has shown a quite large electrical conductivity in comparison to polyacetylene and polyaniline. In addition, the thermal conductivity of PEDOT: PSS is almost two times more than the thermal conductivity of other polymers.

PEDOT: PSS is a polymer electrolyte. This compound is made of conjugated PEDOT with positive charge and saturated PSS with negative charge. The chemical structure of PEDOT: PSS is illustrated in Figure 8 [35].

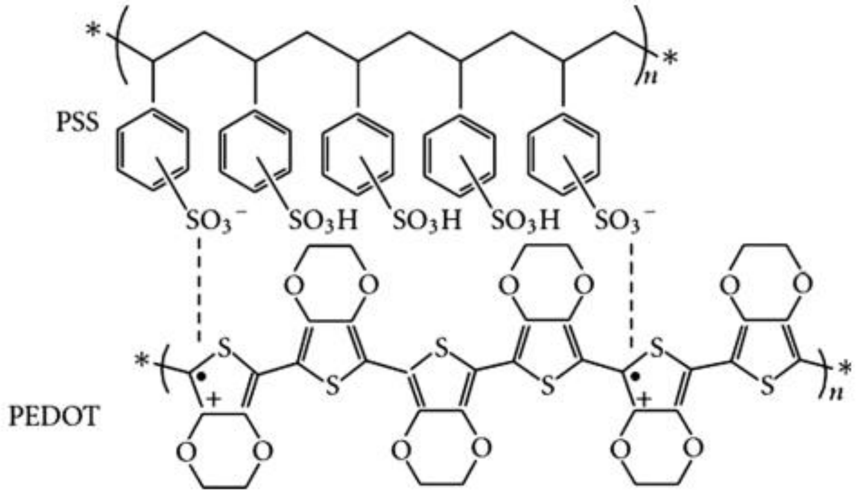


Figure 8.Chemical structure of PEDOT: PSS [35].

It is believed that PEDOT: PSS is by far the most successful conducting polymer used in practical applications. It has a wide range of applications in energy conversion and storage devices [35].

Traditionally, PEDOT: PSS was utilized widely in organic light emitting diodes as a hole injection layer. Then it became popular as a hole transport layer in organic solar cells. Over the past few years, PEDOT: PSS has been able to attract more attention for use as a buffer layer for a variety of devices [35]. PEDOT: PSS is currently commercialized in many applications, such as electrode material in supercapacitors, fuel cells, dye-sensitized solar cells, polymer-based thermoelectric devices, etc. [5]

In general, the characteristics of the PEDOT: PSS material system depends on different factors including post-treatment, composite formation, method of synthesis, doping and de-doping process. Therefore, it is often necessary to tailor its properties to be used in a particular application [41]. It can be predicted that PEDOT: PSS will be used frequently in modern technologies in the near future [35].

3. MATERIALS AND METHODS

To date, several studies have been conducted in which polymers are used as thermoelectric materials. This research has mainly focused on thermoelectric material properties and preparation. However, in this thesis the actual preparation and testing of a thermoelectric module, as well as challenges that are accompanied with its practical use as a technology are described.

As mentioned in the previous chapter, organic thermoelectric materials have unique characteristics, such as cost effectiveness, low thermal conductivity, good flexibility, processability, etc., that makes them potent candidates to be used in thermoelectric devices. However, in spite of the polymer material advantages, there are important criteria that need to be considered in design and fabrication of thermoelectric modules.

When working with organic thermoelectric materials, the environmental stability is one of the major requirements. Some of these materials are not stable in the presence of oxygen or water, especially in high temperatures [42]. Thus, in the fabrication of the thermoelectric module, PEDOT: PSS is a good choice because it possesses stability over a temperature range around room temperature.

In addition, there are some issues that restrict the design of the thermoelectric module. Traditional inorganic thermoelectric devices usually comprise both of the n-type semiconductors and p-type semiconductors. However, when it comes to organic materials, having both p-type and n-type semiconductors in the module structure is challenging since n-type doping of organic TE materials has limited success and often result in less air stable materials [43]. Therefore, in this work, only a thermoelectric module based upon p-type organic material will be used.

This chapter of the thesis covers descriptions of the materials and components used in this work. In addition, methods and fabrication process of the test setup and the thermoelectric device, as well as problems and challenges associated with their manufacturing process are explained.

3.1 Test Setup

The first practical step in this study was the design and fabrication of a test setup which meets the particular requirements of the thesis. In this section, the design and fabrication process of the test setup is described in details. First, the components used in the assembly of the test setup are introduced. The design and manufacturing process of an aluminum test station is explained latter.

3.1.1 Components

Thermoelectric Temperature Controller

The major components of the test setup are two thermoelectric temperature controllers, one for the hot side and another for the cold side. A temperature controller system is usually utilized when maintaining a constant temperature for an object under test The temperature controller is used in combination with a Peltier element in which the controller supplies the needed current to run the Peltier module. The controller regulates the current magnitude and direction according to the measured temperature at the module. In addition, the controllers usually have both heating and cooling abilities, depending on the intended use. There is no need to make any mechanical changes in order to switch from the heating mode to the cooling mode or vice versa. A TEC controller is able to shift the mode merely by altering the direction of the current provided for the Peltier module. Figure 9 indicates one of the temperature controllers (TED200C) used in this work.

Figure 9.TED200C Temperature Controller.

In this experiment, two TED200C thermoelectric temperature controllers, purchased from the Thorlabs Company, are used to provide different temperatures for measurement purposes. This device can be adjusted to different thermal loads and is able to provide a precise temperature across a TEC module with input currents up to ±2 A. The TED200C is also able to support a variety of temperature sensors, including thermistors up to 200 kΩ or temperature sensing ICs.

When the temperature controller is connected to an IC-Sensor, a temperature resolution of 0.01 °C is achievable. The resolution is 1 Ω when a thermistor is used as the temperature sensor. In addition, controlling the temperature set point can be readily done by tuning the control knob in the front panel. When aiming for a constant temperature, the device continuously monitors the TEC module temperature and changes the direction of current to maintain the desired temperature [44].

One of the major challenges that needed to be dealt with while working with the temperature controller was setting the actual temperature with stability to a desirable temperature (Set temperature). To this end, the PID control loop needs to be adjusted to the thermal load of the device under test in order to optimize the response of the controller. PID stands for proportional, integrative and derivative and this controls the time constants that regulate whether the system is overdamped, underdamped (with oscillation), or critically damped.

If the PID control parameters of the feedback loop are not set properly, the system oscillates (passing the set point value) and their amplitudes can make the system instable with a continuous oscillation around the set temperature [44].

The PID control circuits are usually used as closed loop feedback controller in different circuits. The letters P (Proportional), I (Integral), and D (Derivative) presents the 3 control parameters in a PID circuit. PID circuit plays a key role in the system by creating an error signal, e (t), which is actually the difference between the current value and the set point value [45].

The P value is based on the current error. The I value is based on the accumulation of the previous error, and the D value is the anticipation of any future error. The output of the circuit u(t) then will be adapted according to a weighted sum of PID control parameters. Then, u(t) will feed to a control device and its value will be fed backed to the thermal circuit. The primary goal of the whole process is to hold the output of system at the set point for a long period of time [45]. Figure 10 illustrates a simple block diagram which indicates the action of the PID circuit in a nutshell.

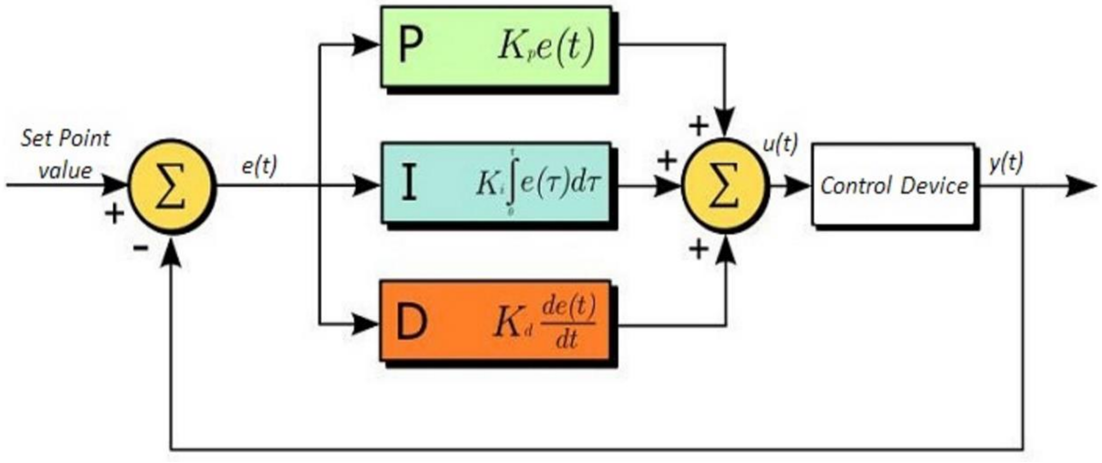


Figure 10.Block diagram of a PID control circuit [45].

By setting proper values of PID parameters for a particular thermal load, a fast response with a minimum number of overshoots can be obtained. Each thermal load should be optimized independently with different PID settings. In the thermoelectric temperature controller, the PID circuit feeds the electrical current to the TEC element. A thermistor is used as a sensor to continuously monitor the actual temperature of the TEC element. As it can be seen from Figure 10, the error signal, e(t), is the difference between the set temperature and actual temperature.

The controller provides the TEC current according to the error input signal. For example, if the TEC surface is too hot, the control circuit will feed less current to the TEC (proportional parameter). Since the proportional parameter (P) is linearly related to e (t), it cannot cool down the TEC surface fast enough. Thus, in order to compensate that, the controller adjusts the output current according to the past errors through the integral parameter (I). Now, as the desired temperature is obtained, the error signal approaches to zero. The derivative control parameter (D) can reduce the current flow to the TEC element while it predicts reaching the actual temperature to the set temperature. PID control parameters need to be adapted independently in order to gain an optimum adjustment [45]. Essentially, with proper PID settings, the solution of the differential equation can be critically damped, versus underdamped or overdamped, and thereby a desired setpoint is reached with minimal overshoots.

Thermoelectric Cooler

TEC modules are one of the most common approaches for maintaining a constant temperature. There are different types of thermoelectric cooler modules available in the market. They are mainly sorted according to their sizes, shapes, and intended applications.

Some of the most common TEC modules are Standard modules, High-temperature modules, Micro modules, Center Hole modules, etc. Each of the modules is accompanied with some pros and cons. One key factor that should be taken into account when choosing a TEC element is the heat load of the system. The heat load of the system is the amount of heat that needs to be transferred away from the device. Additionally, ensuring the appropriate TEC size for the intended use is another major factor [15].

In the case of this work, Rectangular Modules with Center Holes seemed to be the best choice for the following reasons. First of all, the hole in the center of the module can be used as an interface between the temperature sensor and the device under test (DUT), in which the sensor can be in contact with the DUT surface through the hole and detects the actual temperature of it.

Second, the size of the TEC element matched with the intended size of the DUT. The dimensions of the TEC element are 40 mm length, 40 mm width, and 4 mm thickness. In addition, the module was able to achieve the required temperature difference across the thermoelectric device while maintaining low power consumption. Thus, it was compatible with the output current of the temperature controller. In Figure 11, the rectangular module with center hole, used in this work is shown.

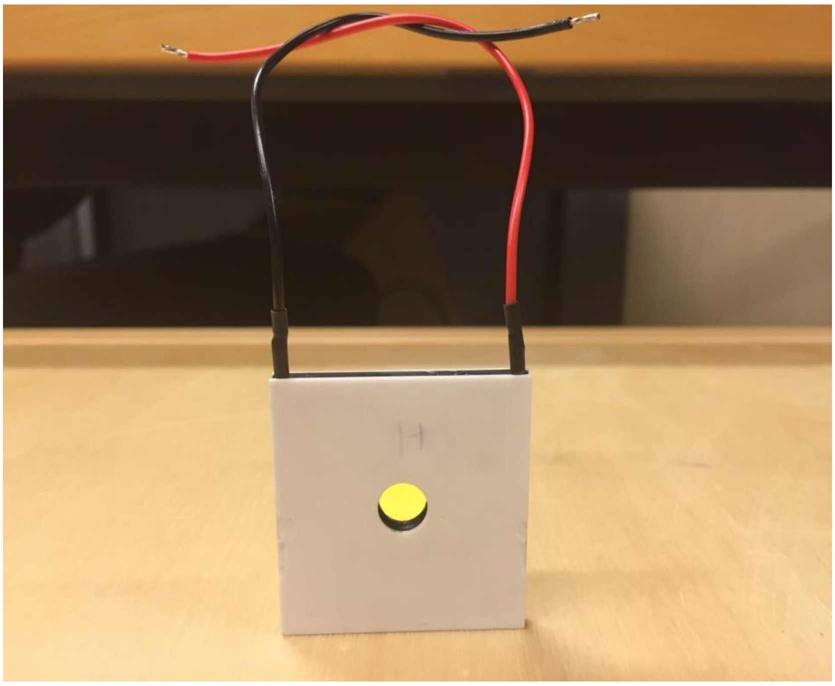


Figure 11.Rectangular thermoelectric cooler.

The TEC modules are able to cool when the electrical current flows in on direction and heat when the electrical current is directed in an opposite direction. However, some environmental factors can limit the performance and accuracy of the elements. For instance, the heat transfer efficiency of thermoelectric modules can be affected by the ambient environment. Major changes in the environment temperature or humidity can prevent proper heat flow. Hence, all the measurements of this experience were implemented in a TUT technical laboratory in which the temperature and humidity is kept constant by an air conditioning system.

Temperature Sensor

In order to have proper control over the TEC element temperatures, a precise temperature measurement is a must. To this end, a temperature sensor is needed to complete a feedback loop between the TEC element and the temperature controller. When the sensor is connected to a TEC element, it detects the actual temperature induced by the TEC module on its surface. This way the sensor allows the temperature controller to constantly monitor the actual temperature and change it according to the set temperature.

The temperature sensor used here is a thermistor. Thermistors are semiconductor elements in which their resistance changes with the change in the ambient temperature. They are used a lot in electronics for temperature measurements.

There are two types of temperature sensors which are compatible with the temperature controller TED200C, AD590 (temperature transducer) and NTC (thermistor). In this thesis, both of the sensors were tested in the setup in order to find the optimum sensor which is able to meet the requirements of the experience and provide the highest thermal accuracy.

The AD590 is an integrated circuit temperature transducer which is able to generate currents linearly proportional to its surrounding temperature. This temperature transducer is able to cover a temperature range of -45 °C to +145 °C. Electrical power needed for the transducer to operate is between +4 V and +30 V which is supplied by the temperature controller [46].

In this experiment, an AD590 transducer was used as the temperature sensor at first. The sensor was placed into the center hole of the TEC element and secured firmly in the place using thermal conductive epoxy glue. However, when the sensor was tested in the setup, it was unable to detect the actual temperature of the intended side of the thermoelectric element. Since the sensor was placed between the hot side and cold side of the TEC element this could result in the confusion of the sensor between the two temperatures and its malfunction.

Another possible option for the temperature sensor was an epoxy coated thermistor (NTC) which is commonly used in thermoelectric applications. This sensor is able to provide 1

°C temperature accuracy and has two ranges of measurements from 0 to 20kW and 0 to 200kW. The measurements ranges can be selected from the front panel of the TED200C temperature controller. However, the exact control range depends on the test setup and thermal load [46].

Among the above mentioned temperature sensors, NTC perfectly matched with the requirements of this experience due to its accuracy and compatibility with the test setup. In order to describe the dependency of temperature vs. resistance, different algorithms and formula can be used. For simplicity, an Excel file provided by the Thorlabs Company was used which was able to calculate temperature for a measured resistance and vice versa.

It is worth mentioning that the temperature measured by the sensor is not necessarily proportional to actual temperature on the DUT. The key to achieve a precise and reliable measurement is to make the temperature of the sensor as equal as possible to the temperature of the DUT. To this end, the sensor needs to be placed as close as possible to the thermoelectric module under test. Hence, to provide a proper measurement, the NTC sensor was attached to the surface of the TEC element in a very close distance to the DUT.

In addition, proper thermal attachment of the sensor plays a leading role in the accuracy of temperature measurement. Thus, thermally conductive epoxy glue was used to secure the sensors on the surface of the TEC element providing an optimal heat transfer between the components.

3.1.2 Test Structure Housing

Design and fabrication of a test station housing made from aluminum was the first practical stage of the thesis. The design and fabrication process was implemented in a way that it met the particular requirements of the experience.

In order to measure the induced voltages within the device under test, a reliable structure is needed which is able to hold the DUT steady between the Peltier modules during the test process. Furthermore, the whole setup needs to be firmly fixed, mainly due to the fact that even a slight unwanted movement of the setup may affect the measured data obtained from the device under test. Therefore, an aluminum weight was designed specifically for this research.

Firstly, a base with a proper weight was required to secure the stability of the test setup and avoid unnecessary, random movement of the components. In the case of the base material, aluminum was an obvious choice due to its reasonable price and proper machinability. The dimensions of the aluminum base are 25 cm length, 20 cm width, and 5 cm thickness. The weight of the base was calculated to be about 7 kg.

The fabricated test structure housing is shown in Figure 12.

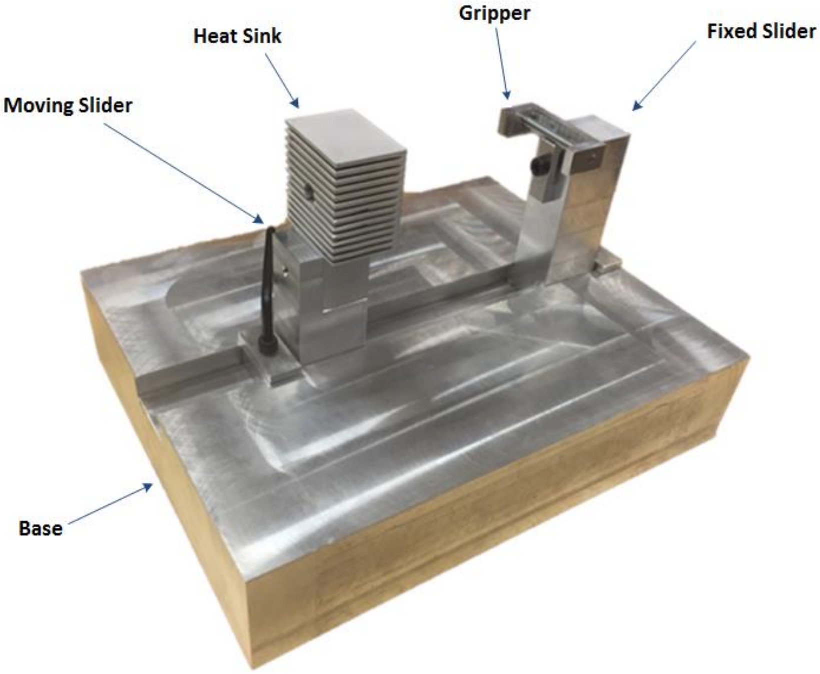


Figure 12. Test structure housing.

As it can be seen from the figure above, the station contains two sliders with a gripper on the top of the right one and a heat sink on the other one. The sliders are designed to hold the Peltier modules steady while the thermoelectric module is kept between them. One of the sliders is fixed at the end of the base while another one has the capability of linear sliding along the base. The location of the moving slider can be adjusted according to the size of the device under the test. Subsequent to the placement of the DUT, the position of the slider can be fixed by using a set screw which is placed at the rear of the slider.

One of the challenges in this stage was to avoid unwanted thermal conductivity between the TEC module and the gripper in the fixed slider. Otherwise, the gripper and the whole slider may act as a heat sink for the TEC module and affect the heating ability of the element. In this regard, a vital step was minimizing the surface in contact between the DUT and the gripper. Therefore, the holder was designed to grip the Peltier module from its sides instead of gripping it from its back which is common in conventional grippers.

Another major challenge in the design of the moving slider was assembly of a heat sink on top of the slider. A heat sink is a device which is usually attached to hot side of the

TEC elements in thermoelectric applications. It provides heat transfer from the hot side of the TEC element to the ambient. When the TEC element is utilized on the cooling mode, one surface of the TEC gets cold while the other side gets hot. If that heat is not transported away from the TEC surface efficiently, the excess heat could leak over to the cool side and limit the cooling performance of the TEC element.

In this work, a large block of aluminum attached to the moving slider was used as the heat sink. In order to facilitate the heat removal, fins were also carved into the aluminum block to more effectively transfer heat to the ambient air. Furthermore, with the aim of maximizing the thermal contact between the TEC element and the heat sink, a thermally conductive double-sided tape was used to attach the TEC element to the heat sink.

3.2 Device under Test

In order to obtain a considerable thermoelectric voltage, a large number of thermoelectric modules should be connected to each other. The design and configuration of the whole device should be in a way that the individual thermoelectric junctions are connected in series electrically while they are thermally connected in parallel [47].

In conventional inorganic TE generators, thermoelectric modules typically have a π-type structure in which both n-type and p-type materials are alternately connected. This results in expensive and inflexible devices with limited number of industrial and commercial applications. However, when using organic TE materials in the thermoelectric device, having the n-type material in the device architecture is not necessary.

In this section, the development of the process flow to synthesize a flexible and light-weight thermoelectric device which only consists of p-type thermoelectric materials is explained. In the first part, materials used in the organic TE module are introduced. In the latter part, the fabrication and characterization of the DUT are discussed.

3.2.1 Materials

In this section, the materials used in the fabrication process of thermoelectric generator are discussed.

Substrate Material

The mass production of TE generators implies the use of flexible and economical substrates in their manufacturing process. There are different, commercially available materials that meet these requirements. One of the most common polymers used in thin substrates in electronic applications is Polyethylene Terephthalate (PET). PET foils are cheap and light-weight which makes them potential candidates for commercial products and mass production.

Production of PET materials is usually done at high temperatures which make them suitable for organic applications using printing methods or evaporation techniques. Another remarkable feature of PET materials is their inherent mechanical flexibility. This trait provides the possibility of folding the substrates in rolls during the manufacturing process. Alternative candidates for the substrates could be thin metal foils or paper sheets. However, the above mentioned properties of PET substrates cannot be easily acquired by them.

Due to the high compatibility of PET films with the requirements of this experiment, two layers of PET material were used as substrates for the electrodes. The PET films were X-478 product from the Folex Company with the thickness of 0.1 mm. All of the X-478 PET films undergo a heat-stabilization process to improve their heat stability which enables them to tolerate temperatures up to 150 °C without any changes in their chemical and physical characteristics. Moreover, they have a good resistance to many liquids and chemical solvents [48].

Electrodes

According to the predetermined design of the DUT, two separate layers of electrodes were needed to be used as bottom electrodes and top electrodes for the PEDOT: PSS material. Different materials were available to be deposited on PET substrates using e-beam evaporation technique, including Gold (Au), Silver (Ag), Aluminum (Al), Copper (Cu), Titanium (Ti). In the DUT fabrication process of this work, Aluminum electrodes were used due to their lower thermal conductivity in comparison with other alternative candidates, as well as their good stability under different temperatures and pressure.

PEDOT: PSS

The organic thermoelectric material used in the fabrication of the DUT was Poly (3,4-ethylenedioxythiophene):poly(styrenesulfonate)(PEDOT:PSS). This material is commercially available from a handful of manufacturers around the world. In this work, the PEDOT: PSS was acquired from the Heraeus Company which is a worldwide, leading company in manufacturing of conductive polymers.

The trade name of the product is Clevios™ S V4 STAB. This product is based on the PEDOT: PSS formulations for transparent conductive materials. The unique properties of this product, such as high conductivity, flexibility, and optical transparency, makes it a potent candidate to be used in a vast range of technically advanced applications, including transparent electrodes, touch panels, and printed electronics. The detailed Information and specification of the Clevios™ S V4 STAB product is demonstrated in table 2.

Table 2. Specification of PEDOT: PSS material

Trade Name	Clevios™ S V4 STAB
Form	Viscous
Viscosity (dPas)	15-60
Resistivity (ohm/sq)	400
Temperature Range (°C)	5-50
Boiling Point(°C)	112
Density at 20 °C (g/cm^3)	1.06
Miscibility with Water	Fully Miscible
Organic Solvent Content	75-80 %
Solid Content	0-5%

The Clevios™ S V4 STAB is available in the form of a blue, opaque solution. This solution can be processed to form a flexible or rigid substrate on the PET transparent films via various processing techniques, such as doctor blading, screen printing, inkjet printing, etc.

3.2.2 Device Fabrication

This section of the thesis includes the description of procedures for the fabrication and characterization of the thermoelectric device which is assembled with different materials and components.

Fabrication Stages

The design of the thermoelectric module comprises two separate layers of PET substrates attached to each other. In order to complete the DUT fabrication process, seven preparation and assembly steps were taken. The DUT sample preparation was done in the following order:

1. Making a shadow mask to form predetermined electrodes on the first PET substrate.
2. The first electrode metal evaporation for the bottom electrodes using the electron beam evaporator.
3. Cutting out two rows of holes with two different alternating sizes (large for TE element and small for electrical feedthrough) on the second PET substrates to be filled with PEDOT: PSS solution and silver paste.
4. Filling large holes with the PEDOT: PSS solution and drying them using a hot-air convection oven.
5. Placement of the PET substrates on the top of each other using adhesive glue in a way that there is a complete overlap of the top and the bottom electrodes on the device.
6. Filling small holes with silver conductive epoxy.
7. Checking the completed device for electrical conductivity and possible open circuits.

In the following section, the above mentioned stages are explained in detail.

Device Preparation

In this work, electron beam evaporation method was used in order to deposit silver electrodes on the PET substrates of the DUT. In the E-beam evaporation technique, a charged tungsten filament is heated in a vacuum chamber in order to emit high-voltage electrons to the target material in a selected crucible. Due to the collision of electron beams and the target material, the material temperature reaches its sublimation temperature and its atoms will be transformed into the gaseous phase. In this process, the target material will be vaporized and coat the inner surface of the vacuum chamber and the target substrates with a thin layer of the target material.

Since in electron beam evaporation technique, the target material will be evaporated to the entire wall of the vacuum chamber, the deposition of thin films on the substrates should be patterned. Patterning can be accomplished by using shadow masking technique in which only the desired parts of the substrates will be coated during the evaporation. The shadow mask can be an etched metal foil or a sheet of patterned paper covering the substrate.

In this work, all of the evaporation stages were completed using a Leybold L560E E-beam evaporator machine which is available in the technical laboratory of the TUT. Figure 13 illustrates the E-beam evaporator. In this figure, the control unit is in the left and the vacuum chamber is in the right side of the picture.

Figure 13. Leybold L560E E-beam evaporator.

In this experiment, an evaporation rate of 2 Å/s was used in order to deposit a thin silver film on the PET substrate. The final thickness of silver film was 100 nm and the vacuum pressure was 10^{-6} mbar in the vacuum chamber.

As mentioned above, the evaporation process was done in two separate stages. At the first evaporation, the bottom electrodes were deposited on the bottom layer of the DUT. Following the first evaporation, the top layer needed to be attached to the bottom layer. To this end, different types of adhesives was tested on PET substrates. In order to find the adhesive that best fits the requirements of this experiment; the performances of adhesives on the DUT samples are compared and demonstrated in Table 3.

Table 3. Adhesives Test results on PET substrates

Trade Name	Company	Flexibility	Strength	Wrinkle Formation
Liquisde	Casco	✓	✓	✗
Power Glue	Loctite	✓	✗	✓
Super Glue	Loctite	✓	✗	✗
Power Epoxy	Loctite	✗	✓	✓
Adhesive Splay	3M	✓	✓	✗
Rubber Cement	Royal Talens	✓	✗	✓
Glue Roller	Kores	✓	✓	✓

As can be seen from Table 3, the best result was achieved through the glue roller from the Kores Company which was able to provide maximum flexibility and strength without blocking small holes.

After filling large holes with the PEDOT: PSS solution, the samples were placed in a hot-air convection oven for thermal drying. The drying process was performed at 130 °C for a period of 10 min. The DUT sample after thermal drying can be seen in Figure 14.

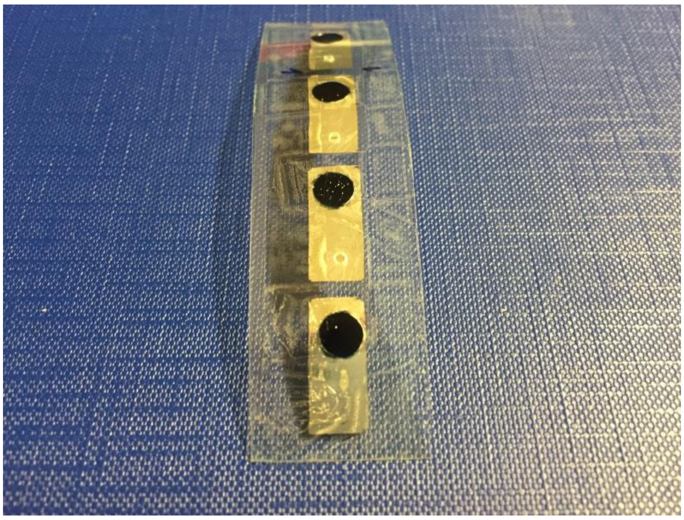


Figure 14. The DUT sample after thermal drying.

After this phase, the second evaporation was performed in order to deposit the top electrodes on the second PET layer. The evaporation condition was similar to the first electrode deposition with a final thickness of 100 nm for silver electrodes.

The next step following the second evaporation was to fill the small holes with a conductive epoxy to complete the structure of the device. To this end, a silver conductive epoxy adhesive from M.G. Chemicals Company was used. In order to provide an optimum conductivity, the device was placed in a hot-air convection oven for heat cure. The cure time was two hours with a cure temperature of 65 °C. The fabricated DUT is illustrated in Figure 15.

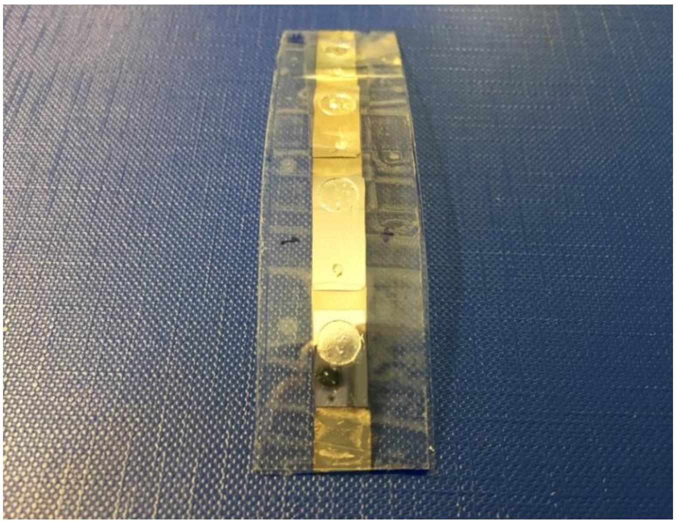


Figure 15. The completed DUT.

The dimensions of the completed DUT are 85 mm length, 20 mm width, and 0.2 mm thickness. Four circular PEDOT: PSS layers with a diameter of 5 mm and a thickness of 0.05 mm was formed on the PET substrate.

4. RESULTS AND DISCUSSION

In this chapter, the DUT test results are presented and discussed in detail. In the first section, the numerical results are demonstrated in a table. In the following, the induced voltage and power output analysis are shown in two different figures in order to see the effect of temperature difference on these parameters. Finally, challenges and future work are discussed in the final section.

4.1 Measurements

In this experiment, all measurements were carried out by using a 34401A digital multimeter from Agilent Technologies. The test was implemented for eight different temperature differences in various temperature ranges. The temperature of both sides of the TE module was monitored constantly during the test via temperature sensors.

The test setup developed in this work can be used in different thermoelectric experiments in which maintaining a temperature difference is required. The test setup is able to establish temperature differences up to 60 °C depending on the thermal load of the DUT. The complete test setup in operation, including temperature controllers, the digital desktop multimeter, the test structure housing, and the DUT can be seen in Figure 16.

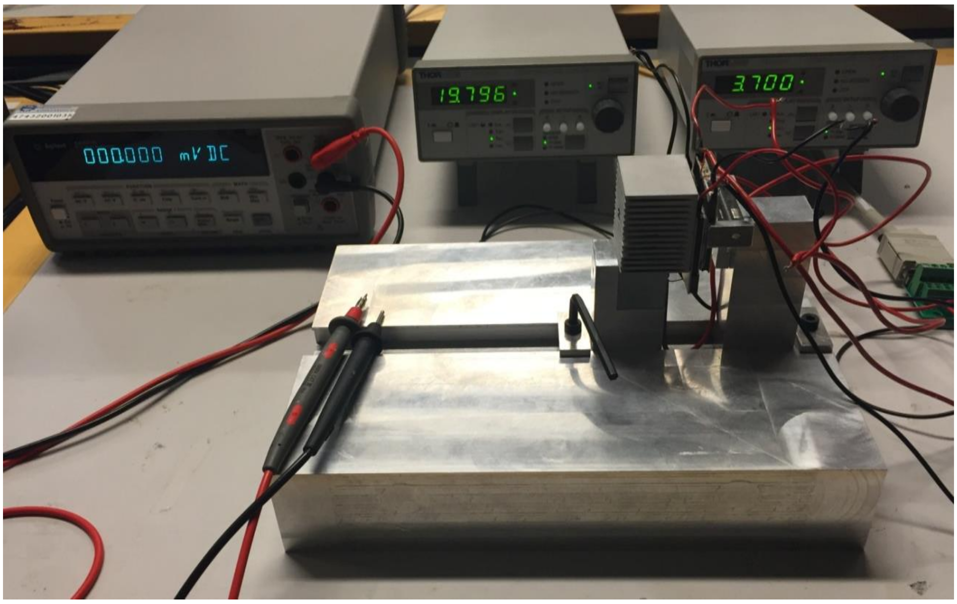


Figure 16. Test setup and the DUT under test.

Table 4 shows the values of voltage and output power acquired by maintaining different temperature differences across the DUT. As shown in table 4, values are measured for temperature differences ranging from 5 °C to 40 °C.

Table 4. Numerical test results

Temperature difference (°C)	**Temperature range(°C)**	**Voltage (µV)**	**Power (nW)**
5	18-23	30	0.3
10	13-23	45	0.7
15	8-23	80	2.4
20	13-33	120	5.5
25	13-38	160	9.8
30	23-53	210	16.9
35	23-58	250	24
40	23-63	280	30

By having a closer look at the voltage values of Table 4, it can be concluded that by increasing the temperature difference across the module, a linearly higher voltage can be generated. However, these results correspond to a temperature gradient applied to the whole device which also includes the adhesive and PET substrates that constitute the majority of the module over which the temperature gradient is established.

In addition, silver is a very good conductor of heat; therefore, silver electrodes can have an adverse effect to the temperature gradient across the thermoelectric device. Moreover, although using the adhesive ensures a proper thermal contact between the two substrates, this increases the amount of non-thermoelectric material in the device.

4.2 Voltage Analysis

The open-circuit voltage as a function of temperature difference between the two sides of the TE device is shown in Figure 16.

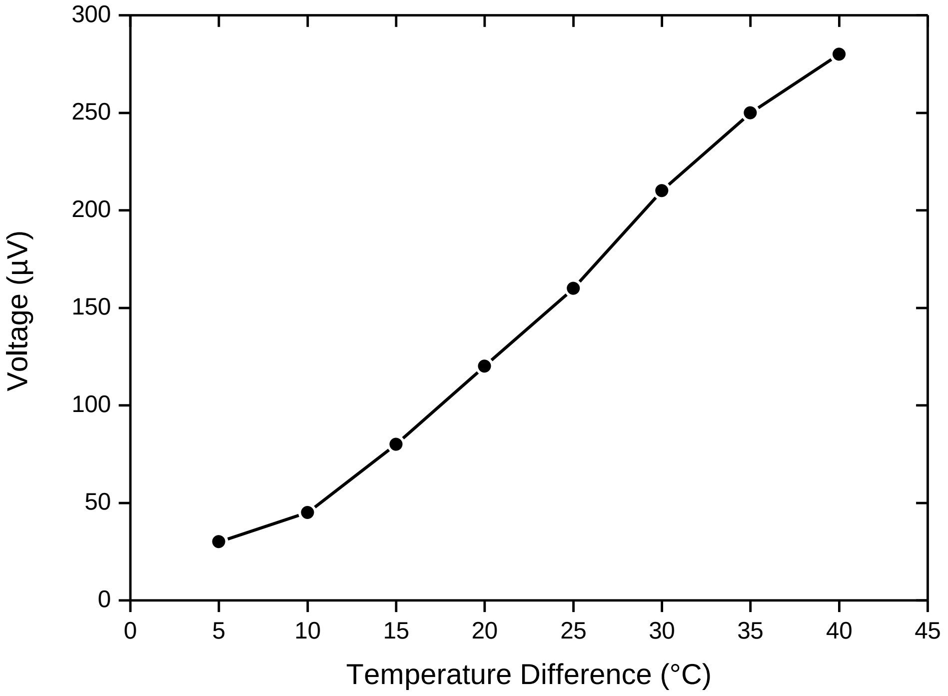


Figure 16. Electrical voltage of the TE module as a function of temperature difference.

As can be seen in Figure 16, the temperature difference is increased by 5 °C in each step of the test starting from 5°C to 40 °C. A constant upward trend for the voltage is noticeable starting from 30 µV for 5 °C temperature difference and reaching the maximum value of 280 °C for 40 °C temperature difference.

In general, it can be concluded that the open-circuit output voltage of the TE device increases in direct proportion to the temperature difference across the two sides of the module. A higher voltage can be also achieved by establishing a higher temperature difference. Since in this work the main objective was harvesting electrical energy from the temperature difference between the human's body skins and ambient in which the difference could not exceed 40 °C in a normal condition, the TE device was tested with a maximum temperature difference of 40 °C.

4.3 Power Analysis

Figure 17 illustrates the generated electrical power as a function of temperature differences across the TE module.

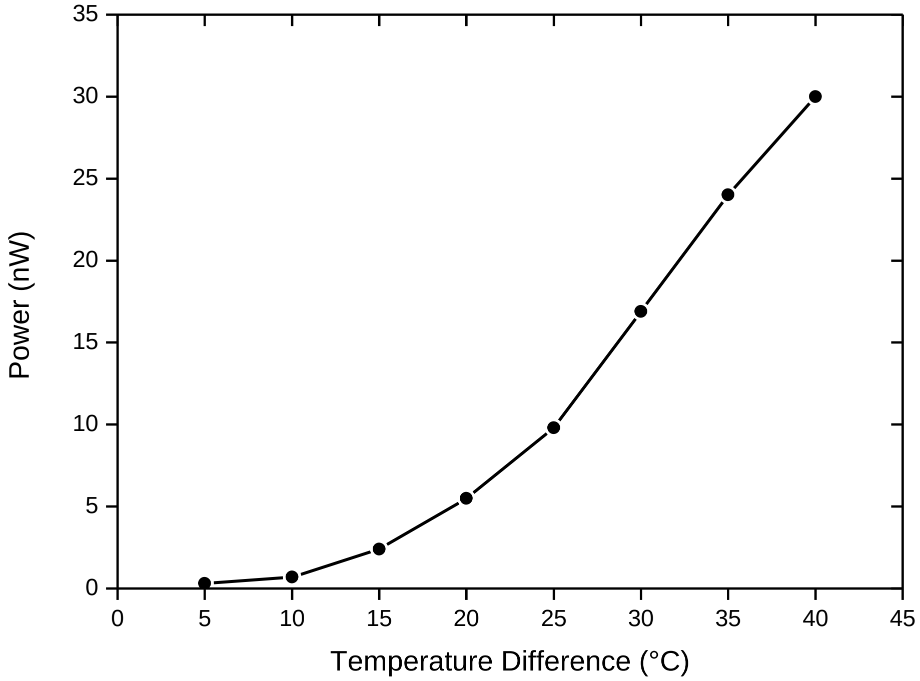


Figure 17. Electrical power of the TE module as a function of temperature difference.

In Fig. 17, it is noticeable that the power increases gradually for 5 °C to 10 °C temperature differences. Then, a sharp increase in the output power can be observed starting from 15 °C temperature difference and above. By having a closer look at the overall graph, it can be stated that the output power increases exponentially as a function of temperature difference.

In general, it can be concluded that the output power of the device is directly proportional to the temperature difference across the two sides of the module. A maximum output power of 30 nW was acquired with a load resistance of 2.6 Ω which corresponds to the internal resistance of the module. Since the electrical power generated by the TE device is in the nanowatt range, it may seem that the efficiency of the thermoelectric device is quite poor. Moreover, the efficiency is highly dependent on the temperature difference between the body and the environment. However, by having a proper power management, this small amount of energy can be stored and accumulated while it is available to harvest.

4.4 Challenges and Future Work

Although generating electrical energy from the body skin based on the thermoelectric principle is a promising approach, harvesting thermoelectric energy mainly required a noticeable temperature gradient across to the sides of the TE module in order to enable the diffusion of charge carriers. Therefore, in the environments in which the temperature difference between the body skin and the ambient is not large enough to establish a significant temperature gradient, alternative energy harvesting strategies should be replaced.

Another serious challenge for state-of-the-art thermoelectric devices is converting from a laboratory-scale device into an actual process which is scalable for manufacture in large volumes. In order to be considered for the mass production, the final TE product requires being low cost, energy efficient, and made from high abundant materials.

For the TE device developed in this thesis, a lot of work and further research is still needed. Operation reliability and air stability of the device needs to be investigated. In addition, most of the area of the TE device shown in Figure 15 merely consists of PET substrates and silver electrodes which have zero contribution to thermoelectric conversion. This area needs to be minimized in the future work. Moreover, using different materials as substrates and electrodes in the fabrication process can have merit in further experiments.

In general, further research is needed to be conducted in order to enable the thermoelectric energy harvesting device to be able to fully supply wearable biomedical devices. These efforts comprise, enhancing the performance of the thermoelectric material, optimization of the power consumption of the electronic components, and improving the design and architecture of the TE device. To this end, the entire scientific community, including chemists, physicists and engineers must cooperate closely with each other to make the thermoelectric generators a successful candidate for green energy harvesting and make our life style more and more sustainable.

5. CONCLUSIONS

Due to the increasing demand for renewable, green energy sources, the generation of thermoelectric power by harvesting heat dissipating from the human's body skin has become one of the most promising strategies to supply wearable electronics. The uniqueness of this approach lies in the direct conversion of temperature difference to electrical power and employing it to run a wearable biomedical device without using any external source of energy. The primary aim in this thesis was the design and test of an organic thermoelectric energy harvesting device.

In this work, an energy harvesting device using PEDOT: PSS as the thermoelectric component was designed and fabricated. Moreover, a test setup was designed and developed in order to test the performance of the device. Due to the many advantages of organic TE materials over conventional inorganic ones, including flexibility and light weigh, only p-type organic semiconductors was used in the fabrication of the TE device. The architecture of the device is in a way that the thermoelectric junctions are connected in series electrically while they are thermally connected in parallel.

The fabricated TE devices were characterized by measuring induced voltage across the TE module. Measurements were carried out for temperature differences ranging from 5 °C to 40 °. Based on the results, it can be concluded that the output voltage of TE device increases in direct proportion to the temperature difference across the two sides of the module reaching a maximum value of 280 μV for a 40 °C temperature difference.

Although the electrical voltage produced by the TE device is in microvolt range, its use for energy harvesting can be encouraged by either serially connecting many more TE elements for a multiplicative effect, and/or coupling it into other components, such as organic supercapacitors for energy storage. This means that the thermoelectric energy generated by the device can be accumulated and stored when a sufficient temperature gradient is available and used when necessary.

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