Thermoelectric Energy Harvesting

A Major Qualifying Project

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Abstract

Thermoelectric devices are considered for many applications including waste heat energy recovery, domestic appliances, solar thermoelectric generators, and biomedical sensors. The goal of this project was to review thermoelectric materials, test a thermoelectric module, and analyze the results. A 5W, 5V thermoelectric module manufactured by TEGProTM was tested to determine the open circuit voltage depending on the temperature gradient. The thermoelectric material in the module was an inorganic, bismuth tellurium (Bi₂Te₃) alloy. T_h, T_c, and V_{oc} were measured as T_h increased. The maximum output voltage, current, and power are 10.8 V, 1 A, and 5.4 W, respectively. Abundant sources of waste heat make thermoelectric energy conversion devices ideal for low power and self-powering applications.

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1. Introduction

The goal of this project was to review thermoelectric materials, test a thermoelectric module, and analyze the results. Thermoelectric materials convert thermal energy to electrical energy. Thermoelectric materials function by a combination of three effects; The Seebeck effect, Peltier effect, and Thomson effect. Thermoelectric materials are evaluated by their figure of merit, *ZT. ZT* improves as thermal conductivity decreases, electrical conductivity increases, and Seebeck coefficient increases. Thermoelectric materials include organics like conducting polymers and carbon nanostructures as well as inorganics like oxides, silicides, and selenides. Thermoelectrics have no moving parts and do not require maintenance, but have low conversion rates. Thermoelectric devices are considered for many applications including waste heat energy recovery from internal combustion engines and other heat sources (energy harvesting), domestic appliances like wood stoves, solar thermoelectric generators (STEGs), and self-powered biomedical devices or sensors.

A 5W, 5V thermoelectric module manufactured by TEGProTM was tested to determine the open circuit voltage depending on the temperature gradient. The thermoelectric material in the module was an inorganic, bismuth tellurium (BiTe or Bi₂Te₃) alloy. Two T-type thermocouples were used to measure the hot side and cold side temperatures (T_h and T_c , respectively). The open circuit voltage, V_{OC} was measured using a multimeter. A heat sink was used to increase the temperature gradient. The heat source was turned on and T_h , T_c , and V_{OC} were measured as T_h increased.

For the 5W, 5V thermoelectric module tested, the maximum output voltage, current, and power are 10.8 V, 1 A, and 5.4 W, respectively. The maximum output values for the module

were achieved at $T_h = 300$ °C and $T_c = 30$ °C. The thermoelectric module can convert up to 6% of the thermal energy to electrical energy, assuming ideal temperature gradient is achieved. Comparable measured data points reached approximately 10% of the open circuit voltage measured by the manufacturer. The most likely reason for the difference in measurements were the T-type thermocouples used to measure T_h and T_c which prevented the thermoelectric module from having a continuous contact surface with the heat source and heat sink. Temperature gradient can be held constant using a phase change material which will maintain temperature until sufficient energy is obtained to completely change phase. Industrial, automotive, and aerospace waste heat sources can produce a significant temperature gradient with sufficient cooling. Abundant sources of waste heat make thermoelectric energy conversion devices ideal for low power and self-powering applications.

2. Background

Thermoelectric materials convert thermal energy to electrical energy. The advantage of thermoelectric materials for thermal-electrical energy conversion is the lack of moving parts. The thermoelectric material simply generates a voltage potential in the presence of a temperature gradient. The disadvantage of a thermoelectric device is low conversion efficiency. Thermoelectric materials function by a combination of three effects; The Seebeck effect (quantitively summarized by the Seebeck coefficient), Peltier effect, and Thomson effect. Each effect describes how a material converts thermal energy to electrical energy or vice versa. Thermoelectric materials are evaluated by their figure of merit, ZT. Materials with high ZT have the best energy conversion efficiency. ZT improves as thermal conductivity decreases, electrical conductivity increases, and Seebeck coefficient increases. Common organic thermoelectric materials include conducting polymers (CP) such as polypyrrole, polyaniline, and polythiophenes and carbon nanostructures (Cowen et al., 2017). Common inorganic thermoelectrics include oxides, silicides, chalcogenides, skutterudites, and Half-Heusler materials (Gaultois et al., 2013; Patil et al., 2018). Thermoelectrics are considered for waste heat conversion, energy harvesting, and other applications.

2.1 History

Conversion of thermal to electrical energy was first discovered by Thomas Seebeck in 1821. During an experiment, Seebeck discovered that two conductive wires exposed to a temperature gradient produce a voltage potential. This phenomenon is described as the Seebeck effect where a temperature gradient produces a voltage potential across a junction between two different materials. In 1834, Jean Peltier discovered a reverse phenomenon of Seebeck effect when an applied voltage to two different materials caused heat transfer. The heat transfer due to an applied voltage on two different materials is described as the Peltier effect. Thermoelectric generators based on Seebeck effect or Peltier effect were first investigated in the 1960s when it was thought that Peltier modules could replace conventional refrigeration devices (Junior et al., 2018). The first materials developed for thermoelectric applications were bismuth telluride (Bi₂Te₃) and silicon germanium (SiGe). Thermoelectric devices based on Seebeck effect have been developed and improved by many methods. Inorganic thermoelectric materials continue to show the greatest thermoelectric properties but are often toxic. Organic thermoelectric materials are being developed as a replacement for inorganics due to their environmental properties and flexibility. The main methods for improving thermoelectric materials are maximizing electrical conductivity and minimizing thermal conductivity. Electrical conductivity is improved by alloying, doping, and electron band alterations while thermal conductivity is improved by phonon scattering due to nanostructures, grain boundaries, surface roughness, and precipitates.

2.2 Seebeck Effect

The Seebeck effect describes the movement of electrons due to a temperature gradient. This phenomenon was named for Thomas Seebeck who discovered the behavior in 1821. The Seebeck effect is observable when different conductors or semi-conductors produce a voltage when the ends are exposed to a temperature gradient (see Figure 1). In the presence of a temperature gradient, n-type semiconductors or n-doped materials transport negative charges (electrons or negative ions) while p-type semiconductors or p-doped materials transport positive charges (positive ions or holes) from high temperature to low temperature (Junior et al., 2018).

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Figure 1: Diagram of Seebeck Effect (Hasan et al., 2020)

A material's ability to produce Seebeck effect/behavior is quantitively designated as the Seebeck coefficient, *S* (sometimes written as α). Seebeck coefficient has the units V/K and is positive for p-type materials or negative for n-type materials. The output voltage produced by Seebeck effect is proportional to the temperature gradient.

$$\Delta V = S \Delta T$$
$$S = \frac{\Delta V}{\Delta T}$$

Efficient thermoelectrics typically have Seebeck coefficients between 100 mV/K and 300 mV/K (Cowen et al., 2017). The Seebeck coefficient has a significant effect on the figure of merit, *ZT*.

$$ZT = \frac{S^2\sigma}{k}T$$

Where *S*, σ , *T* and *k* are the Seebeck coefficient, electrical conductivity, temperature, and thermal conductivity, respectively. To produce more voltage from the same material, p-type and

n-type legs are connected in series (see Figure 2). Thermoelectric modules based on Seebeck effect typically use the alternating structure in series.



Figure 2: Thermoelectric Module with Alternating N-type and P-type legs Connected in Series (Junior et al., 2018)

2.3 Peltier Effect

The Peltier effect is the opposite of the Seebeck effect. The Peltier effect describes the movement of heat from one end of a metallic junction due to an electric current. Jean Peltier discovered the phenomenon in 1834. The direction of the current determines the direction of heat transfer. Heat moves in the direction of current (see Figure 3).



Figure 3: Diagram of Peltier Effect (Junior et al., 2018)

The Peltier coefficient, π is the quantitative representation of a material's ability to produce the Peltier effect. The Peltier coefficient, π has the units W/A. The heat, Q that a material can move is proportional to the current, I.

$$Q = \pi I$$

Modules based on the Peltier effect are used as coolers or heaters in low power applications. In the 1960s, Peltier coolers were suggested as an alternative to conventional refrigeration. The drawback of Peltier coolers, however, is lower heat transfer.

2.4 Thomson Effect

The Thomson effect is similar to the Seebeck effect. The Thomson effect describes the movement of electricity due to a temperature gradient. The difference between the Seebeck effect and the Thomson effect is that the Thomson effect shows voltage generation in one material while the Seebeck effect depends on two different materials. A diagram of Thomson effect is shown in Figure 4.



Figure 4: Diagram of Thomson Effect (Junior et al., 2018)

Thermoelectric energy conversion from thermal energy to electrical energy is based on the combination of Seebeck effect and Thomson effect. The Seebeck effect has a much larger contribution to the voltage generated compared to the Thomson effect.

2.5 Improving Thermoelectric Properties

Maximizing *ZT* is difficult due to the complex relationships between thermal conductivity, electrical conductivity, and Seebeck coefficient. The two most common ways to improve *ZT* are by increasing the electrical conductivity based on band theory or altering carrier concentration/doping and decreasing the thermal conductivity based on phonon scattering (Sharma et al., 2021).

The electrical conductivity, σ of materials is described by band theory. In band theory, atoms in a material possess a valence band and a conduction band. The valence band has the highest occupied energy level of an electron while the conduction band has the lowest unoccupied energy level of an electron. Conduction occurs when an electron moves from the high energy valence band to the low energy conduction band. Conducting materials have overlapping valence and conduction bands, allowing electrons to move from the high energy state to the low energy state easily. Semiconducting materials possess a band gap that allows or prevents the movement of electrons. Insulating materials have a band gap wide enough to prevent electron movement. The band gap of semiconducting materials can be reduced (increasing conductivity) by doping. Since organic thermoelectric devices are made from semiconductors, doping is often if not always included in the production process.

Doping is when electron-removing or electron-donating particles are added to the material to enhance electrical conductivity P-type semiconductors are improved with electron-removing dopants while N-type semiconductors are improved with electron-donating dopants. P-type dopants remove an electron from the highest unoccupied molecular orbital which introduces a positive charge carrier. N-type dopants donate an electron to the lowest unoccupied molecular orbital which introduces a negative charge carrier (Cowen et al., 2017).

2.6 Organic Thermoelectric Materials

Organic thermoelectric materials are typically made from conjugated polymers. Conjugated polymers have a distinct alternating single bond, double bond pattern in the main chain. The alternating pattern enables electrons to flow along the main chain. Polymers that conduct electricity are called conducting polymers. Conducting polymers have a wide variety of smart material applications such as thermoelectric, piezoelectric, magnetoelectric, and electrochromic materials. Thermoelectric conducting polymers include *trans*-polyacetylene, polypyrroles, polyanilenes, polythiophenes, and perlyenediimides (Cowen et al., 2017). Other organic thermoelectric materials include graphene, carbon nanotubes, and other nanocomposites. Thermoelectric devices made from organic materials are less toxic, less expensive, can be flexible, and easier to manufacture. The disadvantage of organic thermoelectric materials is that the Seebeck coefficient, *S*, figure of merit, *ZT*, and electrical conductivity, σ are significantly lower than inorganic thermoelectric materials.

The thermal conductivity of organic thermoelectric materials is difficult to measure experimentally. Since the figure of merit, ZT depends on the thermal conductivity, k, organic thermoelectric materials are compared by the power factor, PF.

$$PF = S^2 \sigma$$

PF can be increased by doping. Improved thermoelectric properties of polythiophene derivatives were observed due to CuTFSI, F4TCNQ, or CN6CP as dopants (Wu et al., 2021). Effective dopants for thermoelectric polypyrrole include dodecylsulfonate, *p*-toluene sulfonic acid, dodecylbenzene sulfonate, perchlorate, and hexafluorophosphate (Kemp et al., 1999). The most common organic thermoelectric material is PEDOT:PSS. This polymer solution is easy to

process, inexpensive, has superior thermoelectric properties, is flexible, and can be adjusted by controlling concentration. Secondary doping of PEDDOT:PSS in a dimethyl sulfoxide (DMSO) solvent further increases conductivity from 0.8 Scm^{-1} to 80 Scm^{-1} (Kim et al., 2002). N-type materials for thermoelectric devices like perlyenediimide (PDI), fullerines, and organometallic coordination polymers (OMCP) are also improved by dopants. Perovskites are another organic material with good thermoelectric properties. Lead halide, lanthanum oxide, and titanium-based perovskites show Seebeck coefficient up to $450 \ \mu V \cdot K^{-1}$ (Cowen et al. 2017).

Graphene and carbon nanocomposites are being studied as an alternative to polymeric and organometallics. The electrical properties of graphene and carbon nanotubes (CNT) are far superior to other organic materials. Composites based on the electrical properties of the carbon nanostructure in PEDOT:PSS matrices have been investigated. Despite the high thermal conductivity of carbon, the significant increase in electrical conductivity compared to pristine PEDOT:PSS improves *ZT* from 0.017 to 0.031 (Yoo et al., 2015). Acid treated PEDOT:PSS-CNT composites show further enhancement of thermoelectric properties.

2.7 Inorganic Thermoelectric Materials

Inorganic materials are the most common in thermoelectric applications due to their higher efficiency and better thermoelectric properties (Seebeck coefficient, electrical conductivity, figure of merit). The main inorganic thermoelectric materials are bismuth telluride (Bi₂Te₃), lead telluride (PbTe), and silicon germanium alloys (SiGe) (Hasan et al., 2020). These thermoelectric materials ideally have a phonon glass-electron crystal (PGEC) property where phonons are scattered, reducing thermal conductivity while improving electrical conductivity (Rashad et al., 2017). Thermoelectric properties can be further improved based on PGEC by including impurities, nanoparticles, or increasing crystal boundaries.

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Bi₂Te₃ has a maximum operating temperature up to 300°C with *ZT* approximately equal to 1 at 50°C (Champier, 2017). Alloying, doping, nano-structuring, and other processes can alter the operating temperature and improve thermoelectric properties. P-type Bi₂Te₃ alloys have large *ZT* values up to 2.42 at 700 K. The thermoelectric properties of n-type Bi₂Te₃ alloys are lower than p-type due to a higher thermal conductivity, *k* (Hasan et al., 2020). Figure 5 shows the thermal conductivity (A) and figure of merit (B) for a selection of Bi₂Te₃ and BiSbTe alloys. Figure 6 shows the efficiency for a selection of inorganic thermoelectric materials. Reducing the thermal conductivity for Bi₂Te₃ alloys is achieved by doping and nano-structuring. The energy gap, E_g in materials describes the driving force for conduction (as E_g increases, the thermal conductivity decreases and electrical conductivity increases). $E_g = -0.13 \ eV$ for n-type Bi₂Te₃. When doped with NaOH, E_q of Bi₂Te₃ increases to 4.8 eV (Rashad et al., 2017).



Figure 5: (A) Thermal Conductivity, *k* vs. Temperature for Bi₂Te₃ and BiSbTe alloys, (B) Figure of Merit, *ZT* vs. Temperature for Bi₂Te₃ and BiSbTe Alloys (Hasan et al., 2020)



Figure 6: Efficiency of Inorganic Thermoelectric Materials and Alloys. A BiTe/Half-Heusler Thermoelectric Device was tested. (Li et al., 2020)

PbTe and SiGe have a greater maximum operating temperature which makes them ideal for high temperature applications. PbTe has a good figure of merit and efficiency for midtemperature applications (see Figure 7). Other thermoelectrics for mid-temperature applications include skutterudites, clathrates, tin selenide (SnSe) and copper selenide (Cu₂Se) (Hasan et al., 2020).



Figure 7: Average Figure of Merit and Efficiency for a Selection of Lead Telluride Alloys

(Sharma et al., 2021)

Lead telluride has excellent thermoelectric properties such as high Seebeck coefficient due to valence band and conduction band properties, high electrical conductivity due to its cubic crystal structure, and low thermal conductivity due to phonon scattering (Sharma et al., 2021). The figure of merit, *ZT* of p-type and n-type PbTe was originally estimated to be ~0.8. With more advanced measurement techniques and electrical and thermal conductivity adjustments from carrier concentration/doping and phonon scattering, *ZT* has been measured up to 2.5 for ptype and 2.0 for n-type PbTe (Sharma et al., 2021). PbTe behaves as a p-type material when Te concentration is increased, but behaves as a n-type material when Pb concentration is increased. Figure 8 shows the figure of merit for a selection of p-type and n-type PbTe materials/alloys at a given operating temperature. Based on Figure 8(a), p-type PbTe alloys shown reach maximum *ZT* (up to ~2.4 for Pb_{0.98}Na_{0.02}Te- 8% SrTe (Tan et al., 2016)) at temperatures around 900 K. Based on Figure 8(b), n-type PbTe materials/alloys reach maximum *ZT* (up to ~2.0 for Bi-PbTe/Ag₂Te (Lee et al., 2019)) at temperatures from 600 to 800 K.



Figure 8: Figure of Merit vs. Operating Temperature for (a) p-type and (b) n-type PbTe Alloys (Sharma et al., 2021)

The thermoelectric properties of PbTe can be improved by several methods. Band flattening improves the Seebeck coefficient by increasing the effective mass, m_d . Doping or alloying PbTe with iodine, lanthanum, or manganese has shown a significant change in the band gap, increasing Seebeck coefficient as an n-type material. PbTe is often doped or alloyed with sodium to improve p-type Seebeck coefficient. Other p-type PbTe alloys that are improved based on electronic band structure include PbTe-PbSe, PbTe-PbS, PbTe-MgTe, and PbTe-SrTe (Sharma et al., 2021). Since ZT is proportional to the square of Seebeck coefficient, improving Seebeck coefficient significantly improves thermoelectric effect compared to improving the electrical conductivity. Another method to improve the figure of merit is band alignment. Band alignment is used to reduce the thermal conductivity by increasing phonon scattering. Band alignment is based on reducing the band gap between materials in a heterogeneous composite. An example of this method is used on PbTe-SrTe composites where strontium atoms replace lead atoms, forming a solid solution (Pb_{1-x}Sr_xTe). The band gap is reduced from 0.06 eV to 0.03 eVwhich slightly reduces the electrical conductivity, but greatly reduces the thermal conductivity due to SrTe precipitates (Sharma et al., 2021).

Decreasing thermal conductivity by phonon scattering is due to defects in the microstructure such as precipitates, nanograins, point defects, and nanostructures. By controlling the architecture of the material at the micro and macroscales together, the thermal conductivity and figure of merit significantly improve as temperature is increased (see Figure 9).



Figure 9: (a) Lattice Thermal Conductivity vs. Temperature of a Selection of Multiscale Architecture Enhanced PbTe Alloys, (b) Figure of Merit vs. Temperature of a Selection of Multiscale Architecture Enhanced PbTe Alloys (Sharma et al., 2021)

Silicon-based alloys and nanostructures are decent thermoelectric materials due to their inherent thermoelectric properties. Silicon nanowires, silicon germanium, and silicides offer the greatest thermoelectric properties at high temperatures >1000 K. The advantages of using silicon-based thermoelectrics is shown in Figure 10. P-type SiGe alloys have lower *ZT* than n-type SiGe alloys. Doping and nanostructuring are used to improve *ZT* in both p-type and n-type SiGe alloys (Hasan et al., 2020).



Figure 10: Advantages of Si-based Thermoelectric Materials (Gadea et al., 2018)

2.8 Thermoelectric Energy Harvesting Applications

Thermoelectric devices convert thermal energy to electrical energy based on Seebeck effect. Thermoelectric technology is used in many applications ranging from smart textiles to solar photovoltaics to internal combustion engines to harvest energy lost due to waste heat. Renewable energy based on solar thermoelectric generators (STEGs) is widely studied (Sundarraj et al., 2014). Energy harvesting from the human body through thermoelectric energy conversion is applied to smart textiles that can produce electrical energy to power cell phones, smart watches, and other devices. Waste heat from vehicles and manufacturing has been investigated as a heat source for thermoelectric generators. Upwards of 60% of fuel energy is lost from internal combustion through exhaust (Patil et al., 2018). Radioisotope thermoelectric generators (RTGs) made from PbTe and SiGe have been used in space exploration applications as early as 1961 (Champier, 2017). RTGs convert the heat naturally generated from decaying radioactive materials, such as plutonium-238, to electrical energy. Industrial processes that use turbines, furnaces, combustion chambers, etc. can also be targeted for thermoelectric applications.

Thermoelectric devices are being considered for many low-power applications where convenience is more desirable than efficiency. In particular, self-powered sensors based on thermoelectric effect have been investigated significantly. Low-power devices, like smart watches or health monitoring devices, have the capability to be powered by the temperature gradient between human skin temperature and ambient temperature. Thermoelectric devices in low-power applications require no maintenance, are reliable, and function over long periods of time without decreasing efficiency and output power. There are many heat sources in industrial applications which produce a large enough temperature gradient for thermoelectric modules to convert a significant amount of energy.

Use of thermoelectric modules to capture waste heat from domestic applications has been developed for cookers and stoves. Many companies have developed cookers or stoves that convert waste heat into electricity. Domestic-sized wood stoves produce a significant temperature gradient up to 150°C enabling thermoelectric modules to produce up to 5 V and 20 W (Junior et al., 2018).

Internal combustion engines are used in cars, planes, helicopters, locomotives, and ships to transport goods and people. An internal combustion engine's maximum efficiency is limited to 40% of the fuel energy used to power them. The remaining 60% of the initial energy is lost due to exhaust or to the environment (Champier, 2017). Thermoelectric generators applied to internal combustion engines, even with efficiencies as low as 3% produce a significant amount of electrical energy at high temperatures and large temperature gradient. Because more power is produced over a large temperature gradient, thermoelectric generators can be small if cooled

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effectively. Recent experiments in the automotive industry have shown thermoelectric devices used in the exhaust system can produce up to 500 W; enough to power onboard electrical devices (Junior et al., 2018). Thermoelectrics can also be applied to the cooling system where a significant temperature gradient is present. Combined thermoelectrics in the cooling and exhaust systems can recover up to 6% of wasted fuel energy.

3. Methods

The goal of this project was to review thermoelectric materials, test a thermoelectric module, and analyze the results. A 5W, 5V thermoelectric module manufactured by TEGProTM was tested to determine the open circuit voltage depending on the temperature gradient. The thermoelectric material in the module was an inorganic, bismuth tellurium (BiTe or Bi₂Te₃) alloy. Graphite sheets are used as the contact plates between the bismuth tellurium and the heat source. The maximum continuous operating temperature of the module was given as 330°C (TEGPro, 2014).



Figure 11: 5W, 5V Thermoelectric Module Dimensions (TEGPro, 2014)



Figure 12: 5W, 5V Thermoelectric Module

The TEG was secured to an aluminum block to conduct heat from the heat source to the module. Two T-type thermocouples were used to measure the hot side and cold side temperatures (T_h and T_c , respectively). An EXTECH® Instruments 7 Thermocouple Type Dual Input Datalogger was used to simultaneously measure T_h and T_c . The open circuit voltage, V_{OC} was measured using an EXTECH® Instruments 410 Multimeter. A heat sink was used to

increase the temperature gradient. The heat source was turned on and T_h , T_c , and V_{OC} were measured as T_h increased.



Figure 13: 5W, 5V Thermoelectric Module Attached to an Aluminum Block with T-type

Thermocouples to Measure Hot Side and Cold Side Temperatures



Figure 14: Thermoelectric Module with Heat Sink



Figure 15: Open Circuit Voltage, Voc Measurements Circuit



Figure 16: EXTECH 410 Multimeter (left) and EXTECH Thermocouple Datalogger (right)

4. Results

The largest delta T measured was 123.5 °C. The highest hot side temperature, T_h, measured was 186.3 °C. The highest Seebeck coefficient, *S*, calculated was 0.087 V/K. The highest open circuit voltage, V_{OC}, was 0.959 V. Without the heat sink, the Seebeck coefficient showed a decreasing trend as delta T increased (Figure 17). With the heat sink, the Seebeck coefficient increased as delta T increased (Figure 18). The most likely cause for the difference in trend is a continuous contact surface. Without the heat sink, the thermoelectric module had a continuous contact surface with the heat source and air. With the continuous contact surface, the entire module would function to its greatest capability even at lower delta T. The decreasing trend is most likely due to delta T increasing more rapidly than the open circuit voltage.



Figure 17: Seebeck Coefficient vs. ΔT (no Heat Sink)



Figure 18: Seebeck Coefficient vs ΔT (with Heat Sink)

The open circuit voltage, V_{OC} , was plotted against the hot side temperature, T_h with and without the heat sink (Figures 19 & 20).



Figure 19: Open Circuit Voltage vs. Hot Side Temperature (with Heat Sink)



Figure 20: Open Circuit Voltage vs. Hot Side Temperature (no Heat Sink)

5. Discussion

For the 5W, 5V thermoelectric module tested, the maximum output voltage, current, and power are 10.8 V, 1 A, and 5.4 W, respectively (Figures 21, 22, & 23). The maximum output values for the module were achieved at $T_h = 300^{\circ}$ C and $T_c = 30^{\circ}$ C. The thermoelectric module can convert up to 6% of the thermal energy to electrical energy, assuming ideal temperature gradient is achieved (see Figure 24).



Figure 21: Open Circuit Voltage vs. Hot Side Temperature of 5W, 5V Thermoelectric Module

(TEGPro, 2014)



Figure 22: Output Current vs. Hot Side Temperature of 5W, 5V Thermoelectric Module

(TEGPro, 2014)



Figure 23: Output Power vs. Hot Side Temperature of 5W, 5V Thermoelectric Module (TEGPro,

2014)



Figure 24: Conversion Rate vs. Hot Side Temperature of 5W, 5V Thermoelectric Module (TEGPro, 2014)

Figures 21 through 24 show that the manufacturer was able to keep the cold side temperature, T_c , constant while increasing the hot side temperature, T_h . Maintaining T_c at 30°C yielded the greatest open circuit voltage, output current, output power, and conversion rate. In comparison to the measured data (Figures 19 & 20), Figure 21 also shows an increase in open circuit voltage as hot side temperature increases. A measured data point to compare to the datasheet is $T_c = 30.1$ °C, $T_h = 90.2$ °C, and $V_{OC} = 0.362$ V. V_{OC} of the measured data point is approximately 10% of the V_{OC} from Figure 21. The most likely cause of this significant difference is the ineffectiveness of the T-type thermocouples used in the experiment. The T-type thermocouple used in the experiment prevented the thermoelectric module from having a continuous contact surface with both the heat source and the heat sink.

Although the maximum output power was achieved at $T_h = 300^{\circ}$ C and $T_c = 30^{\circ}$ C, Figure 24 shows the maximum conversion rate occurs at $T_h = 160^{\circ}$ C and $T_c = 30^{\circ}$ C. The maximum conversion rate occurs at a lower temperature due to the thermoelectric properties of the module.

The conversion rate decreases as the hot side temperature increases due to the electrical and thermal conductivities which reduce the figure of merit and the conversion rate. As temperature increases, electrical conductivity decreases and thermal conductivity increases.

The maximum output power for the module is 5.4 W. At ideal temperature gradient ($T_h = 300^{\circ}$ C and $T_c = 30^{\circ}$ C) the thermoelectric module has a power output per unit area of 4284.9 W/m². Typical engine operating temperature is between 195 and 220°C. Assuming T_c can be effectively kept at 30°C by a heat sink or cooling system, one thermoelectric module produces up to 2380.5 W/m². Another consistent heat source for thermoelectric energy conversion is the external surface of buildings in hot environments or during summer. External building temperatures can reach up to 65°C. At peak temperature gradient for the external surface of a building, the thermoelectric module produces up to 397 W/m². Depending on the power requirements of devices targeted to be powered by thermoelectric modules, the number of modules needed can be calculated using the formula below.

number of modules,
$$N = \frac{P_{target}}{P_{gradient}} \cdot A^{-1}$$

In the formula, P_{target} is the power requirement, in Watts, of the targeted device or appliance to be powered by the thermoelectric modules, $P_{gradient}$ is the power output per unit area (W/m²) of the thermoelectric module depending on the gradient temperature gradient, and *A* is the area of one module (35.5mm by 35.5mm = 1.26×10^{-3} m²). $P_{gradient}$ is calculated using Figure 23 to find the matched load power output for the given T_h and T_c temperature gradient and dividing by the area of one module, *A*.

$$P_{gradient} = \frac{P_{output}}{A}$$

Thermoelectric modules are maintenance free for an indefinitely long time while hot side temperature, T_h does not exceed the continuous maximum operating temperature (330°C in this case). The only cost involved with thermoelectric modules is the initial purchase. The cost of the 5W, 5V thermoelectric module tested in this project was \$18.99 (decreases when buying in bulk). Since installation is very simple (connecting modules in series), cost of thermoelectric energy conversion becomes inexpensive as the modules are used over long periods of time. Due to its easy installation, low initial cost, no long-term cost, and consistent, reliable output power, the 5W, 5V thermoelectric module is an ideal device for long-term applications, especially where maintenance is not possible (sealed compartments like fuselages or walls). Some examples include internal combustion engines, buildings, windows, solar energy conversion and advanced aerospace applications.

The design of the module can be improved by adding another material to the contact surface. A phase change material applied to the contact surface would store thermal energy and maintain the temperature gradient across the module to a constant value. A phase change material stays at a constant temperature until a critical energy level is achieved when the phase change is complete, and temperature can increase or decrease afterwards. Using phase change material layer would be useful for applications requiring a constant voltage, current, or power output.

The 5W, 5V thermoelectric module would be useful for applications that can achieve the ideal temperature gradient of $T_h = 300^{\circ}$ C and $T_c = 30^{\circ}$ C. For example, exhaust gases from internal combustion engines can reach up to 300°C. The issue with the thermoelectric module for this application would be cooling the other side of the module effectively. A well-designed heat sink combined with the forced convection from a moving vehicle in air may be enough to

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generate sufficient electrical energy to power onboard devices and sensors. As for biomedical sensors and devices, a much smaller temperature gradient is available between human skin temperature and ambient air temperature. Although the temperature gradient is smaller and the power output would be less, a thermoelectric module can still provide enough electrical energy to partially or even fully power biomedical sensors and devices. Using thermoelectric devices to power devices eliminates the cost of replacing or recharging batteries and the waste produced from depleted batteries. Abundant sources of waste heat make thermoelectric energy conversion devices ideal for low power and self-powering applications.

References

- Champier, D. (2017). Thermoelectric generators: A review of applications. *Energy Conversion* and Management, 140, 167-181. <u>https://doi.org/10.1016/j.enconman.2017.02.070</u>
- Cowen, L. M., Atoyo, J., Carnie, M. J., Baran, D., & Schroeder, B. C. (2017). Review—Organic Materials for Thermoelectric Energy Generation. *ECS Journal of Solid State Science and Technology*, 6(3), N3080-N3088. <u>https://doi-org.ezpxy-web-p-</u> <u>u01.wpi.edu/10.1149/2.0121703jss</u>
- Gadea, G., Pacios, M., Morata, A., & Tarancon, A. (2018). Silicon-based nanostructures for integrated thermoelectric generators. *Journal of Physics D: Applied Physics*, 51, 423001. <u>https://doi-org.ezpxy-web-p-u01.wpi.edu/10.1088/1361-6463/aad683</u>
- Gaultois, M. W., Sparks, T. D., Borg, C. K. H., Seshadri, R., Bonificio, W. D., & Clarke, D. R.
 (2013). Data-Driven Review of Thermoelectric Materials: Performance and Resource Considerations. *Chemistry of Materials, 25, 2911-2920.* https://doi.org/10.1021/cm400893e
- Hasan, N., Wahid, H., Nayan, N., & Ali, M. S. M. (2020). Inorganic thermoelectric materials: A review. *International Journal of Energy Research*, 44(8), 6170-6222. <u>https://doiorg.ezpxy-web-p-u01.wpi.edu/10.1002/er.5313</u>

- Junior, O. H. A., Maran, A. L. O., & Henao, N. C. (2018). A review of the development and applications of thermoelectric microgenerators for energy harvesting. *Renewable and Sustainable Energy Reviews*, 91, 376-393. <u>https://doi.org/10.1016/j.rser.2018.03.052</u>
- Kemp, N. T., Kaiser, A. B., Liu, C. J., Chapman, B., Carr, A. M., Trodahl, H. J., Buckley, R. G., Partridge, A. C., Lee, J. Y., Kim, C. Y., Bartl, A., Dunsch, L., Smith, W. T., & Shapiro, J. S. (1999). Thermoelectric power and conductivity of different types of polypyrrole. *Journal of Polymer Science Part B: Polymer Physics*, *37*(9), 953-960. <u>https://doiorg.ezpxy-web-p-u01.wpi.edu/10.1002/(SICI)1099-0488(19990501)37:9<953::AID-POLB7>3.0.CO;2-L
 </u>
- Kim, J. Y., Jung, J. H., Lee, D. E., Joo, J. (2002). Enhancement of electrical conductivity of poly(3,4-ethylenedioxythiophene)/poly(4-styrenesulfonate) by a change of solvents, *Synthetic Metals*, 126(2-3), 311-316. <u>https://doi.org/10.1016/S0379-6779(01)00576-8</u>
- Lee, M. H., Yun, J. H., Kim, G., Lee, J. E., Park, S., Reith, H., Schierning, G., Nielsch, K., Ko, W., Li, A., & Rhyee, J. (2019). Synergetic Enhancement of Thermoelectric Performance by Selective Charge Anderson Localization–Delocalization Transition in n-Type Bi-Doped PbTe/Ag₂Te Nanocomposite. *ACS Nano*, *13*(4), 3806-3815.
 DOI: <u>10.1021/acsnano.8b08579</u>.

- Li, W., Poudel, B., Nozariasbmarz, A., Sriramdas, R., Zhu, H., Kang, H. B., & Priya, S. (2020).
 Bismuth Telluride/Half-Heusler Segmented Thermoelectric Unicouple Modules Provide
 12% Conversion Efficiency. *Advanced Energy Materials*, *10*(38), 2001924. <u>https://doi-org.ezpxy-web-p-u01.wpi.edu/10.1002/aenm.202001924</u>
- Mamur, H., Bhuiyan, M. R. A., Korkmaz, F., & Nil, M. (2018). A review on bismuth telluride (Bi₂Te₃) nanostructure for thermoelectric applications. *Renewable and Sustainable Energy Reviews*, 82(3), 4159-4169. <u>https://doi.org/10.1016/j.rser.2017.10.112</u>
- Patil, D. S., Arakerimath, R. R., & Walke, P. V. (2018). Thermoelectric materials and heat exchangers for power generation – A review. *Renewable and sustainable Energy Reviews*, 95, 1-22. <u>https://doi.org/10.1016/j.rser.2018.07.003</u>
- Rashad, M. M., El-Dissouky, A., Soliman, H. M., Elseman, A. M., Refaat, H. M., & Ebrahim,
 A. (2018). Structure evaluation of bismuth telluride (Bi₂Te₃) nanoparticles with enhanced
 Seebeck coefficient and low thermal conductivity. *Materials Research Innovations*, 22(6), 315-323. DOI: <u>10.1080/14328917.2017.1320838</u>

- Sharma, P. K., Senguttuvan, T. D., Sharma, V. K., & Chaudhary, S. (2021). Revisiting the thermoelectric properties of lead telluride. *Materials Today ENERGY*, 21, 100713. <u>https://doi.org/10.1016/j.mtener.2021.100713</u>
- Sundarraj, P., Maity, D., Roy, S. S., & Taylor, R. A. (2014). Recent advances in thermoelectric materials and solar thermoelectric generators – a critical review. *RSC Advances*, 87, 46860-46874. <u>https://doi.org/10.1039/C4RA05322B</u>
- Tan, G., Shi, F., Hao, S., Zhao, L., Chi, H., Zhang, X., Uher, C., Wolverton, C., Dravid, V. P., & Kanatzidis, M. G. (2016). Non-equilibrium processing leads to record high thermoelectric figure of merit in PbTe–SrTe. *Nature Communications*, *7*, 12167. <u>https://doi.org/10.1038/ncomms12167</u>

TEGPro. (2014). TE-MOD-5W5V-35S 5 Watt Thermoelectric Module Product Datasheet. <u>https://www.tegmart.com/datasheets/TGPR-5W5V-35S.pdf</u>

Wu, S., Xing, W., Zhu, M., Zou, Y., Sun, Y., Xu, W., & Zhu, D. (2021). Doped thieno[3,4b]thiophene-based copolymers for p-type organic thermoelectric materials. *Journal of Materials Chemistry C, 12*, 4158-4163. <u>https://doi-org.ezpxy-web-p-</u> <u>u01.wpi.edu/10.1039/D1TC00211B</u> Yoo, D., Kim, J., Lee, S. H., Cho, W., Choi, H. H., Kim, F. S., & Kim, J. H. (2015). Effects of one- and two-dimensional carbon hybridization of PEDOT:PSS on the power factor of polymer thermoelectric energy conversion devices. *Journal of Materials Chemistry A*, *12*, 6526-6533. <u>https://doi-org.ezpxy-web-p-u01.wpi.edu/10.1039/C4TA06710J</u>