Peltier cell's thermoelectric properties study for its possible applications as a thermoelectric device

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The thermoelectric properties of a standard commercial Peltier Cell were studied with the purpose of evaluating its efficiency for its possible applications; these properties included its electrical conductivity, thermoelectric power, thermal conductivity, and internal resistance. It was found that it has a merit figure $Z = S^2\sigma/K = 1.39 \pm 0.07 \times 10^{-3}$ kelvin^{-1} (or unitless $ZT = 0.43 \pm 0.02$), making it a thermoelectric device of moderate efficiency. In addition, under certain assumptions, and when coated with black permanent marker ink, it showed a light absorption capacity of $90 \pm 1\%$. It was concluded that the Peltier cell is suitable for small scale applications, such as a device for measuring the output power of commercially available lasers, or as a cooling system for small spaces.

I. INTRODUCTION

Thermoelectric (TE) devices convert heat energy into electrical energy and viceversa. They are a promising technology for the use of waste heat for generation of electrical power.[6] Their efficiency is evaluated by the value of their figure of merit $Z = S^2\sigma/K$, where S, σ, and K are the thermoelectric power, electrical conductivity and thermal conductivity, respectively.[4, 8] The difficulty is that S, σ, and K are interdependent, and so, the production of a highly efficient TE device is a question of optimizing these three parameters.[5, 13] Nevertheless, new methods have been developed over the last decades to improve the TE efficiency of these devices, such as electron quantum confinement, and phonon scattering in nanostructures.[13] Reducing the dimensions of the TE device to the nano-scale introduces new variables that can be used to improve the TE efficiency.[5] For example, researchers have been able to produce a Bi_2Te_3 with a (unitless) merit figure $ZT \approx 1.5$ through melt spinning nano-structuring processing.[8] (For comparisson, high efficiency TE devices have $ZT \approx 1$.[8]) Other nano-structuring processes include ball milling, thermal forging, and hydrogen synthesis.[8] In the nano-scale, we are not limited by what materials nature gives use; we can now engineer our own for the production of better TE devices.[5] This counterweights the size limitations of highly efficient TE devices. In this report, I assess the efficiency of a standard Peltier cell for its possible applications. Although I do not deal with nano-scale materials, I do explore the underlying physics between the thermoelectric effect.

II. THEORY

I studied the thermoelectric effect with a Peltier cell: a set of alternating n- and p-type semiconductors [10] connected electrically in series [7] and in thermal contact by a series of metal-semiconductor junctions [4]. (See Figure 1.) The n-type semicondcutor has free "excess electrons" for conduction.[7] The p-type semiconductor has a limited number of "vacancies" [7] through which, I suspect, time-constrained impurity conduction can occur. The rest of the conduction in the semiconductors has to occur by intrinsic conduction of electrons above their Fermi energy.

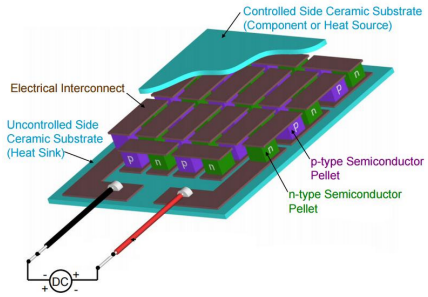

FIG. 1: Typical Peltier cell: an array of n- and p-type semiconductors electrically in series by metal-semiconductor junctions. All this sandwiched between insulators, typically ceramic plates.[10]

For electron conduction between a metal and a semiconductor in contact, their Fermi levels must be equal at thermodynamic equilibrium.[9] I suspect that electron flow in a Peltier cell is determined by the electron density difference between the n- and p-type semiconductors; electron conduction in a circuit is aided by the semiconductors' doping (n or p), and this would determine the direction of electron flow. It would be easier to start a current in the direction n $\rightarrow$ p since the n-type has "excess" electrons, and therefore a larger electron density.

Heating one side of the cell gives the metals' electrons enough energy to jump into the conduction band of the n-type semiconductor. These electrons would run freely throughout the cell above its Fermi level, according to the Pauli exclusion principle [9], and so, there would not be any electron build-up in the metals and semiconductors.

For constant pressure, the Gibbs energy equation is [9]:

$$dG = -S_E dT + \mu dN, \tag{1}$$

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where G, S_E, T, μ, and N are the Gibbs free energy, the entropy, the temperature, the chemical potential, and the number of particles in the system, respectively.

Eq. (1) applies to the Peltier cell, since its faces were in contact with pressure and heat reservoirs [9]. For a reversible addition of an electron, $dG = 0$ [9], and so, the change in electron number and temperature have the same sign. Applying a voltage throughout the cell allows the metals' electrons flow through the excess electrons "spaces" in the n-type semiconductor, decreasing the metal's electron number, and therefore, its temperature would also decrease. I suspect that these electrons are below the Fermi level, and so, they do not have enough energy to jump into the conduction band of the p-type semiconductor. This would cause an electron build-up on the metal on the other "face" of the cell, raising its temperature. This temperature rise would give some electrons in the metal enough energy to jump into the p-semiconductor's conduction band, adding them to the current.

The merit figure Z and coefficient of performance β are parameters determining the performance of a thermoelectric device. High performance thermoelectric materials have a *unitless* merit figure $ZT \approx 1$ [8], with a small thermal conductivity and a large electrical conductivity and thermoelectric power [4]:

$$Z = S^2\sigma/K, \tag{2}$$

where S, σ, and κ are the Seebeck coefficient (or thermoelectric power), the electrical conductivity, and the thermal conductivity, respectively. T in (unitless) ZT is for temperature.

The coefficient of performance is [4]:

$$\beta = \frac{\Pi I_p - {I_p}^2 R_p/2 - \kappa\Delta T}{S I_p \Delta T + {I_p}^2 R_p}, \tag{3}$$

where Π, I_p, R_p, κ are the Peltier coefficient, the current produced by the cell at a certain ΔT (temperature difference between cell's faces), its internal resistance and its thermal conductance, respectively.

The evaluation for possible applications of the Peltier cell depends on its Z and β values.

III. EXPERIMENTAL DETAILS

The goal of this experiment was the evaluation of the possible application of the Peltier cell (of unknown materials[endnote1]) as a thermoelectric device. The experiment consisted in measuring the following electric and thermal properties of the cell for the calculation of Z and β:

(i) its Seebeck coefficient, (ii) electrical conductivity, (iii) thermal conductivity, (iv) internal resistance, (v) and its Peltier coefficient.

The theoretical assumptions regarding the Gibbs' energy (eqn. (1)) were carefully observed. At all times, both sides of the Peltier cell were kept in contact with a common pressure reservoir and each with its own heat reservoir. (See Figure 2.) The pressure reservoir was made of the composite system atmosphere and sandwiching plates. The upper heat reservoir was the atmosphere, and the bottom one, a heat sink made of metal and filled with room temperature water. Water has a large isochoric heat capacity (4.1570 kJ/(kg·kelvin) [3]), and therefore, filling the sink with water allowed us to dump more heat into it without raising its temperature significantly; this reduced the heat back-flow inside the cell, specially when using it as a heat pump or refrigerator.

Although heat back-flow in the cell was reduced, it was not eliminated. A correction attributed to the heat flux inside the cell was added to the equations used for the calculation of the properties of the cell affected by it. The majority of our measurements were timed; heat back-flow meant that the measurement of a value, say the current produced by the cell, at a given moment would not be the same at another. This variation in values was not true for the quantities listed above, except (v); since they were calculated from the parameters of a straight line (intercept and slope) from linearisation techniques, we just had to ensure that the $y-$ and $x-$values were gathered at the same time intervals to obtain a good linear fit.

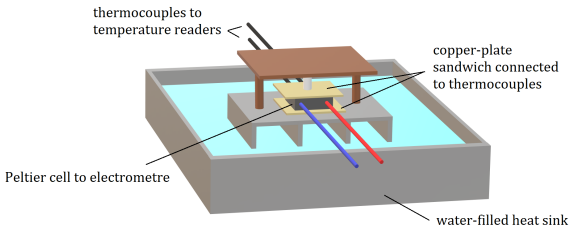

FIG. 2: Setup model (self-made). To use the Peltier cell as a heat engine: attach resistor on top of it. To use it as a heat pump or refrigerator: apply a voltage.

IV. ANALYSIS AND RESULTS

The value of the merit figure Z of the Peltier cell was determined to be $Z = 0.139 \pm 0.007 \times 10^{-3}$ K^{-1} (or equivalently, (unitless) $ZT \approx 0.43 \pm 0.02$ [11]). For reference, a high efficiency thermoelectric device has $ZT \approx 1$ [8] ($\approx 3.24 \times 10^{-3}$ [11]).

The main difficulty in the determination of the parameters of Z (eqn. (2)) was dealing with heat flow inside the cell. I accounted for this by timing the measurements. The collection of data at definite time intervals for the determination of the Seebeck coefficient S and the thermal conductivity K was the best way to proceed. These two quantities are given by [4], respectively,

$$V_s = S\Delta T \tag{4}$$

$$K = \kappa\frac{L}{A}, Q = \kappa\Delta T, \tag{5}$$

where V_s was the voltage generated by the cell due to the temperature difference ΔT between its sides when it was used as a heat engine (see caption of Fig. 2). κ is the thermal conductance, the slope of the line of the plot for the heat power supplied to the resistor, Q, vs. ΔT. A and L are the area of the cell's sides and its thickness, respectively. I obtained $S = 0.01368 \pm 0.00007$ volts/K and $K = 1.94 \pm 0.06$ watts/(K·m).

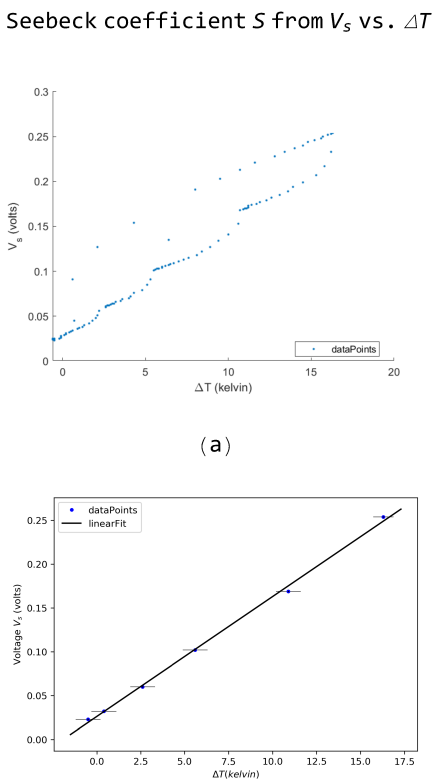

FIG. 3: Measurements for the determination of the Seebeck coefficient as in eqn. (4). (a) Data behaviour in time. (b) Selected data at kinks.

The $x-$ and $y-$values of eqn. (4) fluctuated in time for a fixed voltage and current applied to the resistor. This was expected: heat flow inside the cell was present at *all* times, so I could not obtain a constant ΔT, and therefore, a constant V_s, for certain heat power values Q. To fix this, I studied the evolution of the graph V_s vs. ΔT in time for different Q-values (see Fig. 3a). I chose V_s and ΔT values at fixed times for different Q's and plot them; I obtained a linear behaviour (see Fig. 3b). Although choosing V_s and ΔT meant that the graph of eqn. (4) would possibly be displaced with respect to the one expected from the real values of V_s and ΔT, the slope S of the regression line would not be affected significantly.

A similar observation applied for the determination of the thermal conductance κ, used to determined the value K above. This time, the $y-$value in eqn. (5) was constant while ΔT, the $x-$value, varied in time (see Fig. 4).

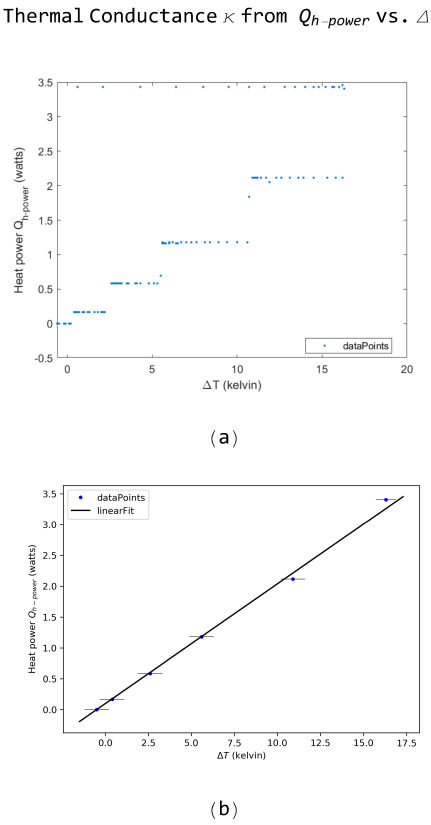

FIG. 4: Measurements for the determination of the thermal conductance of the Peltier cell as in eqn. (5). (a) Evolution of the data in time. (b) Data selected from jump discontinuities.

The electrical conductivity σ was determined from [4]:

$$\sigma = \frac{L}{R_p I_p}, \tag{6}$$

where R_p is the internal resistance of the Peltier cell given by [4]:

$$V_p - S\Delta T = R_p I_p, \tag{7}$$

where V_p and I_p are the applied voltage and current, respectively, when using the cell as a heat pump (refer to Fig. 2). Statistical methods for the determination of R_p failed due to the lack of enough data. Instead, I used linearisation methods: I studied how ΔT varied in time for fixed V_p and I_p values. As time passed, ΔT became more stable, and by the end of the run, it would fluctuate *around* a particular value, which meant R_p did the same. I averaged the last values of ΔT from different runs and plot eqn. (7) (see Fig. 5); I obtained a linear behaviour and found $R_p = 0.690 \pm 0.008$ ohms from the slope. Reasons to suspect this value is correct are presented in the "Discussion" section.

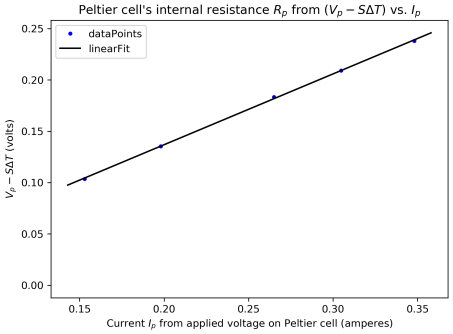

FIG. 5: Determination of the internal resistance of the Peltier cell from linearization as in eqn. (7); errorbars are very small.

Having a value of R_p allowed me to test the correctness of my calculation of the Peltier coefficient given by the $y-$intercept in the equation [4]:

$$\frac{Q}{I_p} = \Pi - \frac{1}{2}R_p I_p - \frac{K\Delta T}{I_p}, \tag{8}$$

where $\Delta T = 0$ when the cell was used as both a heat engine and heat pump at the same time. The rest of the variables are as defined before. The correctness of the fit results of the graph produced from eqn. (8) could be tested with the value of its slope, $-\frac{1}{2}R_p$. Obtaining $\Delta T = 0$, however, was difficult, and the temperature readers were not calibrated properly: they disagreed when reading the same temperature. Because of this, there was heat back-flow inside the cell for $\Delta T = 0$ readings and some of the data broke the linear trend expected from eqn. (8) (see Fig. 6a). I fixed this partially by adding a heat flux term ϕ to the heat power term Q; I obtained Figure 6b, and the value $R_p = 3.2 \pm 0.4$ ohms. Compare this value to the $R_p = 0.690 \pm 0.008$ given before. Rearranging eqn. (8) with $R_p = 0.690 \pm 0.008$ ohms failed the Chi-squared test. This is understandable: Figure 6b is obviously not completely linear; underlying systematic errors (treated in the "Discussion" section) must have been present in the data collection. Without a $\Pi-$value, I cannot provide a value for the coefficient of performance β of the Peltier cell.

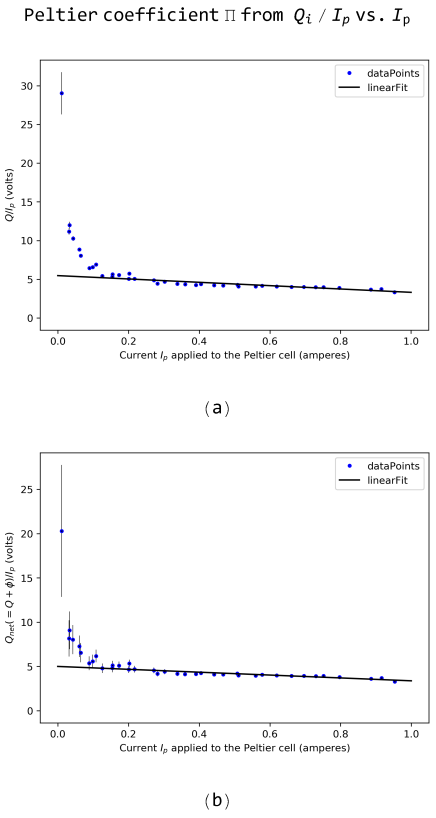

FIG. 6: Measurements for the determination of the Peltier cell's Peltier coefficient for (a) Heat power Q supplied to the cell by a 200 ohms resistor, and for (b) net heat power through the cell $Q_{net} = Q + \phi$, where ϕ is the heat power back-flow (or flux) through the cell due to the temperature gradient between its "faces".

V. DISCUSSION

The Peltier cell used in this experiment can be classified as a moderate efficiency thermoelectric device given its (unitless) figure of merit $ZT \approx 0.43 \pm 0.02$, which is almost half of that of a high efficiency thermoelectric device [8]. Its electrical conductivity $\sigma = 14.5 \pm 0.5$ W·m is about seven times larger than its thermal conductivity $K = 1.94 \pm 0.06$ watts/(K·m). Considering these data, the possible applications of the Peltier cell should be considered.

One of the questions regarding the applications of the cell is whether it should be set up as a continuous power generator (heat engine setup) or as a heat pump or refrigerator. The former has the complication of the need of a constant heat power supply, which means that, in most cases (specially during Winter time) we would be using energy from another source, a DC power supply, for example, that could be used directly instead to produce the desire electrical energy. Nevertheless, the Peltier cell *could* make use of waste heat [2] for short-timed power generation. The latter setup is more attractive as long as we have a sink of large heat capacity where to dump heat with.

Another option is using the Peltier cell not as a device from which one plans to *draw* electrical energy for *use*, but as one from which one could determine the properties of another device. Such an application is using the Peltier cell as a laser-output-power measuring device. As a final part of this experiment, this application was explored. One of the sides of the Peltier cell was coated with a layer of Sharpie® permanent marker black ink to increase its absorption of the green light shone onto it from a laser device. The maximum output power of

this laser, as measured by a photodetector of (assuming) about $99.0 \pm 0.5\%$ of light absorption capacity connected to a powermetre, was $P_{max-photodetector} = 74.0 \pm 0.1$ mW.

The maximum power read by the Peltier cell, as calculated from equation (9) [12], where R_p is the internal resistance of the cell and I_s, its generated current, was $P_{max-PeltierCell} = 67.2 \pm 0.8$ mW. This means that the cell, coated with black ink, showed a light absorption capacity, under the assumptions above, of approximately $90 \pm 1\%$.

$$P = R_p {I_s}^2 \tag{9}$$

It is reasonable that $P_{max-Peltiercell} < P_{max-photodetector}$, and this suggests that $R_p = 0.690 \pm 0.008$ ohms is indeed the value of the internal resistance of the Peltier cell. Employing the cell, one could find the output power of a laser from the equation

$$P \approx R_p {I_s}^2 (1 + \frac{10\%}{90\%}). \tag{10}$$

I also considered exploring the use of the Peltier cell as a refrigerator (same setup of a heat pump). By connecting the Peltier cell to a microcontroller, such as an Arduino®, one could control the temperature of a small chamber. For example, a temperature sensor inside the chamber could send feedback to the Arduino® to keep the chamber at, say, 5°C. Every time the temperature of the chamber exceeded 5°C, the Arduino® could command the supply of electric current to the Peltier cell via a Tolako® 5V relay module [1]. Once the temperature dropped back to 5°C, the current would be cut. Unfortunately, I have not finished setting up this application by now, but I will continue working on it for future exploration.

It is important to add that some materials show a high figure of merit Z but a low thermoelectric performance and viceversa.[6] For a complete assessment of the quality of the Peltier cell, one must determine its coefficient of performace β as well. I failed in doing so, due to the employment of improper methods in the take of measurements for the calculation of the Peltier coefficient Π, upon which β depends. Among these methods was the improper timing of measurements and rushing the acquisition of data. In addition to such sources of systematic errors, I faced the difficulty of working with non-calibrated temperature readers; although I calibrated them at some point, a full study on how they affected our measurements for the determination of Π, however, was not possible: the day I planned to study how the readings between the two temperature readers differed as a function of temperature as measured by a third (alcohol) thermometer, it was found that one of the temperature readers had been rescaled; the reasons how this happened are unknown. The technicians could not fix it and the reader was replaced by another one.

VI. CONCLUSIONS

The efficiency of a Peltier cell is assessed with the value of its figure of merit $Z = S^2\sigma/K$ [endnote2]. The Peltier cell used in this experiment is a thermoelectric device of moderate efficiency; its figure of merit is $Z = 1.39 \pm 0.07 \times 10^{-3}$ 1/kelvin (equivalently, $ZT = 0.43 \pm 0.02$). This makes it suitable for small-scale applications. These include its use as a device for measuring the output power of a laser, as a waste heat user for short-timed power generation, or as a cooling system for small spaces or devices.

VII. ACKNOWLEDGEMENTS

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NOTES

[14] The materials of the Peltier cell's semiconductors were not mentioned in its specifications document.

[15] S, σ, and K are the thermoelectric device's Seebeck coefficient (or thermoelectric power), electrical conductivity, and thermal conductivity, respectively.