PRELIMINARY DESIGN OF A CRYOGENIC THERMOELECTRIC GENERATOR

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A cryogenic thermoelectric generator is proposed to increase the efficiency of a vehicle propulsion system that uses liquid nitrogen as its fuel. The proposed design captures some of the heat required for vaporizing or initial heating of the liquid nitrogen to produce electricity. The thermoelectric generator uses pressurized liquid nitrogen as its cold reservoir and ambient air as the high-temperature reservoir to generate power. This study concentrated on the selection of thermoelectric materials whose properties would result in the highest efficiency over the operating temperature range and on estimating the initial size of the generator. The preliminary selection of materials is based upon their figure of merit at the operating temperatures. The results of this preliminary design investigation of the cryogenic thermoelectric generator indicate that sufficient additional energy can be used to increase overall efficiency of the thermodynamic cycle of a vehicle propulsion system.

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Symbol	Meaning
A	Area
h	Convective heat transfer coefficient
k	Thermal conductivity
K	Kelvin temperature
kW	Kilo watt
L	Length
LN_2	Liquid nitrogen
M Pa	Mega Pascal
Micro	10^{-6}
n - type	n type thermoelectric material
Nano	10^{-9}
NIST	National Institute of Standards and Technology
PTFE	Polytetrafluoroethylene
p - type	p type thermoelectric material
PF	Packing fraction
$\dot{Q}$	Rate of heat transfer
R	Thermal resistance
v	Volts
T	Temperature
ΔT	Change in temperature
t	Thickness of the material
Z	Figure of merit
α	Seebeck coefficient
ρ	Electrical resistivity
η	Efficiency of the generator

CHAPTER 1

INTRODUCTION

At the present projected rate of power consumption, petroleum deposits will be exhausted within the next 200 years. Scientists and engineers are seeking new ways to obtain power from a variety of sources of energy. Most of the hydrocarbon fuels being used now were deposited in the earth millions of years ago and cannot be increased or restored quickly [1].

One alternative proposal to obtaining power is to store energy from-non carbon-based sources in cryogens. One line of investigation is focused on making high-efficiency air motors in the power range of 15 to 25 KW. The proposed research focuses on increasing the overall process efficiency by converting some of the enthalpy of cryogen vaporization to electrical energy in a way that is additive to the energy of the expansion of gas.

Liquid nitrogen, a cryogen, offers many advantages such as environmental friendliness, non-flammability, non-toxicity, inexpensive production, and easy renewability. Liquid nitrogen can be used as a primary energy carrier to drive a vehicle and thus has become an important source of energy for transportation. To date, propulsion of cryogenic vehicles has been only from the expansion of vapors of cryogenic liquids [2]. This study focuses on exploring ways to obtain additional energy from the heat of vaporization of the liquid cryogens.

The basic thermoelectric generator consists of thermocouples, which have both p-type and n-type elements and are connected electrically in series to obtain the desired output voltage and thermally in parallel. Heat flows into the hot side of the thermocouple and is rejected from the cold side, which produces an electric potential.

The electric potential is proportional to the temperature difference between the hot and the cold junctions. The basic thermoelectric generator is shown below.

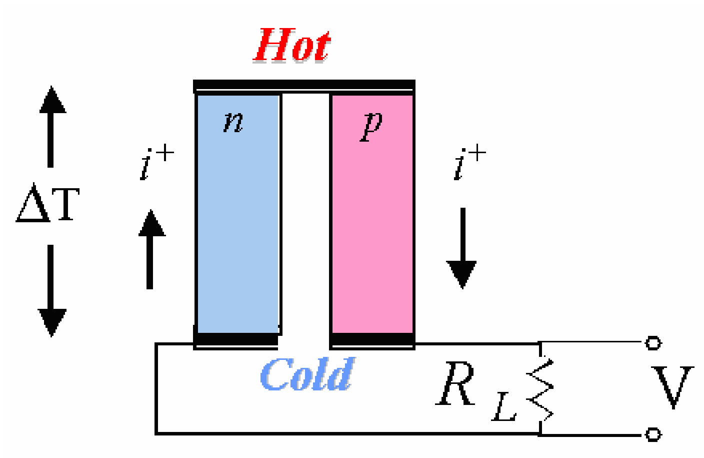


Figure 1.1: Basic conventional thermoelectric generator [3, 4].

In a conventional thermoelectric generator, the hot ends of both p-type and n-type materials are connected electrically, and a load is connected across the cold junction to produce a voltage (Seebeck effect). In a cryogenic thermoelectric generator, the load is connected at the hot end for ease of connection. The voltage produced causes current flow through the electrical load, thereby providing electrical power.

Making liquid nitrogen (LN_2) is a method of storing energy. Energy can be recovered by evaporation and expansion of the gas. Liquid nitrogen, when exposed to ambient heat, produces nitrogen gas that can be used to power a piston or turbine engine. The maximum amount of energy that can be extracted is 628-kilojoules per kilogram. Roughly equivalent amounts of energy are available in the filling of the piston and the expansion process. A Liquid nitrogen vehicle with a 90-gallon tank can achieve useful ranges similar to those of a gasoline-powered vehicle. Advantages are zero harmful emissions, energy densities superior to compressed air and fast refilling (in a matter of minutes) [4-8].

Background of the Problem

There is increasing interest by researchers to develop cars powered by Liquid nitrogen and other alternative fuels [9,10]. Currently, four different groups are researching alternative fuels: two in the United States, one in the Ukraine, and one in India. The principle of operating Liquid nitrogen engines is that heat from the atmosphere vaporizes Liquid nitrogen under pressure to produce compressed nitrogen gas. This compressed nitrogen gas drives a pneumatic motor and the exhaust product is nitrogen gas.

Purpose of the Study

The purpose of this study is to design a thermoelectric generator that can be used at cryogenic temperatures and to determine whether significant additional energy can be obtained by use of a suitable thermoelectric generator. The results of this study will determine whether a thermoelectric generator can contribute significantly to the overall efficiency of a liquid-nitrogen-based power system. This study will also consider recent advances in materials available for a cryogenic thermoelectric generator. “Significant energy addition” is defined as greater than 2.5 % of the total energy available in the thermodynamic cycle without a thermoelectric component.

Problem Statement and Statement of Need

The need for additional efficiency is dictated by the comparatively low specific energy of cryogens and the subsequent need to fully utilize all available energy from that source. This study focuses on investigating the possibility of increasing the efficiency of the current process in which energy is extracted only from expanding gases. By adding a cryogenic thermoelectric generator, it might be possible to convert some of the enthalpy of vaporization to electrical work.

Scope of the Study

The scope of this study is to determine whether significant additional energy can be obtained through the addition of a thermoelectric generator to capture some of the enthalpy of vaporization of a cryogen.

Significance of the Study

Cryogenic-powered vehicles must carry an auxiliary battery for electric services [11]. The development of a cryogenic thermoelectric generator can minimize the need for auxiliary batteries. The study investigates one promising method for raising the efficiency of cryogenic power systems for use in cryogenic vehicles with the hope of increasing their acceptance for use in general transportation. If successful, a possible benefit of using cryogenic vehicles is the reduction of emission of green house gases from transportation sources. The ultimate aim of the study is to create a cleaner environment that depends less on petroleum, with the ultimate goal of slowing or halting global warming.

Research Question

The research question to be addressed during this study is as follows: Can significant energy be obtained from a cryogenic thermoelectric generator to provide more than 2.5% additional energy in a two-stage expansion process at power levels of up to 25 kW?

Methodology

The methodology used during this research study will encompass the following:

1. Select suitable thermoelectric materials (bismuth telluride, $CsBi_4Te_6$) that can be used at cryogenic temperatures. This selection of thermoelectric materials is based on the figure of merit at the proposed operating temperatures.
2. Collect material properties from NIST reference software, research papers on thermoelectric materials, *Handbook of Heat Transfer*, and the *Handbook of Thermoelectrics* by D. M. Rowe.
3. Calculate thermal resistances per square meter across the thermoelectric generator.
4. Calculate temperature difference across the thermoelectric material.
5. Calculate the total weight of the assembly.
6. Calculate the overall efficiency of the generator.
7. Calculate the energy output of the generator.
8. Reference the total energy outputs from the expansion processes.
9. Calculate the percentage increase in overall efficiency.

The collected data includes temperatures and material properties at cryogenic temperatures. The effect on generator efficiency by all these variables is also considered.

Limitations

The scope of this study is limited to an assessment of the value of adding thermoelectric generators to cryogenic energy recovery systems. This study is limited to proposed systems whose maximum power is less than 25 kW. This study is limited to vehicles of total engine power less than 25 kW. This research study is limited only to the library sources which includes both printed and electronic resources available at the University of North Texas Library.

Assumptions

The following assumptions are made in this thesis:

- The outside wall thickness. 1/8 inch, is strong enough to hold the assembly together; and the inside wall thickness, 1/4 inch, holds the pressure of the Liquid nitrogen.
- Electrical insulator (PTFE) thickness is 0.05 cm, electrical conductor (copper) thickness is 0.1 cm, and thermoelectric material ($CsBi_4Te_6$) thickness is 5 cm.
- The temperature difference across the thermoelectric generator is 223 K.
- Condensation or the boiling heat transfer coefficient of LN_2 is the same as for water.
- The engineered computer models can accurately represent real phenomena in the development of cryogenic thermoelectric generators.
- The material data are accurate and appropriate.

CHAPTER 2

REVIEW OF THE LITERATURE

A thermoelectric generator can be used at cryogenic temperatures to generate power which adds to power from an energy recovery system. When interest in electric power grew from 1885 to 1910, following Seebeck's discovery of the effect that bears his name, many investigators looked at thermoelectricity. In 1910, E. Altenkirch, a German scientist, developed methods to calculate the efficiency of thermoelectric generators. An efficiency of 0.6% for a thermoelectric generator was considered to be good during those early periods. Metallic conductors were the only materials available. In 1940, a unit with an efficiency of 4% had been developed using semiconductors. The improved efficiency indicates that semiconductors are the best-suited materials for attaining higher efficiencies. During the late 1980s, researchers found that specialized semiconductor materials offered improved efficiencies. Efficiencies of up to 10% were achieved. Research continues in pursuit of higher efficiency and better materials [12].

A review of the literature was conducted to select the best materials to use in the design of a cryogenic thermoelectric generator. The literature looked at various materials such as aluminum, copper, steel, and silver for use in the design of structural walls. According to the literature, aluminum is well suited for the design of structural walls because it is lightweight, offers good thermal conductivity value, is easily manufactured, and has good corrosion resistance. Polytetrafluoroethylene (PTFE) and copper are recommended for the electrical insulator and the electrical conductor because of their good thermal conductivity and good electrical resistivity values. The selection of thermoelectric material is based on its figure-of-merit value at mean operating temperature. According to the literature, the condensation/boiling heat transfer coefficient value of LN_2 is taken as the value of condensation/boiling heat transfer coefficient of water; and the low end of the molecular weights of both water and LN_2 is found to be close enough. A review of literature was conducted in the following areas: cryogenic thermoelectric generator design; thermophysical properties of conductors, insulators, and various thermoelectric materials; and the efficiency of generator design. This data was used to estimate the total weight of the assembly, total power generated by the assembly, and quantity of thermoelectric material required.

Seebeck Effect

The Seebeck effect is the development of a voltage difference that is proportional to the temperature difference between two different materials. The Seebeck effect was discovered by Thomas Johann Seebeck in 1821.

Seebeck discovered that when a closed loop is formed using two different metals at two junctions, with a temperature difference between the junctions, a compass needle placed near the loop is deflected. This deflection indicates that two metals at different temperatures produce a voltage that induces a current when the circuit is completed and the current produces a magnetic field [13].

The Seebeck effect is the voltage created in the presence of a temperature difference between junctions of two different metals. Thus, when the metals form a closed loop, the voltage causes continuous current to flow in the conductors. The voltage developed will be reflect a temperature difference of the order of several microvolts per degree temperature difference [13]. In modern semiconductors, the voltage developed can be of the order of 100 microvolts per degree C, a major improvement.

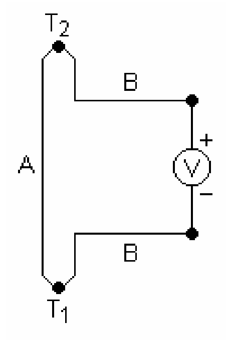


Figure 2.1: Seebeck effect [13].

Contribution of This Study

This study contributes to understanding the design of a cryogenic thermoelectric generator. Conductors, insulators, and thermoelectric materials are selected to optimize total generator efficiency. The selection of conductors and insulators is based upon their properties and usage. The selection of thermoelectric material is based upon a parameter called the figure-of-merit value at 200 Kelvin (the approximate average operating temperature).

Summary of the Chapter

The literature review is adequate for a preliminary design study. Further, the field is somewhat narrow, and the literature is focused into specific topics. The review of the literature indicates that there is progress in making improved materials for thermoelectric generation that attained efficiencies of 10% or even higher. Thermoelectric generators were developed for space applications. Thermoelectric materials also found widespread applications in small refrigerators.

CHAPTER 3

METHODOLOGY

This chapter deals with the individual thermal resistances, design of thermoelectric generator, all the thermal resistances across the thermoelectric generator, heat flux calculation results, and the temperature difference across thermoelectric materials.

Convective Heat Transfer

The transfer of heat energy between a surface and a moving fluid at different temperatures is called convection. Convective heat transfer is of two types:

- Forced convection
- Free convection

Forced convection occurs when fluid flow is induced by an external force, such as a pump or a fan. Free convection occurs naturally. In this design, forced convection due to vehicle movement is considered.

Thermal Resistance Circuits

$\dot{Q}$ is the heat-transferred rate and $T_1 - T_2$ is the temperature difference between opposite sides of a slab, then we can say that slab is a pure resistance to heat transfer and $\dot{Q}$ can be defined as follows [14]:

$$\dot{Q} = \frac{T_1 - T_2}{R},$$

where

$T_1 - T_2$ = Temperature difference between opposite sides of a slab, where slab is a pure resistance to heat transfer.

R = $L/(k \times A)$, the thermal resistance [14].

L = Length of the material (m)

k = Thermal conductivity of the material [w/(m.K)]

A = Area of material (m^2)

As Equation (1) indicates, the thermal resistance R depends on length (L), thermal conductivity (k), and area (A) of the material. The value of R increases when the L value increases, area decreases, and thermal conductivity value decreases.

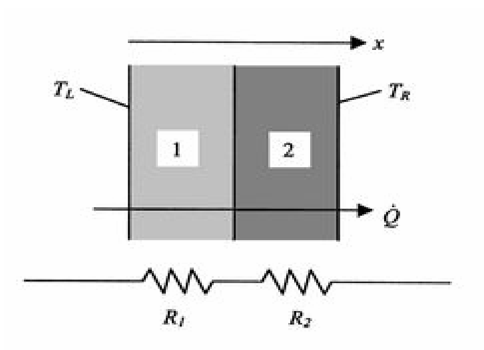


Figure 3.1: Heat transfer across a composite slab (series of thermal resistances) [14].

Thermal resistances in Fig. 3.1 of heat transfer across the slab are given by the following:

- $R_1 = L_1/ (k_1 A_1)$
- $R_2 = L_2/ (k_2 A_2)$
- $R_{total} = R_1 + R_2$
- $\dot{Q} = (T - T\infty)/ R_{total.}$

Similarly, if there are four different materials, the total thermal resistance is found by adding up all four resistances. A schematic diagram of a cryogenic thermoelectric generator is shown in Fig. 3.2.

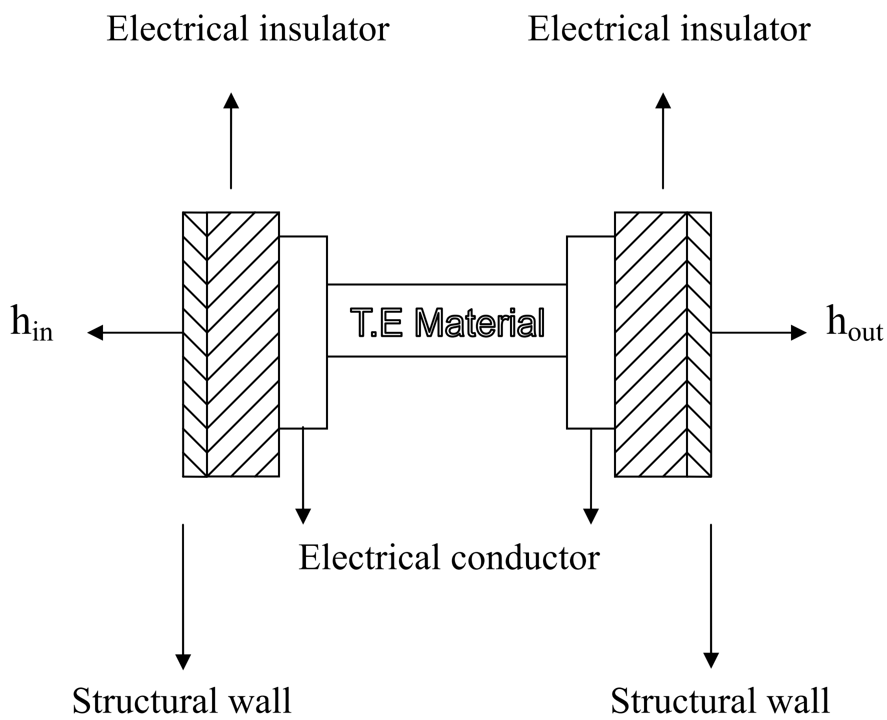


Figure 3.2: Cryogenic thermoelectric generator.

In the design of a cryogenic thermoelectric generator, there are a series of thermal resistances consisting of wall, electrical insulator, electrical conductor, and thermoelectric material. Heat transfer through each of these resistances can be found and summed to get a total thermal resistance. The total thermal resistance is substituted in the formula to get the total heat transferred.

In the design of the proposed cryogenic thermoelectric generator, the walls are made of aluminum, the electrical insulator is PTFE, the electrical conductor is aluminum, and the thermoelectric material is $CsBi_4Te_6$. The heat transfer that occurs between the outside atmosphere and the walls of generator is convective. So, in order to find the total thermal resistance, both the convective and conductive heat transfer processes are considered. The thermal resistance across the wall is considered to be 1/ h, where h is the convective heat transfer coefficient across the wall. The thermal resistance across the electrical insulator, electrical conductor, and the thermoelectric material is L/ k, where L is the thickness of the material and k is the thermal conductivity of the material. Consider an example to find the thermal resistance of an electrical insulator for 1-m^2 area.

$$R = L / k$$

where

R = thermal resistance across the electrical insulator.

L = length or thickness of the electrical insulator.

k = thermal conductivity of electrical insulator.

Material properties collected are shown in the following table:

Material	Thickness	K	Density
Units	m	w/(m.K)	kg/m^3
Aluminum Inside Outside	 0.006 0.003	237	2700
Copper	0.001	398	8920
PTFE	0.0005	0.2	2200
$CsBi_4Te_6$	0.05	1.48	7088

Table 3.1: Properties of component materials [16- 21, 23, 32].

The outside wall thickness, 1/8 inch, is strong enough to hold the assembly together; and the inside wall thickness, 1/4 inch, holds the pressure of the Liquid nitrogen.

Here, L = 0.0005 (m) and

k = 0.35 (W/ m K).

Substituting all the values in thermal resistance equation results in the following:

R = 0.0005 (m) / 0.35 (W/ m K)

= 0.0012638 (K/W)

Thermal resistance for 1-m^2 area across the electrical conductor (copper) is

R = L / k,

where

R = Thermal resistance across electrical conductor material (copper).

L = Length or thickness of electrical conductor.

k = Thermal conductivity of electrical conductor.

Here, L = 0.001 (m)

k = 398 (W/m K)

R = 0.001 (m) / 398 (W/m K)

= 2.5 E-06 (K/W)

Similarly, thermal resistance across the thermoelectric material is calculated using the formula R = L / k, where the values of L and k are the values of the thermoelectric material; and the area is the range of 0.4(A) to 0.6(A), where 0.4 to 0.6 is the range of packing fractions of thermoelectric material reported as feasible by a Marlow Industries representative.

Heat Transfer Coefficient

Heat transfer coefficients (h) have two different values, h_{inside} and $h_{outside}$, which have a value of 8517.3 W/m^2.K [15] and 54 W/m^2.K, respectively [15]

The value for h_{inside} (8517.3 W/m^2.K) was taken as the value for condensing or boiling water in the absence of data for Liquid nitrogen. The value for $h_{outside}$ (54 W/m^2.K) was taken as an average value used for the external surfaces of houses.

The tabular form showing all the thermal resistances across the generator is shown below.

R_1, R_9 = Thermal resistances at the wall surface.

R_2, R_8 = Thermal resistances across the wall (Al).

R_3, R_7 = Thermal resistances across the insulator (PTFE).

R_4, R_6 = Thermal resistances across the conductor (Cu).

R_5 = Thermal resistance across the thermoelectric material ($CsBi_4Te_6$)

R_1	R_2	R_3	R_4	R_5	R_6	R_7	R_8	R_9
1/h (K/W)	L / k (K/W)	L / k (K/W)	L / k (K/W)	L / k (K/W)	L / k (K/W)	L / k (K/W)	L / k (K/W)	1/h (K/W)
Outer wall surface	Outer wall	Electrical insulator	Electrical conductor	Thermoelectric Material P.F.	Electrical conductor	Electrical insulator	Inner wall	Inner wall surface
0.01852	1.3E-05	0.0025	2.5E-06	0.4 0.0844 0.6 0.0563	2.5E-06	0.0025	2.5E-05	0.00012

Table 3.2: Thermal resistances per square meter across the thermoelectric generator.

In thermal resistances across the thermoelectric generator, R_1 and R_9 are not equal because the heat transfer coefficient across the wall is not same on both sides. The heat transfer coefficient for inside is much greater than the heat transfer coefficient for outside because it reflects boiling heat transfer; whereas the outer side reflects forced convection of air. R_2 and R_8 are not equal because the thickness of the wall (aluminum) is not the same on both sides. R_3 and R_7 are equal because the thickness of insulator (PTFE) is the same on both sides. R_4 and R_6 are the same because the electrical conductor (copper) has the same thickness on both sides. R_5 is the thermal resistance across the thermoelectric material.

Packing Fraction	R_{total} (K/ W)	ΔT(300–77) (K)	Heat Flux $\dot{Q}$ / m^2 =ΔT/ R_{total} (W)	$\dot{Q}$ =(ΔT/R)A (W)
0.4	0.10	223	2062	2062
0.6	0.08	223	2788	2788

Table 3.3: Heat flux calculation results.

After calculating all the individual thermal resistances across the generator, one can find the R total by adding all the individual thermal resistances values. The temperature at the cold end of the circuit is of the order 77 K to 100 K. The other end is at room temperature, which is of the order 300 K. The change in temperature across the circuit is the difference of the temperatures, which is 200 K to 223 K. The heat flux is defined as the heat transfer per unit cross-sectional area. Later, heat flux is multiplied by area to get the heat transfer rate for the desired cross-sectional area.

After the values of heat flux are determined, the temperature drop or change in temperature across the thermoelectric material is determined. The packing fraction values of 0.4 and 0.6 are shown in the Table 3.4

Packing Fraction Value	R_{total} (K/W)	Heat Flux (W)	Temperature difference across thermoelectric material (K)
0.4	0.10	2062	174
0.6	0.08	2788	157

Table 3.4: Change in temperature over thermoelectric material with packing fraction values of 0.4 and 0.6

The temperature difference across thermoelectric material is calculated using the following formula [14]:

$$\Delta T = \frac{\dot{Q} \times L_{TE}}{k\,(P\,F)\,A},$$

where $\dot{Q}$ is total heat transfer rate, the value from Table 3.3; and $L_{T\,E.}$ is the length of the thermoelectric material. The thermal conductivity (k) of thermoelectric material is 1.48 W/mK. The packing fraction of the thermoelectric material is in the range of 0.4 to 0.6, and it is the ratio of the area occupied by the thermoelectric material to the area of the heat transfer path.

Here, $\dot{Q}$ = 2062.17 w.

L_{TE} = 0.05 m.

k = 1.48 w/ (m.K)

P F = 0.4

A = 1 m^2

$$\Delta T = \frac{2062.17 \times 0.05}{1.48 \times 0.4} = 174.17 \text{ K}$$

Similarly, the ΔT value with a packing fraction value of 0.6 is 156.98 K.

The temperature difference is found to be 174.17 K when the packing fraction value is 0.4 and 156.98 K when the packing fraction value is 0.6 and the length of thermoelectric material is 5 cm.

CHAPTER 4

DATA COLLECTION

Calculation of the power of the generator, the efficiency of the thermoelectric generator, and the total weight of the assembly requires collection of the thermoelectrical properties of the conductors, insulators, and thermoelectric materials to be used in the design of the generator. Aluminum and copper are the best electrical conductors for use in designing a generator.

Structural Walls

Aluminum: Aluminum is a soft, lightweight metal with a silver-colored appearance caused by thin layers of oxidation when the metal is exposed to air. Aluminum is about one-third as dense as steel and copper. Aluminum has excellent corrosion resistance and durability because of the protective oxide layer. Aluminum is also a good heat conductor.

Aluminum, which is one of the best thermal conductors available, has the following structural properties [16-19]:

- Density: 2700 kg/m^3
- Electrical resistivity: 26.50 nano-ohm m at 300 K
- Thermal conductivity: 237 W/(mK) at 300 K

Electrical Conductor

Copper: Copper is a reddish metal with high electrical and thermal conductivity. Copper is malleable and ductile and is a good conductor of heat and, when very pure, a very good conductor of electricity [20, 21]. The properties of copper are as follows:

- Density: 8920 kg/m^3
- Electrical resistivity: 16.67 nano ohm m at 300 K.
- Thermal conductivity: 401 W/(m K) at 300 K

Electrical Insulator

PTFE: Polytetrafluoroethylene, which is popularly known as PTFE, is one of the best electrical insulating materials [22]. The characteristics of PTFE are as follows:

- Resistance to many chemicals
- Weather and ultraviolet resistance
- Outstanding performance at extreme temperatures

The properties of PTFE [23] are as follows:

- Density: 2200 kg/m^3
- Electrical resistivity: 1×10^{22} to 1×10^{24} ohm m.
- Thermal conductivity: 0.2 W/(m.K)

Thermoelectric Material

The thermoelectric material selected for use in the generator is expected to operate at an average temperature of 200 K based upon its properties at cryogenic temperatures. The figure of merit is the best criterion by which to select a thermoelectric material. Figure of merit is a function of the Seebeck coefficient, electrical conductivity, and thermal conductivity. The formula for the figure of merit [24] is as follows:

$$Z = \frac{\alpha^2}{\quad}$$

k ρ

So, the thermoelectric material selected for the generator is based upon its figure-of-merit value [25]. The following figure shows the figure of merit of various thermoelectric materials at cryogenic temperatures.

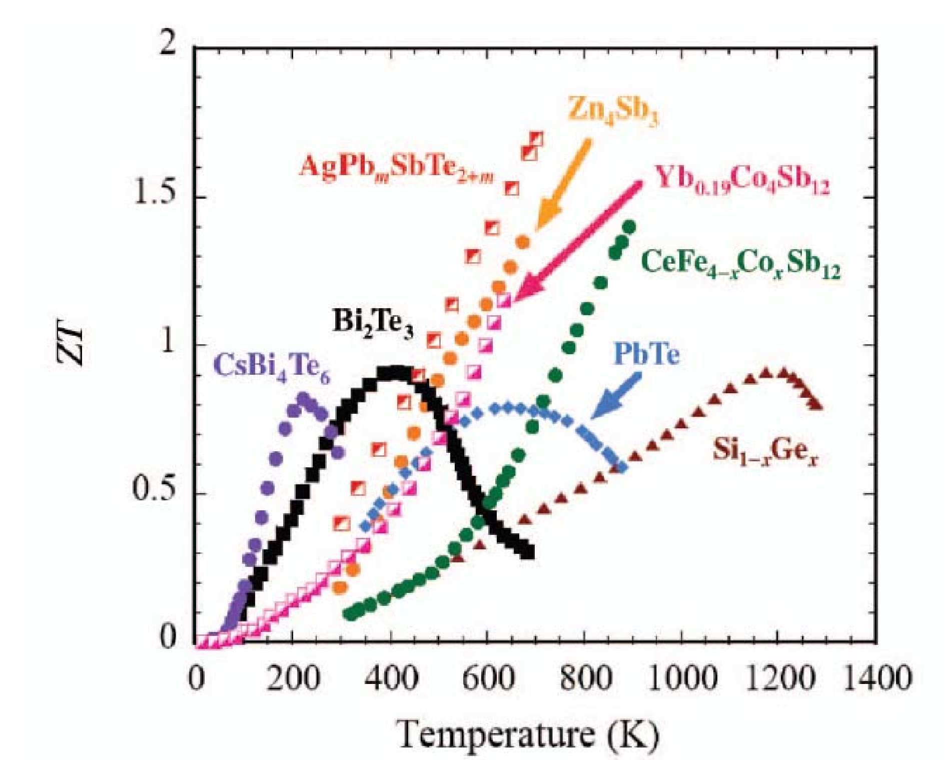
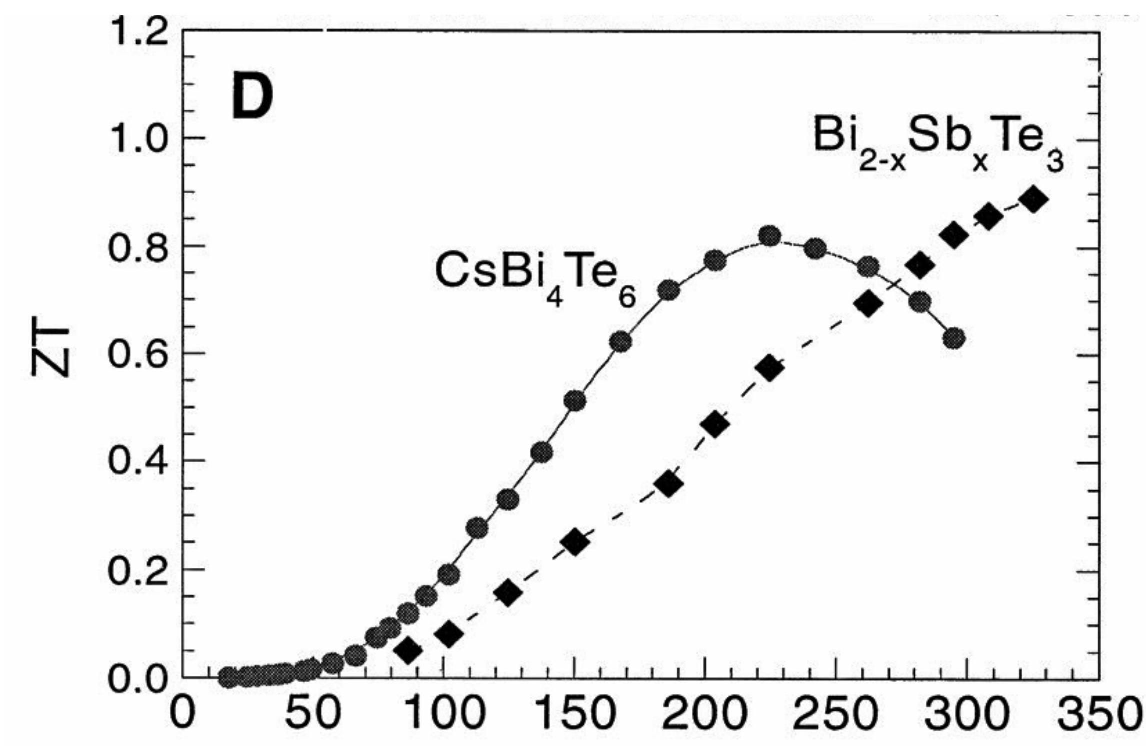


Figure 4.1: Figure of merit ZT shown as a function of temperature for several bulk thermoelectric materials [26].

Earlier bismuth telluride alloys were the best available thermoelectric materials at room temperature and lower. After the recent discovery (2004) of the new thermoelectric material $CsBi_4Te_6$, in most of the applications involving temperatures approaching the cryogenic range, $CsBi_4Te_6$ is available as a substitution for bismuth telluride. To compare the figure-of-merit (ZT) values of these two thermoelectric materials, a curve is plotted in Figure 4.2.



TEMPERATURE (K)

Figure 4.2: Comparing ZT values of bismuth telluride alloys and $CsBi_4Te_6$ [27].

It can be clearly seen that at temperatures below room temperature (300 K), $CsBi_4Te_6$ has a higher figure-of-merit value than bismuth telluride alloys. It has a higher figure-of-merit value throughout the range of cryogenic temperatures [28].

At 200 K, the average operating temperature of our proposed generator, $CsBi_4Te_6$ has a higher figure-of-merit value than that of the bismuth telluride alloys. The thermoelectric material, $CsBi_4Te_6$, has its highest figure-of-merit value of 0.82 in the range from 225 K to 200 K. At cryogenic temperatures, the thermoelectric properties of $CsBi_4Te_6$ appear to exceed those of bismuth telluride alloys, except in the range over 275 K [29-31].

The thermal conductivity values at room temperature or lower of oriented ingots of $CsBi_4Te_6$ measured along the b-axis are in the range of 1.25 to1.85 W/(m.K), depending on the doping level. An average value of 1.48 W/(m.K) at 200 K is taken as reference for calculation purposes. These thermal conductivity values are very low when compared with the bismuth telluride alloys [32].

The properties of $CsBi_4Te_6$ are as follows:

- Density: 7088 kg/m^3
- Thermal conductivity: 1.48 W/(m K) at 200 K

The components of the thermal conductivity of the thermoelectric material over the cryogenic temperature range are shown in Fig. 4.5:

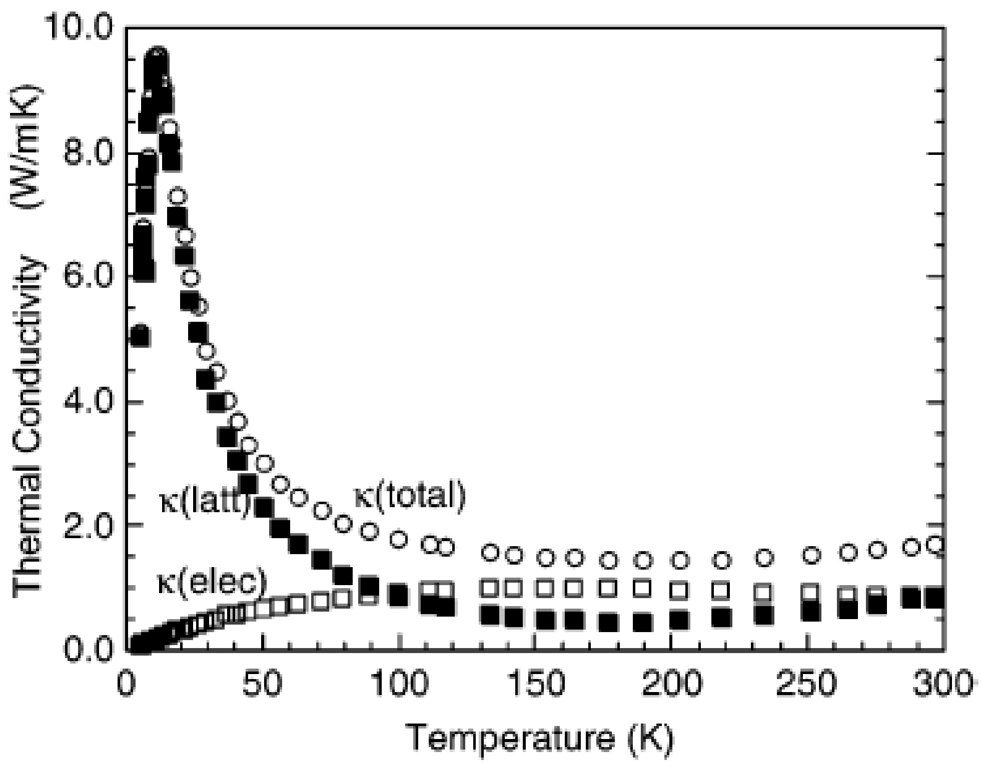


Figure 4.3: Total thermal conductivity of $CsBi_4Te_6$ [34].

CHAPTER 5

RESULTS AND ANALYSIS

The cryogenic thermoelectric generator, which was built with aluminum as the wall material, copper as the electrical conductor, polytetrafluoroethylene (PTFE) as the electrical insulator, and $CsBi_4Te_6$ as the thermoelectric material, was used to make the estimates. The efficiency of the generator was found for $CsBi_4Te_6$. The efficiency of the generator mainly depends upon the figure-of-merit (ZT) value of the thermoelectric materials used and the geometry.

The total temperature change across the generator is about 200 K. It is desirable that a large fraction of the temperature drop be across the thermoelectric material. The thickness of the thermoelectric material can be varied to produce that result. The packing fraction (P.F.) of the thermoelectric material is assumed to be 0.4 to 0.6, based on industrial practice. So, with this data, the thickness of the thermoelectric material was calculated by using the formula [14],

$$\dot{Q} \text{ x } L_{TE} / k\,(P.F.)\,A = \Delta T.$$

Here, $\dot{Q}$, the rate of heat transfer, is a known value; the length of the thermoelectric material is varied; thermal conductivity is a known value; 0.4 to 0.6 is the P.F. of the thermoelectric material; and A is the area of thermoelectric material. The change in temperature could be in a range of 60% to 80% of the total temperature drop, which would be 120 K to 160 K.

The ZT value of $CsBi_4Te_6$ is found to be maximum at 225 K. The thermoelectric material shows the same value of ZT at 200 K. So, by using a ZT value of 0.82, one can calculate the efficiency of the generator by using the following formula [34]:

$$\eta = \frac{(T_1 - T_2)}{T_1} \times \frac{(M-1)}{(M + T_2/T_1)},$$

where $M = (1 + ZT_M)^{1/2}$

Efficiency of the Generator

The efficiency is equal to $W/\dot{Q}$, and its value depends to some extent on the way that the electrical load is matched to the resistance of the generator. The condition for maximum power transfer is obtained if R_L (load resistance) and R (total electrical resistance of the generator) are made equal to one another. However, if this condition is satisfied, the efficiency can never exceed 50% of the ideal thermodynamic value. Therefore, it is assumed that the load resistance is chosen to yield maximum efficiency. If the ratio R_L/R is denoted by m, it is required that $d\eta/dm = 0$. The optimum value of m, identified as M, is given by

$$M = (1 + ZT_M)^{1/2},$$

where Z is the figure of merit of the thermoelectric material. In the case of two materials such as p type and n type, the figure-of-merit value is calculated by using this formula [24]:

$$Z = \frac{(\alpha_p - \alpha_n)^2}{[(k_p \rho_p)^{1/2} + (k_n \rho_n)^{1/2}]^2}$$

where α_p = Seebeck coefficient of p-type material.

k_p = Thermal conductivity of p-type material.

ρ_p = Electrical resistivity of p-type material.

α_n = Seebeck coefficient of n-type material.

k_n = Thermal conductivity of n-type material.

ρ_n = Electrical resistivity of n-type material.

The efficiency of the generator is given by [34]

$$\eta = \frac{(T_1 - T_2)}{T_1} \times \frac{(M-1)}{(M + T_2/T_1)}.$$

Here, for the thermoelectric material, the $CsBi_4Te_6$, ZT_M value is 0.82; so the value of M is obtained by substituting in the equation $M = (1 + ZT_M)^{1/2}$

$$M = (1 + 0.82)^{1/2}$$

$$M = 1.349$$

$$\eta = \frac{(T_1 - T_2)}{T_1} \times \frac{(M-1)}{(M + T_2/T_1)}$$

$$= \frac{300-77}{300} \times \frac{(1.349 - 1)}{(1.349 + 77/300)}$$

$$= 0.743 \times 0.2173$$

$$= 16.14\%$$

So, the efficiency of the generator is found to be 16.14% of the total heat going through the generator.

Weight of the Assembly

The total weight of the assembly estimated for an area of 1 m^2 is

$$= (\rho_{Al} \times t + \rho_{Cu} \times t + \rho_{PTFE} \times t + \rho_{T.E.\ material} \times t \times P.F.)\ A.$$

Here, ρ_{Al}, ρ_{Cu}, ρ_{PTFE} $\rho_{T.E.\ material}$ represents the densities of aluminum, copper, PTFE, and the thermoelectric material $CsBi_4Te_6$. The letter *t* represents total thickness (sum of inside and outside) of the materials. The total weight of the assembly of a 1-m^2 area, estimated by assuming a P.F. value of 0.4, is

$$= (2700 \times 0.009 + 8920 \times 0.002 + 2200 \times 0.001 + 7088 \times e\ 0.05 \times 0.4)$$

$$= 24.3 + 17.84 + 2.2 + 141.76$$

$$= 186.1 \text{ Kg}$$

The total weight of the assembly of a 1-m^2 area, estimated by assuming a P.F. value of 0.6, is

$$= (2700 \times 0.009 + 8920 \times 0.002 + 2200 \text{ x } 0.001 + 7088 \times 0.05 \times 0.6)$$

$$= 24.3 + 17.84 + 2.2 + 212.64$$

$$= 256.98 \text{ kg}$$

The total weight of the assembly assumed for an area of 1 m^2 is estimated to be in the range of 186.1 Kg to 256.98 Kg based upon the P.F. value chosen from 0.4 to 0.6.

The expected flow rate of LN_2 is 4 liters/minute; 1 liter of LN_2 weighs 0.7 kg. Then, the mass flow rate of LN_2 is 2.8 kg/minute. The properties of LN_2 collected from the NIST software [35] are as follows:

Temperature (K)	Pressure (MPa)	Enthalpy (kJ/kg)
123	3.0	65
124	3.1	58
125	3.2	49.3

Table 5.1: Properties of LN_2 [35].

The energy required to boil LN_2 is the product of mass flow rate and enthalpy change of vaporization. An operation pressure of 3.0 MPa is assumed.

$$\text{Energy} = \frac{2.8\ \text{kg}}{\text{minute}} \times \frac{65\ \text{kJ}}{\text{kg}} \times \frac{1\ \text{minute}}{60\ \text{sec.}}$$

$$= 3.03\ \text{kJ/sec.} = 3.03\ \text{kW}$$

The required boiling energy is 3.03 kW. If the thermoelectric generator is to provide that level of energy, the area will have to be increased by the ratio of 3.03 kW / 2.78 (kW/ m^2), which is 1.09 m^2. The range of weights for P.F. values of 0.4 and 0.6 are 202.8 kg to 280 kg.

Number of Thermoelectric Junctions

According to the Seebeck effect, voltage developed in a thermoelectric junction when there is a temperature gradient across the junction is given by the following formula [13]:

$$V = (S_p - S_n)(T_2 - T_1),$$

where

V = voltage developed across the thermoelectric junction.

S_A = Seebeck coefficient or thermopower of material A.

S_B = Seebeck coefficient or thermopower of material B.

T_1 = temperature at the first junction (77 K).

T_2 = temperature at the second junction (300 K).

When $CsBi_4Te_6$ is doped with 1% Te, it results in the formation of n-type $CsBi_4Te_6$ thermoelectric material, whose S_n (thermopower) value is found to be -90 μ V/K at 200 K. Similarly, when $CsBi_4Te_6$ is doped with 0.1% Bi, it results in the formation of p-type $CsBi_4Te_6$ thermoelectric material, whose S_p (thermopower) value is found to be 120 μ V/K at 200 K. By substituting all these values in the voltage-generated formula, one derives the following:

$$V = [120 - (-90)]\ 10^{-6}\ (300 - 77)$$

$$= 210 \times 223 \times 10^{-6}$$

$$= 0.047 \text{ volt.}$$

Therefore, the voltage generated for one thermoelectric junction is of the order of 0.047 volt. The required voltage to be generated from the thermoelectric generator is 13.5 V, which is equivalent to a 12-V battery. The number of thermoelectric junctions required to generate 13.5 V is calculated as follows:

$$\text{Number of thermoelectric junctions} = \frac{13.5 \text{ V}}{0.047 \text{ V}} = 288.2$$

Therefore, 288 thermoelectric junctions are required to generate 13.5 V at a temperature difference of 223 K. As a preliminary design approximation, 300 junctions could be used to guide further design.

The expected flow rate of LN_2 is 4 liters/minute; 1 liter of LN_2 weighs 0.7 kg. Then, the mass flow rate of LN_2 is 2.8 kg/minute. The properties of LN_2 collected from the table 5.1

The energy required to vaporize the LN_2 is the product of mass flow rate and enthalpy change of vaporization. An operation pressure of 3.0 M Pa. is assumed.

$$\text{Energy} = \frac{2.8\ \text{kg}}{\text{minute}} \times \frac{65\ \text{kJ}}{\text{kg}} \times \frac{1\ \text{minute}}{60\ \text{seconds}}$$

$$= 3.03\ \text{kJ/sec.} = 3.03\ \text{kW.}$$

The energy produced from the thermoelectric generator is the product of the energy required to vaporize the LN_2 and the efficiency of the thermoelectric generator.

Energy produced = energy required to vaporize boil LN_2 x efficiency of the generator

$$= 3.03 \times 0.1614$$

$$= 0.489\ \text{kW.}$$

Therefore, a 0.489-kilowatt of energy is produced from the thermoelectric generator. The estimated energy in the expansion process is 300 kJ/kg [36]. Then, energy produced by expansion process is a product of mass flow rate and estimated energy, which is:

$$\frac{2.8\ \text{kg}}{\text{minute}} \times \frac{300\ \text{kJ}}{\text{kg}} \times \frac{1\ \text{minute}}{60\ \text{seconds}} = 14\ \text{kW.}$$

The additional energy required for the use of thermoelectric generator is the ratio of energy produced from the thermoelectric generator and the energy produced from the expansion processes.

$$\text{Additional energy} = \frac{0.4890}{14} = 0.0349 \text{ or } 3.49\%$$

Therefore, the use of a thermoelectric generator will provide more than 2.5% of additional energy in vehicle engines whose power is 14 kW.

CHAPTER 6

SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

Summary of the Study

The purpose of this research study was to design a thermoelectric generator that can be used at cryogenic temperatures. An additional purpose of this study was to determine whether sufficient energy can be obtained from a cryogenic thermoelectric generator to significantly improve the efficiency of cryogenic energy recovery systems.

This study identified materials for use in the generator's design. After the generator's design, the efficiency of the generator and the total weight of the generator were determined. The efficiency of the generator was maximized by use of the thermoelectric material with the greatest ZT value (figure of merit) at 200 K. It was found that two thermoelectric materials could be used in designing the generator. The materials are bismuth telluride and $CsBi_4Te_6$. When the two thermoelectric materials were compared, it was concluded that $CsBi_4Te_6$ is more effective because it has higher ZT values than bismuth telluride at low temperatures. Both thermoelectric materials are promising thermoelectric materials at temperatures lower than room temperature, but $CsBi_4Te_6$ has a higher figure-of-merit value at 200 K than bismuth telluride.

Answer to the Research Question

Q. Can sufficient energy be obtained from a cryogenic thermoelectric generator to significantly raise the overall efficiency of a cryogenic energy recovery system?

Regarding the research question, we were studying if use of cryogenic thermoelectric generator, sufficient energy can be obtained to raise the overall efficiency by 2.5 %. After the cryogenic thermoelectric generator design was analyzed, it was found that the power generated from vaporizing the Liquid nitrogen was sufficient to add to the overall efficiency of the generator.

Conclusions Based on Results and Analysis of the Study

After analyzing the research study, it was concluded that the thermoelectric generator may be too heavy even if the thickness of the thermoelectric material can be reduced to 2 to 3 cm.

Strengths of the Study

The main strength of the study is that a design of a cryogenic thermoelectric generator using currently developed materials can add significantly to the total efficiency of the generator. The efficiency of the generator whose design is being planned is generally proportionate to the total temperature difference between the two junctions. Here, the total temperature difference is assumed to be 223 K. The efficiency obtained justifies consideration of building the generator.

Recommendations for Further Research

Once the cryogenic thermoelectric generator is designed and its efficiency and total assembly weight are determined, additional studies are recommended using different thermoelectric materials with lower densities to reduce the total assembly weight.

APPENDIX

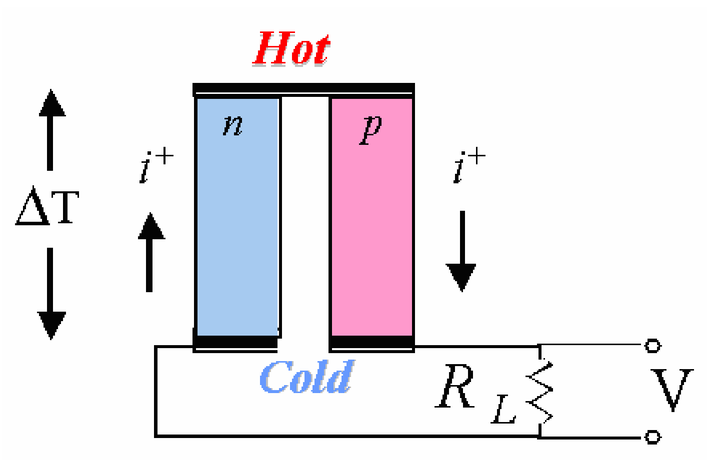
DEFINITIONS

1. Thermoelectric materials:

Thermoelectric materials turn heat into electricity. These materials can be used either for cooling or for power generation.

2. Thermoelectric generator:

The basic thermoelectric generator consists of a thermocouple, which has a p-type and an n-type thermoelement connected electrically in series and thermally in parallel. Heat is pumped into one side of the couple and rejected from the opposite side. An electrical current is produced, proportional to the temperature gradient between the hot and the cold junctions. The basic thermoelectric generator is shown below [3, 4]:



3. Conductors:

Materials through which electric current can pass are classified as conductors. Metals are considered to be the best examples of conductors.

4. Insulators:

Materials that offer resistance to the flow of electric current are classified as insulators.

5. Semiconductors:

The materials that are neither conductors nor good insulators are called semiconductors.

6. Cryogenic temperature:

Cryogenic temperature is the temperature below -150° C or 100 K.

7. Cryogenic Thermoelectric Generator:

A thermoelectric generator that can be used between ambient and cryogenic temperatures is defined as a cryogenic thermoelectric generator.

8. Figure of merit:

The figure of merit of a thermoelectric material is defined as

$$Z = \frac{\alpha^2}{k\rho},$$

where

Z = Figure of merit of thermoelectric material

α = Seebeck coefficient of the material (microvolts/K)

ρ = Electrical resistivity of the material

k = Thermal conductivity of the material

The figure of merit of a thermoelectric material with both p- and n-type materials is

$$Z = \frac{(\alpha_p - \alpha_n)^2}{[(k_p \rho_p)^{1/2} + (k_n \rho_n)^{1/2}]^2},$$

where α_p = Seebeck coefficient of p-type material.

k_p = Thermal conductivity of p-type material.

ρ_p = Electrical resistivity of p-type material.

α_n = Seebeck coefficient of n-type material.

k_n = Thermal conductivity of n-type material.

ρ_n = Electrical resistivity of n-type material.

A good thermoelectric material should have a large Seebeck coefficient, low electrical resistivity, and low thermal conductivity. As Z varies with temperature, a useful dimensionless figure of merit can be defined as ZT [24].

9. Heat transfer:

Heat transfer is a passage of thermal energy from a hot body to a cold body. When a physical body is at a different temperature from its surroundings or another body, energy from that body is transferred to another body or surroundings. Transfer of energy always takes place from a hot body to a colder one. This transfer of energy occurs through conduction, convection, or radiation. This study focused on conductive and convective heat transfer [37].

(a) Conduction

This type of heat transfer occurs mainly in solids, where atoms are in contact with each other. Metals are the best conductors of thermal energy.

(b) Convection

This type of heat transfer occurs between a fluid and a solid.

(c) Radiation

No medium is necessary for this type of heat transfer to occur; in fact, radiation works even in and through a perfect vacuum. Heat is transferred by photons leaving the hot surface.

10. Packing fraction:

The packing fraction of a material is defined as the area occupied by that material to the total area in which the material is present.

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