
A Re-Review of Thermoelectric Module

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ABSTRACT

In 21st century there are major two problem energy shortage and environmental defects. Thermoelectric cooler is the best solution for those two problems. This review is explaining about basic concept of thermoelectric and thermoelectric generator, including the structure optimization which significantly affects the thermoelectric generator, the low temperature recovery, the heat resource and its application area. Then it reports the recent application of the thermoelectric cooler including the thermoelectric model and its application area. It ends with the discussion of the further research direction.

Keywords: Cooling system, Peltier effect, Thermoelectric cooler.

1. INTRODUCTION

Extensive fossil fuel consumption by human activities has led to serious atmospheric and environmental problems. Consequently, global warming, greenhouse gas emission, climate change, ozone layer depletion and acid rain terminologies have started to appear frequently in the literature. To abate the impact of the above disasters, the thermoelectric (TE) energy converter is proposed as one of the possible technologies for this aim, which currently gains the most popularity owing to its capability in converting the heat given off from vehicles, electrical instruments, etc., into the electricity [1].

In 1823, a German scientist Thomas Seebeck discovered that, in a closed circuit made up of two dissimilar metals an electric current is generated continuously provided that both the junctions of the metals were maintained at different temperatures. After some years in 1834, a French watchmaker, Jean Charles Athanase Peltier (1785-1845) discovered thermoelectric cooling effect which is also known as Peltier effect. Who discovered that when an electric current is passed through junction which is made up of two dissimilar metals, then one side of the junction becomes hot while the other end of the junction becomes cold. By changing the polarities of electric current supplied the hot side becomes cold while the cold side becomes hot. After four years in 1838, Emil Lenz made clear about the true nature of Peltier effect by placing a bismuth-antimony junction to freeze the water by passing of an electric current through the junction. He also observed that the ice could be melted if the current was reversed. In 1950's, Bismuth-Telluride replaced bismuth-antimony and began to be used as the primary material in the thermoelectric cooling.

Thermoelectric (TE) property was discovered earlier about two centuries but (Thermoelectric cooler) TEC was commercialized in recent years. The applications of TE ranges from small sized devices like refrigerators and electronic devices to big sized devices like Avionic instrumentation illumination control and thermal imaging cameras. Recently there is a tremendous increase in the applications of TE coolers in water chillers, medical chillers, semiconductor chillers, food and beverage chillers, etc. [16].

2. WORKING PRINCIPLE

TEC works on the principle of Peltier effect, when a DC is supplied from a 12V battery to TEC module then, heat is absorbed at one junction and dissipated at the other junction. Depending on the direction of applied DC power source and the relative Seebeck coefficient of the two materials, the direction of the heat flow is regulated. TEC can be used either for heating or for cooling, while the main application is cooling. TEC module is a solid-state active heat pump which contains number of p- and n- type semi-conductor which are coupled in series and

sandwiched between two thermally conductive and electrically insulated ceramic substrate. The main advantages of a TEC compared to a vapor-compression refrigerator are its lack of moving parts or circulating refrigerants, flexible shape, invulnerability to potential leaks and its smaller size. The "hot" side is attached to a water cooled heat sink so that it remains at ambient temperature, while the "cold" side goes below room temperature. Multiple coolers can be cascaded together for lower temperature for some applications.

There are various thermoelectric materials which include Lead Telluride (Pb-Te), Silicon Germanium (Si-Ge), Bismuth-Antimony (Bi-Sb) and Bismuth Telluride (Bi-Te) alloys that may be used according to the situations. Conventional R&AC system uses refrigerant to carry the heat from refrigerated space while TEC uses electrons rather than refrigerant as a carrier of heat. TEC is the emerging green R&AC technology which can be used to couple with Solar PV cell generated DC power, which makes them complete environmental friendly [16].

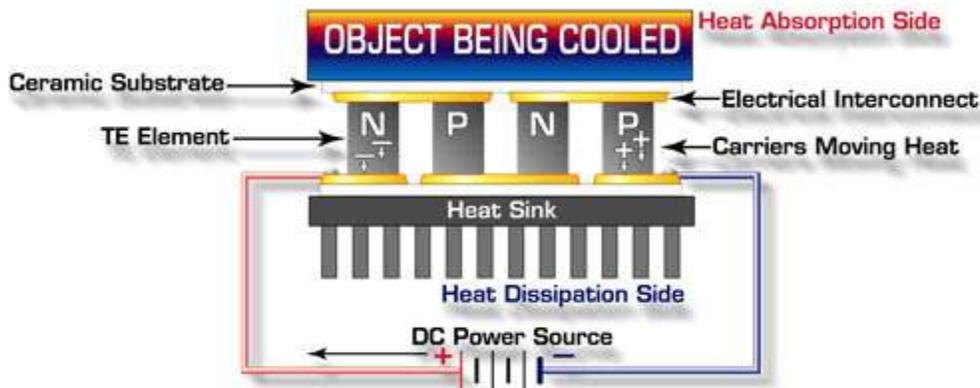


Fig-1: Working principle of TEC module [16].

Seebeck effect was found in 1821 which disclosed that two joint dissimilar metals have the different temperatures (ΔT) at the joints, and the corresponding current and electromotive force existing in the joint circuit are called the thermo-current and thermo-electromotive force. Increasing the voltage difference (ΔV) enlarges the temperature difference between two joints (ΔT). The proportional constant related to the intrinsic property of the material is known as the Seebeck coefficient. This coefficient is relatively low for materials like metals at approximately $0\mu V/K$, while it would be much larger at around $\pm 200\mu V/K$ for these semiconductor[1].

$$\alpha = \Delta V / \Delta T \dots\dots\dots (1)$$

Peltier effect, which was discovered in 1834, is the phenomena that when there is the current in the circuit, the joint of different conductors absorbs or rejects the heat depending on the direction of the current. This phenomenon is largely due to the difference of the Fermi energies between two materials. The capacity of the heat absorption or rejection is largely related to the property of the twodissimilar conductors and the temperature of the joint. When defining the heat absorbed in per area of the joint per second, a dimensionless parameter, ZT , is usually used to determine the Peltier performance of a thermoelectric material.

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3. MATERIAL RESEARCHES OF THERMOELECTRIC

The TE materials can be classified into 3 catalogues: semiconductors, ceramics and polymers. Recently, certain polymers, i.e. ethylenedioxythiophene, carbon fiber polymer-matrix structural composites, have also been shown to exhibit interesting thermoelectric material properties [1].

3.1. Semiconductor

Semiconductor materials are promising for the construction of thermocouples because they have large Seebeck coefficients in excess of $100 \mu\text{V}/^\circ\text{C}$, and one proper way to reduce j without affecting a and s in bulk materials, thereby increasing ZT , is to use semiconductors for its high atomic weight, such as Bi_2Te_3 and its alloys with Sb, Sn, and Pb. A high atomic weight reduces the speed of sound in the material and thereby decreases the thermal conductivity. A solid state or semiconductor electronics component, for example, can perform well and reliably for many years when it is operating at or near the ambient temperature. The best- ZT materials are found to be heavily doped, small bandgap semiconductors. The intermetallic compounds such as Mg_2X ($\text{X} = \text{Si}, \text{Ge}, \text{Sn}$) (the figure of merit, ZT , for Mg_2Si is 0.86 at 862 K. And their solid solutions are semiconductors having the antiferroelectric structure and have been proposed to be good candidates for high-performance thermoelectric materials, because of their superior features such as its large Seebeck coefficient, low electrical resistivity, and low thermal conductivity. The highest ZT for Bi_2Te_3 and its dopant has been reported to be 2.4 in p-type $\text{Bi}_2\text{Te}_3/\text{Sb}_2\text{Te}_3$ superlattices at 300 K by growing phonon-blocking electron transmitting hetero-structures by the low-temperature metal organic chemical vapour deposition (MOCVD) technique. Pei et al. have found that the transport properties of PbTe alloyed with MnTe result in a ZT as high as 1.6 at 700 K which can be explained by alloy scattering and multiple band model, as shown in Fig. 3. As mentioned before, lowering the thermal conductivity can enhance the ZT . Pei et al. have found that Ca-doped BiCuSeO can intrinsically have low thermal conductivity thus boost the ZT - 0.9 at 923 K for $\text{Bi}_{0.925}\text{Ca}_{0.075}\text{CuSeO}$. Rhyee et al. have discovered that the binary crystalline n-type material, In_4Se_3 have the ZT value of 1.48 at 705 K, which is the result of the high Seebeck coefficient and the low thermal conductivity in the plane of the charge density wave.

J. de Boer et al. [5] have investigated that material magnesium alloy have different characteristics than can help in thermoelectric module. In this section we want to give an overview over the elements that have been successfully employed to p-dope Mg_2X . The optimization of the carrier concentration is a fundamental prerequisite for good thermoelectric properties and one of the fundamental optimization parameters for any thermoelectric material. For p-type Mg_2X the issue is of particular importance: first, the experimental realization of samples with sufficient number of charge carriers has been proven to be difficult, often leading to samples with too low p and hence un-optimized thermoelectric properties. Secondly, the choice of the dopant might influence the material properties more than for the n-type material. For the n-type material the most popular dopants Sb and Bi seem to obey the rigid band picture, i.e., addition of dopants shifts the chemical potential of the electrons and enhances the number of charge carriers but the band structure itself remains unaffected. Disregarding small differences in carrier mobility and lattice thermal conductivity the choice of the dopant does not significantly influence the thermoelectric properties. This has been confirmed experimentally for Sb and Bi for n-type Mg_2X where $ZT > 1:2$ has been found for both dopants. For the p-type it has been argued repeatedly that the rigid band model is not applicable for all dopants. In this case the choice of dopant is naturally of utmost importance for the optimization of the thermoelectric material.

3.2. Ceramics

TE materials in practical applications are always based on alloy materials, such as SiGe and Bi_2Te_3 . In comparison with TE alloys, metal oxides have advantages in better chemical stability, oxidation resistance, less toxic and low cost, so their use enables the fabrication of more durable devices. Ceramic is an important thermoelectric material for thermoelectric energy conversion to retrieve high-temperature waste heat from incinerators or combustion engines. However, oxides had not been considered to be candidates as TE materials due to their low carrier mobility, until the high performance TE oxide of $\text{Na}_x\text{Co}_2\text{O}_4$ appeared [1]. Now cobalt-based oxides, such as $\text{Ca}_3\text{Co}_4\text{O}_9$, NaCo_2O_4 , have been fabricated as p-type legs in TE modulus. As a counterpart, n-type SrTiO_3 , ZnO and CaMnO_3 ceramics have also been studied. Among them, CaMnO_3 can be synthesized in ambient atmospheric condition and shows excellent TE properties, which make the CaMnO_3 a prospective candidate as n-type oxide TE material. Compared with their p-type counterparts, most n-type oxide TE materials are inferior due to their high thermal conductivities. Up to now, several n-type oxide materials such as SrTiO_3 , CaMnO_3 and ZnO have been

reported having good thermoelectric properties. Cadmium oxide (CdO) is an n-type semiconductor that is widely used as a transparent conductive material [13]. Nonstoichiometric CdO usually exhibits very good electrical conductivity due to the native defects of oxygen vacancies and Cd interstitials, and its resistivity can be further decreased by appropriate doping with high-valence elements, such as rare-earth elements. The conduction type of SnO₂ is n-type. Moreover, it is known that the doping of Sb₂O₅ in SnO₂ can increase the electrical conductivity. The carrier mobility of SnO₂ is known to be as large as oxide material. Wang et al have studied the high-temperature thermoelectric properties of Cd_{1-x}Pr_xO ceramics. The results show that the dimensionless figure-of-merit ZT of the 0.1% Pr-doped CdO sample reaches 0.38 at about 1000 K. Zhu et al have studied the TE properties of CaMnO₃ ceramics doped by Lanthanides and other rare-earth elements the results show that the optimized dopants were found and the highest ZT of 0.20 can be achieved with the substitution of either Dy or Yb. A suitable dual-doping results in a remarkable increase of figure of merit. The highest ZT = 0.21 at 973 K is obtained for Ca_{0.96}Dy_{0.02}Bi_{0.02}MnO₃[1].

3.3. Polymers

The widely investigated, developed and used inorganic thermoelectric materials involve issues such as toxicity, a shortage of natural resources, and complicated manufacturing processes with high cost. Thus it is of great importance to develop or find new types of materials to further improve their properties. The conductive polymer composites family containing insulating polymer matrices and conducting fillers have been studied for its advantages of mechanical flexibility, low-cost synthesis, solution processability, inexpensive, lightweight, and more environmentally friendly alternatives to common thermoelectric devices. Wang et al have investigated the thermoelectric behaviour of segregated conductive polymer composites with hybrid fillers of carbon nanotube and bismuth telluride

Table 1
The value of ZT of the Bi–Te based material [1][9].

Authors	Published year	Material	ZT	Temperature (K)
Jong Gil Park	2016	P-Bi _{0.5} Sb _{1.5} Te ₃	0.86	325
		N-Bi ₂ Te ₃	0.52	473
Wei Zhu	2015	P-Bi _{0.5} Sb _{1.5} Te ₃ / N-Bi ₂ Te _{2.7} Se _{0.3}	2.2	915
Ming Tan [24]	2014	Bi ₂ Se _{0.5} Te _{2.5}	1.28	Room temperature
Y.H. Yeo [25]	2014	(Bi,Sb) ₂ Te ₃	1.41	Room temperature
Ming Ma [26]	2014	Bi ₂ Te _{2.7} Se _{0.3}	1.27	Room temperature
Z. Chen [27]	2014	Bi _{0.4} Sb _{1.6} Te ₃	1.26	Room temperature
Xi'an Fan [28]	2014	p-type (Bi,Sb) ₂ Te ₃ Thermoelectric material	1.17	323
Ming Tan [29]	2014	Bi ₂ (Te,Se) ₃	1.01	Room temperature
Zhijun Xu [30]	2012	P-type (Bi _{0.26} Sb _{0.74}) ₂ Te ₃ + 3% Te ingots	1.12	Room temperature
J. Seo et al. [38]	1997	Bi ₂ Te ₃	1.62	693
Jun-Ho Seo et al. [39]	1996	Bi ₂ Te _{2.85} Se _{0.15}	1.86	93
Venkatasubramanian et al. [5]	2001	p type Bi ₂ Te ₃ /Sb ₂ Te ₃	2.4	300

4. TE APPLICATION

The thermoelectric effect can convert heat to electricity, etc. vice versa. Thus the TE applications are mainly based on those two aspects by either converting heat to electricity (TEG) [13] or converting electricity to heat (TEC).

4.1. TEG

TEG can directly converse the heat to the electricity with solidstate which makes it adaptable in many areas from the space nuclearauxiliary power (SNAP) program applied for space and the militaryuse to the building and the automobile daily commonly used stuffs.And the heat sources for TEG are also various from solar, biomassand the earth. It should be point out that the temperature rangesfor TEG recently are relative low. The higher the temperature is,the less competitive the TEG is. It is true that the conversion efficiencyof the TEG is rather small because of the material properties.However, the efficiency can be improved by enhancing the intrinsic of the TE material which has been discussed early and optimizingthe structure of the TEG.

Niu et al have investigated the TEG with the parallel-plate heat exchanger.The results show that the hot fluid inlet temperature and flowrate significantly all affect the maximum power output and conversionefficiency. Karabetoglu et al have investigated thecharacterization of a commercially available and the cheapest versionsBi₂Te₃ based TEG at low temperatures in the temperaturerange of 100–375 K.In the experiment, two parameter Seebeck coefficient and electricalconductivity of a Bi₂Te₃ based TEG are examined. Fig.6 isdimensionless maximum power output vs. mean temperature for $\Delta T = 200$ K. The result shows that 250 K seems a critical meanoperating temperature for the considered Bi₂Te₃ module.The results also give correlations for temperature dependencyof material quantities in the temperature region of 100–375 K. Lesage et al have studied a forty Bismuth Telluride basedmodule TE liquid-to-liquid generator which is optimized for thepeak power output via changing the electrical load resistance

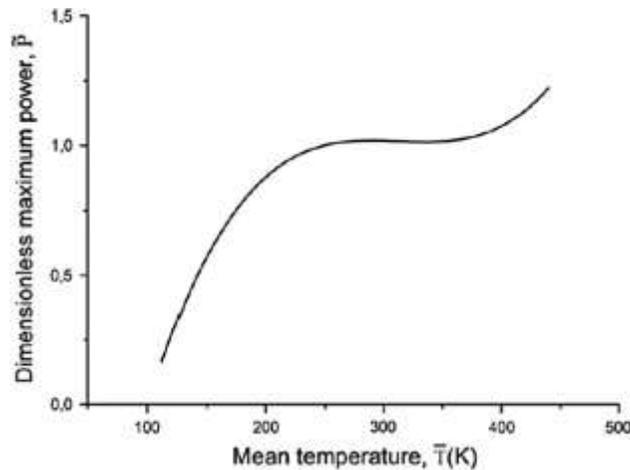


Fig.2. Dimensionless maximum power output vs. mean temperature for $\Delta T = 200$ K [1].

Abu Raihan Mohammad Siddiqueet. al have discuss about wearable power generators are one of the more recent technological advancements in the field of portable electronics. Wearable TEGsuse the temperature difference between any living body and surroundingenvironment to harvest energy and convert it to useful electrical output. The core temperature of a human body varies from 28 °Cto 37 °C with a change in the room temperature from 0 °C to 35 °C. Moreover, the heat flow varies from 50 to 150 Wm⁻² duringregular activities of the body. Wearable TEGs can theoreticallygenerate a maximum of 180 μ Wcm⁻² power from skin (considered skintemperature and heat flow are 34 °C and 20mW cm⁻², respectively) at 22 °C ambient temperature. Table 2 presents the power generationcapabilities of different parts of the human body.

Table 2
Possible capabilities of harvesting power from human body parts [12].

Body part Power generation	(mW)
Forehead	2.3–27.6
Chest	3.1–36.6
Arm	1.7–20.2
Forearm	1.3–16.1
Abdomen	3.1–36.6
Thigh	2.4–28.8
Foot	2.1–25.2

One growing area of application for TEGs is for powering biomedical devices using body heat. Mitcheson et al reported that a TEG was more suitable than a motion energy harvester for bio-sensors since the power density of a TEG harvester was $20\mu\text{W cm}^{-3}$, while $10\mu\text{W cm}^{-3}$ for the motion energy harvester used during walking and running [3]. Yang et al investigated the use of TEGs to power implantable medical devices (IMD). Different thermal conditions of a patient (e.g. environmental and physical) were investigated and the results indicated that close to the skin surface was the best part of the human body to harvest power [14]. In another application study, Ekuakille et al concluded that a TEG could be used to provide sufficient energy for a hearing aid device. An additional power management circuit and battery were used as a backup power source. In the interest of improving the efficiency of a TEG at lower body temperatures, Udalagama et al used resonance and voltage set up techniques to increase the power harvesting capability of the system. An ADC-DC boost converter was used as a setup transformer in the power management circuit (also used by Lossec et al. in their power management circuit). A new parameter Z_E, which depends on the physical properties of materials, was used to optimize the power output of the TEG during poor thermal coupling [14]. An additional heat sink was attached to the TEG to increase the productivity of the TEG as shown in Fig. 3(b). Different thermoelectric materials (e.g. bismuth telluride), have been investigated by Funahashi et al who used Ni_{0.9}Mo_{0.1} for the n-type and La_{0.035}Sr_{0.965}TiO₃ for the p-type for fabricating their prototype generator. An Y_{0.03}Zr_{0.97}O₂ insulator was placed between the n-type and the p-type elements. Multilayer co-fired ceramic technology was used for fabricating the generator. At a 10 °C temperature difference, the prototype (see Fig. 3(a)) produced 100 μW which is sufficient for powering a radio transmitter [12].



Fig.3. A hearing aid powered by a TEG. (b) Fin was attached to the cold surface of the module (two TEG modules were connected in series) to harvest energy from hand [12].

4.2 TEC

TEC, compared to the traditional refrigeration or heat supplying devices, has many advantages such as solid-state, no vibration, simplicity and environmentally friendly. TEC models and its application areas are discussed. It is easy to discover that the main disadvantage of the TEC is its low efficiency, which causes its limitation in commercial application. Thus, the optimization of the TEG models has been done to maximum the COP.

Raghied Mohammed Atta has investigated about new system Solar-driven Thermoelectric Dehumidifiers. An additional key concern water scarcity is the water consumption during energy generation. Solar energy has the distinct advantage of low water consumption during its use-phase, making it ideal for installation in locations that have a highly variable or scarce freshwater supply. However, close attention was not paid to solar refrigeration until the energy crisis in 1970s. Research in a Peltier's cooling effect integrated with Photovoltaic (PV) also developed around that time, primarily for the cold chain project of the World Health Organization and the international Health Organization specifically for rural areas. Solar cells were used to power small TE operated fridges [15]. Experimental investigation and relevant analysis on a solar cell driven, thermoelectric refrigerator has been conducted. The main components of the solar PV/battery thermoelectric dehumidifying system are the PV cell (including the PV array, the storage battery and the controller), the thermoelectric refrigeration system and the cooled object (e.g., a cooling box). The PV array is installed outdoors and the storage battery stores the excess electricity produced during sunshine periods. This stored energy is used for running the system during the

The technique used in the assembly of a TE system is as important as the selection of the proper device. It is imperative to keep in mind the purpose of the assembly, namely to move heat. All of the mechanical interfaces between the objects to be cooled and ambient are also thermal interfaces. Similarly all thermal interfaces tend to inhibit the flow of heat or add thermal resistance. Again, when considering assembly techniques every reasonable effort should be made to minimize thermal resistance. Mechanical tolerances for heat exchanger surfaces should not exceed 0.001 in/in with a maximum of 0.003" Total Indicated Reading. If it is necessary to use more than one module between common plates, then the height variation between modules should not exceed 0.001" (request tolerance lapped modules when ordering). Most TE assemblies utilize one or more "thermal grease" interfaces. The grease thickness should be held to 0.001 ± 0.0005 ". When these types of tolerances are to be held, a certain level of cleanliness must be maintained. Dirt, grit and grime should be minimized; this is very important when "grease" joints are utilized due to their affinity for these types of contaminants [15].

5. CONCLUSION

The thermoelectric technology can be used in globally for energy conservation without any pollution. The research reviewed on thermoelectric module of existing work shows potential, theory, material, model, energy resources, construction and applications for electricity generation and cooling. Some appropriate research directions were further proposed by authors [1]

- TE potential in current electricity generation and cooling. The TE technology can be applied in many areas, although recently it is still utilized in niche fields such as out-space mission and distant area. With the increase of the figure of merit and advancement in the devices, it can be applied in the domestic building as air conditioner and the power generator. It can also be applied to the areas where the temperature of the waste heat is relatively low. In those areas the traditional generator is low efficient and cost relatively high. Another potential field is self-cooling system, especially a fairly small device where TEC compared to the traditional cooler has many unique advantages.
- For the structure of the TEG and TEC, with the optimization of the TEG devices for wood stove, the output power gradually grows from 1W per module in 2003 to 9W per module in 2014. Thus the priority for efficiency of TE devices is to optimize the influence of heat exchange.
- For TEG, the temperature plays a significant role for TEG application. The low temperature recovery especially converting the waste heat to the electricity is feasible. The efficiency of the low temperature device is among 1% and 2%. For TEC, the COP is a significant parameter to evaluate the performance of the cooler. The COP is generally among 1 and 2 when the temperature is between 313 K and 293 K. And theoretical COP for $ZT = 2.4$ at the same temperature is 3.97. There is still improvement for the device to gain better performance [1].
- In recent work from 2015 to 2017 that explaining new thing than can introduce to increase its application and improve its performance.

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