A short review on recent trends and applications of thermoelectric generators

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Abstract. The basic needs of the society were food, water and energy. The nexus between food, water and energy is unavoidable. Energy is the key element for the survival of all the living beings on the Earth. Energy crisis and environment deterioration are the two most faced glitches of the current scenario. Thermo electricity is one of the promising solutions for energy crisis that is experiencing in this 21st century. This particular article gives the brief description about the principle of thermoelectric devices and their necessity, classification and the applications of thermoelectric generators (TEG’s). Also, this paper gives a short description on materials, design and optimization of TEG’s. It concludes with the future research direction in the realm of thermo electricity generation.

Keywords: Thermo electric power generation; thermo electric generators; thermo electric materials; Applications.

1. Introduction
Extensive usage of fossil fuels for sustenance of human life has led to severe atmospheric and ecological problems. Subsequently, the terminologies like greenhouse gas, global warming, ozone depletion, climate change, acid rains, etc., were evolved and now they are the trending glitches of our world, in which the solutions for them are not up to the mark. One of the most reasonable solutions for lessening the fossil fuels usage is thermoelectricity, where it is gaining its popularity because of its impeccable advantages. Thermo electricity is an approach that converts the heat available from automobiles, industries etc., into electricity. Likewise, thermoelectric technology, also converts the electricity into required thermal energy for the demanded heating or cooling applications. The key benefits of this approach are that it converts thermal energy into electric energy directly without any intermediate conversion, it has no moving parts or no working fluids inside the equipment, the operation is noiseless and maintenance free, it is emission and chemical reaction free, it is harmless to the environment and it has long reliable operation. Regardless of these benefits, the application of this approach is limited mainly because of the low conversion efficiency and high cost which have been a hurdle to its advancement for most common applications from over decades. Accordingly, wide investigations into the TE technology and its materials have been carried out for attaining the high conversion efficiency and to expand its wings for all applications. The phenomenon of Thermoelectricity was discovered in the early 18th century, which generates the voltage between two dissimilar materials and was most
commonly utilized as thermocouples. Even though, novel materials are yet under the development, the elementary concept behind the TE approaches are all rely upon the principles of Seebeck effect and Peltier effect. Thermo Electric Generators (TEGs) generally comprises of a set of thermoelectric modules embedded between two heat exchangers. Each thermoelectric module then comprises of some hundreds of thermoelectric couples connected together thermally in parallel and electrically in series which directly converts the thermal energy that passes through it into electrical energy. This review thus gives the brief discussion on the thermoelectric principles, materials and applications. It would help the fellow researchers to demonstrate the thermoelectric approach and identification of techno-glitches in the technology along with the future directions of research.

2. Working Principle

The Seebeck effect came into existence in 1821 which revealed that two dissimilar metals have the distinct temperatures at the junctions, and the respective electromotive force (emf) and current in the junction circuit are called as thermo-emf and thermo current. Enhancing the temperature difference increases the temperature difference between two junctions. The proportional constant associated to material property is acknowledged as Seebeck coefficient. This coefficient is low for metals and high for semiconductors i.e., for metals it is approximately 0 µV/K and for semiconductors it is about ±200 µV/K

\[ \alpha = \frac{\Delta V}{\Delta T} \]  \hspace{1cm} (1)

Where
- \( \alpha \) = Seebeck Coefficient,
- \( \Delta V \) = voltage difference,
- \( \Delta T \) = temperature difference.

Peltier effect came into existence in 1834 that when there is current in the circuit, the junction rejects or absorbs the heat depends on the current direction. This is mainly due to the Fermi energy difference between two materials. The capability of heat rejection or absorption is mainly correlated to the temperature of junction and property of different conductors. For defining the absorbed heat per area of junction per second, \( ZT \), a dimensionless parameter is most commonly used to evaluate the Peltier performance of a thermoelectric material.

\[ ZT = \frac{\alpha^2 \sigma T}{k} \]  \hspace{1cm} (2)

Where
- \( \alpha \) = Seebeck coefficient,
- \( \sigma \) = electric conductivity,
- \( k \) = thermal conductivity. Accordingly, the thermoelectricity approach is divided into two categories according to Peltier and Seebeck,
1. Thermo electric generators (TEGs) for generating electricity when two materials are disclosed in two distinct temperatures,
2. Thermo electric coolers (TECs) for cooling applications when voltage is added onto the materials used. The TEG efficacy can be evaluated by:

\[ \eta_{max} = \frac{T_H - T_C}{T_H} \times \frac{\sqrt{1+ZT}-1}{\sqrt{1+ZT}+\frac{T_C}{T_H}} \]  \hspace{1cm} (3)

Where \( T_H \) is temperature on the hot side and \( T_C \) is temperature on the cold side and the maximum coefficient of performance of the TEC is evaluated by:

\[ COP = \frac{T_C}{T_H - T_C} \times \frac{\sqrt{1+ZT} - \frac{T_H}{T_C}}{\sqrt{1+ZT} + 1} \]  \hspace{1cm} (4)
Corresponding to equations (3) and (4) it is seen that when the value of ZT is infinite, the efficacy or COP is Carnot. Thus, it was said that, TEGs are Carnot hot engines, where electrons can work as working medium. On contriving Thermoelectric modules, both p- and n-type materials are essential [1, 2].

3. Materials
Meanwhile the later 1950s, the semiconductor TE appliances have been employed for cooling and power generation and subsequently for space power production because of their impeccable energy conversion and some interesting capabilities compared to the conventional power generators. During early 90’s, there was an enthusiastic curiosity in the stream of thermoelectricity which is greatly powered by the necessity for more distinct materials for electricity generation and electronic refrigeration. In this regard, thermoelectric materials are broadly classified into three types, namely:

1. Semiconductors,
2. Polymers and
3. Ceramics [3].

3.1. Semiconductors.
The semiconductor materials are best suitable and capable for developing the thermocouples because they have higher Seebeck coefficients and also the way to reduce $k$ without influencing $\alpha$ and $s$ in bulk materials, thus increasing the value of ZT, is to utilize the semiconductors for its greater atomic weight like Bi$_2$Te$_3$ and the alloys with Sn, Sn and Pb. A semiconductor or solid-state electronics component can perform good and with greater reliability for many years when it is operating at near ambient temperatures. The materials with best ZT are found as heavily doped and small bandgap semiconductors [4]. The highest value of ZT for Bi$_2$Te$_3$ has been noticed as 2.4 in p-type Bi$_2$Te$_3$/Sb$_2$Te$_3$ at 300K [5]. Pei et al. [6] found the transport facilities of PbTe alloyed with MnTe resulted in a high ZT value of 1.6 at 700K. As said earlier, decreasing the thermal conductivity can enhance the value of ZT, Pei et al. [7] found that Ca – doped BiCuSeO can lower the thermal conductivity and can rise the ZT to 0.9 at 923K for Bi$_{0.92}$Ca$_{0.07}$CuSeO. Rhyee et al [8] discovered the ZT value of 1.48 at 705K for binary crystalline n-type material In$_3$Se$_3$ and Hsu et al. [9] noticed the ZT value of 2.2 at 800K for AgPb$_3$SbTe$_2$-m.

3.2. Ceramics
Thermoelectric materials in real-time operations are invariably based on the alloy materials like Bi$_2$Te$_3$ and SiGe. In comparison with other thermoelectric alloys, metal oxides have some benefits such as chemical stability, less toxic, low cost and oxidation resistance so their use enables the manufacturing of more reliable and durable equipment [10]. Ceramic is a chief thermoelectric material for thermoelectric energy transformation to recover waste heat of high temperature from engines and incinerators [11]. However, these oxides are not considered as thermoelectric materials due to their low carrier mobility till the high operative thermo electric oxide of Na$_x$Co$_2$O$_4$ came into view. Presently, cobalt based oxides like Ca$_3$CoO$_9$, NaCo$_2$O$_4$, have been manufactured as p-type legs in thermoelectric modules. Parallely, n-type ZnO, SrTiO$_3$ and CaMnO$_3$ ceramics also been considered. Among them, CaMnO3 can be synthesised at ambient conditions showed the extraordinary thermoelectric properties which in turn made it as a potential n-type oxide material [12]. Tsubota et al. [13] examined the TE properties of LaCoCO$_3$ with addition of B$_2$O$_3$-CuO and resulted that the material ha value of $ZT = 0.073$ at 373K, which was almost 1.5times greater than that of pure LaCoCO$_3$ sintered at 1473K. Butt et al. [14] evaluated the thermoelectric properties of (La, Fe) co-doping of Ca$_3$Co$_6$O$_9$ and results revealed that the value of ZT= 0.32 at 1000K which is 70% greater than that of pure Ca$_3$Co$_6$O$_9$.

3.3. Polymers
The broadly examined, developed and utilized inorganic materials associated with complicated issues such as dearth of natural resources, toxicity and manufacturing methods involved with high economy. Therefore, there exists a great need of developing a new type of material for further enhancement of properties[15]. The group of conductive polymer composites comprising conducting fillers and
insulating polymer matrices have been examined for the benefits of inexpensive, solution processability, flexibility, lightweight, low cost synthesis and more eco-friendly substitutes to conventional thermoelectric modules. Further investigations on the behaviour of segregated conductive polymer composites with hybrid fillers of carbon nanotube and bismuth telluride resulted that segregated composite containing 2.6 vol% CNTs and 5.1 vol% Bi\textsubscript{2}Te\textsubscript{3} exhibit the value of $ZT = 3 \times 10^{-5}$ at room temperature [16]. However, currently there is advancement in the polymers ZT, Kim et al. [17] stated that the value of ZT of dopant poly (styrenesulphonate) in poly (3,4-ethylenedioxythiophene) as 0.42 at room temperature. For polymers, ceramics and some semiconductors, though the value of ZT is low, other influencing properties like temperature resistivity and flexibility made them as intriguing thermoelectric materials.

Among all, semiconductor is widely used but still the value of ZT is not so as high enough to make them as competitive among conventional generator and cooler materials. Other major disadvantage of semiconductors is that they are resistive of high temperatures and they do lack of flexibility. Hence, ceramics and polymers are alternatives for them.

4. Applications of Thermo Electric generators (TEGs)

Thermoelectric generators are basically categorized according to the heat source type and applications where it is utilized. Some of them are as follows:

1. Waste Heat Recovery
2. Space applications
3. Solar Thermo Electric Generators (STEGs)

4.1. Waste Heat Recovery:

4.1.1. Automobiles: One of the major challenges experiencing currently is to reduce the energy that is being wasted in the form of heat energy. Automobile industry is one among them for the utilization of TEGs. Almost 65 percent of the heat generated in the internal combustion engines is being wasted as of the survey noted [18]. However, for the installation of the TEGs in automobiles, it has to meet some conditions. They are: it should not affect the operation of the vehicle. The materials should be recyclable and eco-friendly. It should be economically viable [19].

The Ford group in association with the department of energy (DOE) has conducted a research on the v 6 engine equipped with TEGs with an objective to produce 500 W but the results published by Maranville in 2012 showed that the generated output was 250 W which is 50 percent of the target [20,21]. Generator is protected by installing a bypass in the exhaust system. Also, Volvo, Renault trucks worked on the RENOTER (recovery of energy from exhaust of an engine from 2008 to 2011). This project inferred that TEG can generate up to 130 W from a passenger car exhaust. Renoter 2 project started in year 2013 targets the usage of TEGs in industrial gas exhaust recirculation and on the hybrid gasoline engines [22]. Similarly, for aircrafts, a study conducted by boeing research and technology showed that by using TEGs, fuel reductions of 0.5% can be achievable which will reduce the operating costs of the flights significantly[19]. Subsequently, shipping is one of the largest sources of greenhouse gas emissions. Kristiansen et al. [23] studied the possibilities of using TEGs for large ships. The heat that is released by the engine is used to purify the water and to heat the accommodation areas. so the temperatures of the waste heat will get significantly reduced. Also, the weight is one of the main concerns in the heavy ships. TEGs are also an excellent opportunity in the smaller ships since the weight is not a problem, cold source (water) is free [24].

4.1.2. Industries: Heat is a by-product in almost all the industries. In some of the industries, this heat is used for some heating networks and in some industries, it is converted into electricity by using steam turbines. KELK LTD. did the experiment on the usage of the thermo electric generation at komatsu ltd., Awazu plant. The results shown that the efficiency is 5% [25]. Aranguren et al. [26] had conducted experiments on a TEGs dedicated to convert the waste heat from a combustion chamber. TEGs are being used in some of the steel industries to convert the radiant heat from molten metal into electricity.
In Japan, JFE steel corporation did the studies on TEGs using radiant heat from slabs. TEG is connected to the grid [27]. Luo et al. [28] studied the usage of TEGs in Portland cement manufacturing and reported that around 10-15% of the energy is dissipating into atmosphere. This kind of wasted heat is difficult to recover as the kiln rotates permanently. The heat loss from a kiln of length 72 m and diameter 4.80 m is approximately 10000 kW. They have taken a kiln which is surrounded by a coaxial shell having thermo electric modules and performed the experiments. The results showed that TE system can produce 210 kw and it also saves approximately 3280 KW due to insulation provided by the shell around the kiln. Hesham Khalil et al. [29] investigated about the influence of the tilt angle on waste heat recovery system from a chimney placed vertically by employing TEGs cooled at their cold sides through natural convection and also the aspect ratio performance of Thermo Electric Generator has been studied. Later, the whole scenario was studied numerically in ANSYS-Fluent software and results were best fitted with the experimental outcomes. The tilting of chimney wall towards the flue gases had a positive influence on the output power of TEGs and an angle of 15° degree augments the power of upper TEGs by 5% with a nominal influence on the power of TEGs equipped at lower side. Souvik Biswas et al. [30] numerically investigated on the design and development of waste heat recovery utilization system through a heat exchanger made of Bi2Te3 material and got the best fit of results for industrial use.

4.2. Space Applications

Electricity production in some of the drastic environments should meet strict specifications. Weather conditions can be extreme, either very hot or cold etc. also the maintenance should be minimum as it is difficult in such type of environments. the space industries are using the radio isotope thermo electric generators (RTGs). Heat is generated by the natural radioactive decay plutonium-238 [31]. US NAVY’S transit navigation satellite first used this technology back in 1961. They equipped the satellite with the SNAP-3 nuclear auxiliary generator which generated the power of about 2.7 W only but worked for about 15 years [32]. RTGs are used in space applications because of their low weights, good reliability and also, they can work even for several years. The voyager I and II are launched in 1997 also equipped with these RTGs because of their extreme reliability to power the instruments and systems in the craft. The capacity of generation decreases gradually by 7W a year due to decay of the plutonium. NASA launched the Cassini-Huygens orbital probe in association with European space agency in 1997 to explore about Saturn and its satellites. This is also powered by RTGs [33,34].

4.3. Solar Thermo Electric Generators (STEGs)

In these generators, the heat from the sun is used as heat source. the maximum efficiency which can be obtained by using TEGs are around 5-10%. But the solar cell will have an efficiency more than that of TEGs by 3-5 times. The efficiency of the solar TEGs can be increased by increasing the temperature difference across the thermo elements. This can be achieved if a concentrating lens is used to concentrate the solar beams. [3]. The device consists of thermal concentration absorber and optical concentration system. To reduce the losses, they created a vacuum by enclosing the STEG with glass.[35,36]. Kraemer et al. [37] did the research to integrate STEGs in solar hot water vacuum tube system for co-generation application to create a device that has the potential to provide cost effective hot water and electricity. Baranowski et al. [38] did the research and proved that by using the available thermo electric materials an efficiency of 14.1% can be achieved with a temperature difference of 1000[degree centigrade] and concentration of solar intensity by 100. Wei He et al. [39] did the research on coupling of the solar water heating with a TEG. A heat pipe is used to transfer the heat and the TEG is used to exchange the heat from heat pipe to water. Electric efficiency is around 1-2%, the hot water production efficiency is around 55%. Khanmohammadi [40] investigated the novel model of solar-based integrated energy systems (IES) for hydrogen yield with and without thermoelectric generators (TEGs) waste heat recovery system (WHRS). The proposed approach has an increase in out power by 17.6%, efficiency by 1.2% and hydrogen production is increased by 16% when compared to conventional system.
5. Future Scope
So as to be compete with conventional devices, the analysis revealed that the value of ZT should be greater than 3 [41]. Though the highest ZT ever found at the normal temperature is about 2.4. Therefore, it is even crucial to invent the highly efficient thermoelectric materials among several materials like ceramics, semiconductors and polymers. Also, it is also very essential to augment the thermoelectric devices by enhancing and optimizing the structure of heat exchangers, the operating parameters and the geometry design, because these aspects obviously influence the whole system efficiency. The field of applications can be broadening such as heat load reduction in automobiles, energy storage, thermal energy management and recovery from the manufacturing. Lastly, the long-term operation and stability assessment can be more investigated for better potentiality.

6. Conclusions
In the current discussion, a brief elucidation on the principle, working and applications of thermoelectric materials and thermoelectric generators has been presented. Also, novel materials with improved ZT, high temperature resistive materials with greater reliability also been discussed. Later the application in sector wise and the developments of TEGs was reviewed which allows the researcher to get a concise knowledge on the TEGs. At the end, the future direction in this allows the reader to enhance the researching path in the particular gaps discussed.

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