The History of Thermoelectrics: From Discovery to Modern Advancements

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Abstract - This paper provides a thorough examination of the history of thermoelectricity, spanning from its discovery in the early 19th century to the latest advancement in the field. Thermoelectricity, the direct conversion of heat into electricity or vice versa, has undergone significant transformations over the years, driven by breakthroughs in materials science, solid state physics, and engineering. The paper chronicles the key milestones, from the discovery of the Seebeck and Peltier effects to the development of modern thermoelectric materials and devices. The evolution of thermoelectric materials from traditional semiconductors to novel nanostructural materials is discussed. It also explores the diverse application of thermoelectricity including waste heat recovery and space exploration. By tracing the history of thermoelectricity, this paper aims to provide a deeper understanding of the scientific and technological advancement that have shaped the field. By understanding the history and evolution of thermoelectricity, we can appreciate the progress made so far and look forward to future advancements that will shape the field. The potential for thermoelectricity to contribute to sustainable energy solutions and reduce greenhouse emissions is vast, making it an exciting and important area of research.

Keywords: Thermoelectricity, Seebeck Effect, Peltier Effect, Nanostructural Materials, Greenhouse Emissions.

I. INTRODUCTION

Thermoelectricity refers to the conversion of thermal gradient into electrical potential (Seebeck effect) or the creation of a thermal gradient by passing electric current (Peltier effect). Since the early work of Thomas Johann Seebeck in 1821, researchers have explored how dissimilar conductors generate voltage under temperature gradients (Uchida & Heremans, 2022).

The potential to harvest waste heat or enable solid state cooling makes thermoelectrics relevant to modern energy and sustainability challenges (Tritt, 2011). Traditional thermoelectrics were limited by low conversion efficiency.

Today, advanced materials and processing methods aim to push the thermoelectric dimensionless figure of merit, ZT beyond 1 (i.e. $ZT > 1$) to enable economic viability (Zoui et al, 2020).

II. CHRONOLOGICAL DEVELOPMENT

2.1 Early Discoveries (1820 – 1920)

Thermoelectricity has long been discovered as a potential source of greener energy by researchers and scientists in Western Europe predominantly Berlin, Germany prior to the world wars.

2.1.1 Seebeck Effect

Thomas Johann Seebeck in 1821 discovered that a circuit of two different metallic conductors produces a magnetic deflection through a compass magnet (Seebeck, 1895) when one junction is at a higher temperature, making the first observation of thermoelectric voltage (Zoui et al, 2020). Initially Seebeck assumed that his observation was as a result of magnetism induced by the temperature difference, and later agreed it might be related to the Earth's magnetic field.

Seebeck later, opined that the magnetic deflection as supported by Ampère's law occurred due to an electric current induced by the thermoelectric force. This is today known as the Seebeck Effect. The early instrument used by Seebeck to observe the deflection of a compass needle is shown in Figure 1.

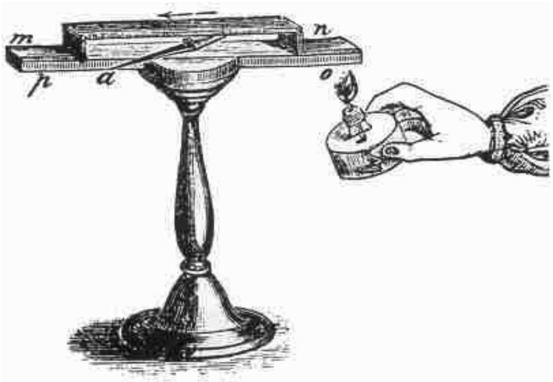

Figure 1. Seebeck's early instrument for observing the deflection of a compass needle (Seebeck, 1895).

The voltage produced is proportional to the temperature difference between the two junctions. The resultant constant of proportionality is known as the Seebeck coefficient, also known as thermopower.

$$\frac{\Delta V}{\Delta T} = S \qquad 1.0$$

where ΔV is the voltage difference, ΔT is the temperature difference and S is the Seebeck coefficient expressed in units of μV/K or μV/°C of the circuit.
The voltage difference ΔV produced across the terminals of an open circuit made from a pair of dissimilar metals or conductors, A and B whose junctions are held at different temperature is directly proportional to the difference between the hot and the cold junction temperatures,

$$T_h - T_c \qquad 2.0$$

where T_h and T_c are hot junction temperature and cold junction temperature, respectively and this is illustrated in Figure 2.

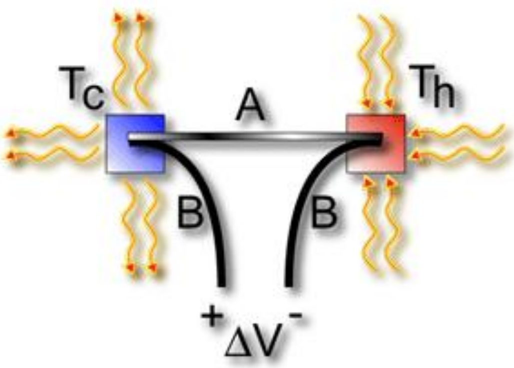

Figure 2. The voltage difference ΔV produced across the terminals of an open circuit made from a pair of dissimilar metals, A and B whose junctions are held at different temperatures (Magnus, 1851).

Gustav Magnus in 1851 discovered that the Thermopower is a thermodynamic state function since the Seebeck voltage is independent on the temperature distribution along the metals between the junctions. On this basis, thermocouple becomes a regular temperature measuring device nowadays.

Seebeck's Analysis
Seebeck analysed numerous materials such as elements, alloys and minerals, e.g. zinc antimonide, chalcogenide minerals (e.g. lead sulphide and cobalt arsenide) and subsequently made a qualitative comparison of their Seebeck effect.

Werner Haken following the studies of Becquerel in 1910 (Becquerel, 1866) on ZnSb and CdSb characterized the Seebeck coefficient and electrical conductivity of many elements, alloys and compounds. This study led to the identification of Sb_2Te_3, Bi_2Te_3, $Bi_{0.9}Sb_{0.1}$, SnTe, PbTe and Cu-Ni alloys as good thermoelectric materials (Haken, 1910).

2.1.2 Peltier Effect
Jean Charles Attanase Peltier, a French physicist in 1834 found that an electrical current would produce heating or cooling at the junctions of two dissimilar metals (Wu, 2014; Pickett & Moodera, 2001). Peltier effect therefore is the presence of heating or cooling at the junction of two different conductors (Patel & Mehta, 2015). Peltier in his study observed that an electrical current would produce a temperature difference or gradient at the junction of two different conducting materials.

Illustration of Peltier Effect
When an external electromotive force (emf) source is applied across the open ends of two coupled materials as shown in Figure 3, current, I flows in a clockwise direction around the circuit. Therefore, a temperature difference, ΔT is developed, while heat is generated or absorbed kniown as rate of heating $(\Delta Q/\Delta t)$ at one junction and on the junction, heat is released or removed, and it's known as rate of cooling $(-\Delta Q/\Delta t)$.

The heat absorbed or created at the junction is proportional to the electrical current, I and it's represented as:

$$\frac{\Delta Q}{\Delta t} = \pi_{AB}.I \qquad 3.0$$

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where, π_{AB} is the Peltier coefficient of the A-B circuit, and it is measured in W/A or V.

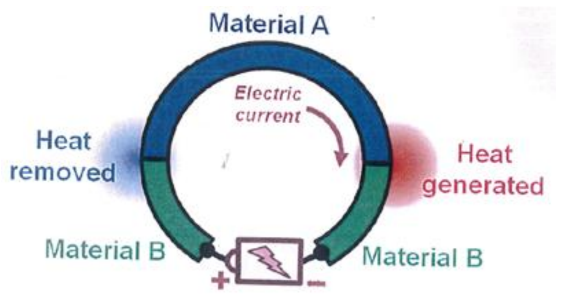

Figure 3. Schematic illustration of Peltier effect (Wu, 2014).

2.1.3 Thompson Effect

In 1854, about thirty years after the discovery of Seebeck effect, a British Physicist, William Thomson, who later became Lord Kelvin (Thomson, 1857) described a detailed explanation of the Seebeck and Peltier effects together with analysis of their correlation. The study gave rise to what is today known as the Thomson effect.

Illustration of Thomson Effect

In this study, heat is absorbed or released when a current flows in a conducting material with a temperature gradient ($\Delta T/\Delta x$). The rate of the heat absorbed or released ($\Delta Q/\Delta t$) is proportional to the electric current, I and the temperature gradient ($\Delta T/\Delta x$). This is represented in equation 4.0.

$$\left(\frac{\Delta Q}{\Delta t}\right) = \mu . \mathrm{I} . \frac{\Delta \mathrm{T}}{\Delta \mathrm{x}} \quad 4.0$$

where μ is the Thomson coefficient (V/K).

The value of μ is positive when current flows from the hot end to the cold end (heat generation). When current flows in a reverse direction (heat absorption), the μ becomes negative. The Thomson effect with a Thomson coefficient, μ of negative value is illustrated as shown in Figure 4.

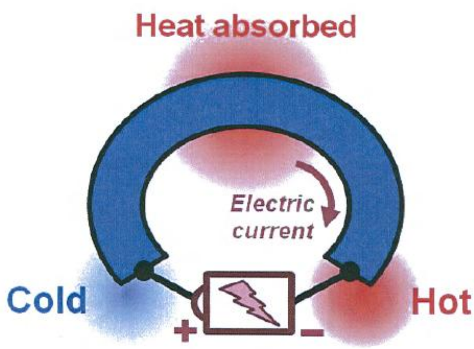

Figure 4. Schematic illustration of Thomson effect (Wu, 2014).

Seebeck, Peltier and Thomson effects are collectively known as thermoelectric effect. Thus, thermoelectric effect is inter-related in Kelvin's relations as derived from thermodynamics. The equation is as shown below:

$$\pi_{AB} = S_{AB}T \quad 5.0$$

The expression (equation 5.0) above implies that Peltier coefficient is simply the product of Seebeck coefficient and absolute temperature.

2.1.4 Development of Thermoelectric Figure of Merit

Edmund Altenkirch, a German Engineer in 1909 was the first to derive the maximum efficiency of a thermoelectric generator using the constant property model. In 1911, he also studied the performance of a cooler when the design and operating conditions are optimized (Altenkirch, 1909; Altenkirch, 1911). This correlation however, was later developed into the thermoelectric figure of merit, ZT. The optimal performance of thermoelectric materials and devices depends on the ZT. The higher the ZT, the better the efficiency of the TE materials to convert heat energy into useable electricity.

ZT contains both electrical and thermal contributions to the properties of the TE materials and is given as:

$$\mathrm{ZT} = \frac{\mathrm{S}^2 \sigma \mathrm{T}}{\mathrm{K}} \quad 6.0$$

where S is the Seebeck coefficient, σ is the electrical conductivity, T is the absolute temperature at which the properties are measured and $k = k_L + k_E$ (Tritt & Subramanian, 2006) is the total thermal conductivity. k_L and k_E are the lattice thermal conductivity and electronic thermal conductivity, respectively.

ZT describes the material's performance, hence is a prerequisite for a good thermoelectric material. Hence, ZT is a measure of the struggle existing between electronic transport (power factor) and the thermal transport (total thermal conductivity) in a material (Dehkordi , 2014). According to Carmo et al (2011), thermoelectric figure of merit is the electric power through which the heat flows between the hot and cold sides per unit temperature gradient.

Early conductivity measurements on solids by A.Eucken (Eucken & Kuhn, 1928) revealed that point defects found in alloys significantly reduces the lattice conductivity, hence;

$$K_L = K - K_E \qquad 7.0$$

The concept of ZT was first used in 1949 by Abram Fedororich Ioffe, a Russian physicist when he developed the modern theory of thermoelectricity (Vedernikov & Iordanishvili, 2012), hence culminating in the classic texts on semiconductor thermoelements and thermoelectric cooling. Ioffe and his Institute in Saint Petersburg vigorously worked on the research and development of TE in USSR, and this led to the first commercial TE power generation and cooling devices.

For a high ZT to be achieved, the following parameters are essential (Tritt & Subramanian, 2006; Nemir & Beck, 2010):

i. Large Seebeck coefficient to produce a required high voltage for a given temperature difference.
ii. High electrical conductivity to minimize Joule heat due to electrical resistance, and
iii. Low thermal conductivity to minimize heat loss and restrict diffusion of heat across the device.

In 1954, Julian H. Goldsmid carried out one of the earliest demonstrations of 0 ºC cooling using Bi_2Te_3 based thermoelements (Goldsmid & Douglas, 1954). Goldsmid therefore became of the first to utilize the thermoelectric quality factor, identifying the importance of high mobility and effective mass combination in semiconductors that when properly doped, make good thermoelectric materials. Goldsmid is the author of many books on thermoelectrics including Introduction to Thermoelectricity published in 2010.

2.2 Advancement and Applications of Thermoelectrics

Thermoelectricity technologies such as cooling and power generation have been studied both for military and civilian utilization during and after the World wars. Unfortunately, the political and economic importance of these devices made advancement more complex and slow to public glare especially between the Eastern European and Western countries.

By the 1950's, generator efficiencies had reached 5 % and cooling from ambient to below 0ºC was demonstrated , and this led to some notable viable industries. According to public projections, thermoelectrics would soon replace conventional heat engines and refrigeration since interest and research in the area grow rapidly at major Corporations such as Westinghouse, universities and national research laboratories (Heikes & Ur, 1961; Cadoff & Miller, 1960; Egil, 1960). Regrettably, at the end of the 1960's, the pace of progress began to slow and many research programs were dismantled despite several reports of ZT > 1.

In the quest for higher ZT Materials, a general strategy guided by the quality factor has been to look for a small bandgap semiconductor made from heavy elements. Glen Slack summarized the material requirements succinctly in the concept of "Phonon-Glass Electron-Crystal "that the phonons should be disrupted like in a glass while the electrons should have high mobility like they do in crystalline semiconductors (Slack, 1995). This concept implies that outstanding thermoelectric materials require crystalline solids with low thermal conductivity such as glass and scatter phonons without significantly hindering the electrical conductivity, but maintains charge carriers of high mobility or electronic transport as expected of a crystal (Slack, 1995; Mahen, 1998).

2.3 Specialized Applications of Thermoelectrics

Thermoelectricity is a solid-state technology known for its easiness, reliability and simplicity. These qualities put together account for its niche applications even when conventional processes are more efficient. For example a small and stable industry produces variety of products such as optoelectronics, small refrigerators and seat cooling/heating systems based on Bi_2Ti_3-Sb_2Te_3 compounds. Equally, the need for reliable, remote power sources provides some niche or specialized applications for thermoelectric power generation.

Despite the low energy conversion efficiency, niche applications and slow technological progression associated with thermoelectric devices, it is paramount to state that thermoelectric devices or generator are still in their developmental stage with numerous potential applications (Patel & Mehta, 2015).

Outside power generation, TE materials have attracted potential applications in solid state cooling or thermoelectric refrigeration using the Peltier effect. The effect of low energy conversion efficiency has constrained the use of TE devices and generators to specialized areas where reliability other than cost is a major consideration (Ismail, 2011). These specialized applications include:

i. Providing power for cathodic protection systems in gas well casings and pipelines (Patel & Mehta, 2015; Karschinia & Chakraborty, 2013).

ii. Self-powered systems for wireless data communications or gatherings (Karschinia & Chakraborty, 2013; Rowe, 1995).

iii. Powering of automotive and deep space explorations such as Radioisotope Thermoelectric Generators, RTGs (Rowe, 1995).

iv. Ventilation fans, navigation equipment and landing lights in airports (Karschinia & Chakraborty, 2013).

2.4 New Concepts in Thermoelectricity

New concepts in thermoelectricity have emerged since 2000 focusing on improving efficiency and developing sustainable materials. The key advancements include:

i. Thermoelectric materials: Researchers have explored various materials such as skutterudites, half-Haussler compounds, oxides and organic-inorganic hybrids to enhance thermoelectric performance (Snyder & Toberer, 2008; Casper et al, 2012). Nanostructuring and defect engineering have also shown promise in improving the properties of thermoelectric materials.

ii. Device development: Advances in device design and fabrication have led to improved performance and efficiency. For example, thin-film TE devices have been developed for wearable electronics and energy harvesting (Yadav et al, 2008; Liu et al, 2018). Also developed is segmented thermoelectric generators (STEGs) aimed to improve efficiency by optimizing material properties and device design (Ursell & Snyder, 2002).

iii. Thermoelectric applications: Thermoelectric generators and devices have been explored for various applications, including waste heat recovery, solar energy harvesting, etc. (Rowe 2006; Nozariasbmarz et al, 2021).

iv. Thermal modeling and simulation: Advances in computational modeling and simulation have enabled the prediction of thermoelectric properties and the optimizatuion of device performance (Luo et al, 2022; Gorai et al, 2017).

III.CONCLUSION

The history of thermoelectricity is a proof to the power of scientific discovery and innovation. From its humble beginning to the current state-of-the-art materials, and devices, thermoelectric research has come a long way. As we look to the future, it is clear that thermoelectricity will play an increasingly important role in addressing global energy challenges and enabling sustainable development. Further research and development are needed to overcome the remaining challenges and unlock the full potential of thermoelectricity.

By understanding the history and evolution of this field, we can appreciate the progress made so far and look forward to the exciting advancements that will shape the future of energy materials in general and thermoelectricity in particular.

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