



Quadrennial Technology Review 2015

Chapter 6: Innovating Clean Energy Technologies in Advanced Manufacturing

Technology Assessments



Additive Manufacturing

Advanced Materials Manufacturing

*Advanced Sensors, Controls, Platforms
and Modeling for Manufacturing*

Combined Heat and Power Systems

Composite Materials



Critical Materials

***Direct Thermal Energy Conversion
Materials, Devices, and Systems***

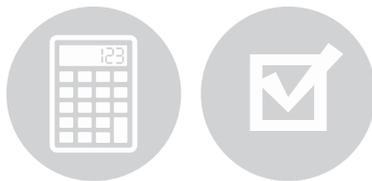
Materials for Harsh Service Conditions



Process Heating

Process Intensification

Roll-to-Roll Processing



*Sustainable Manufacturing - Flow of
Materials through Industry*

Waste Heat Recovery Systems

*Wide Bandgap Semiconductors for
Power Electronics*



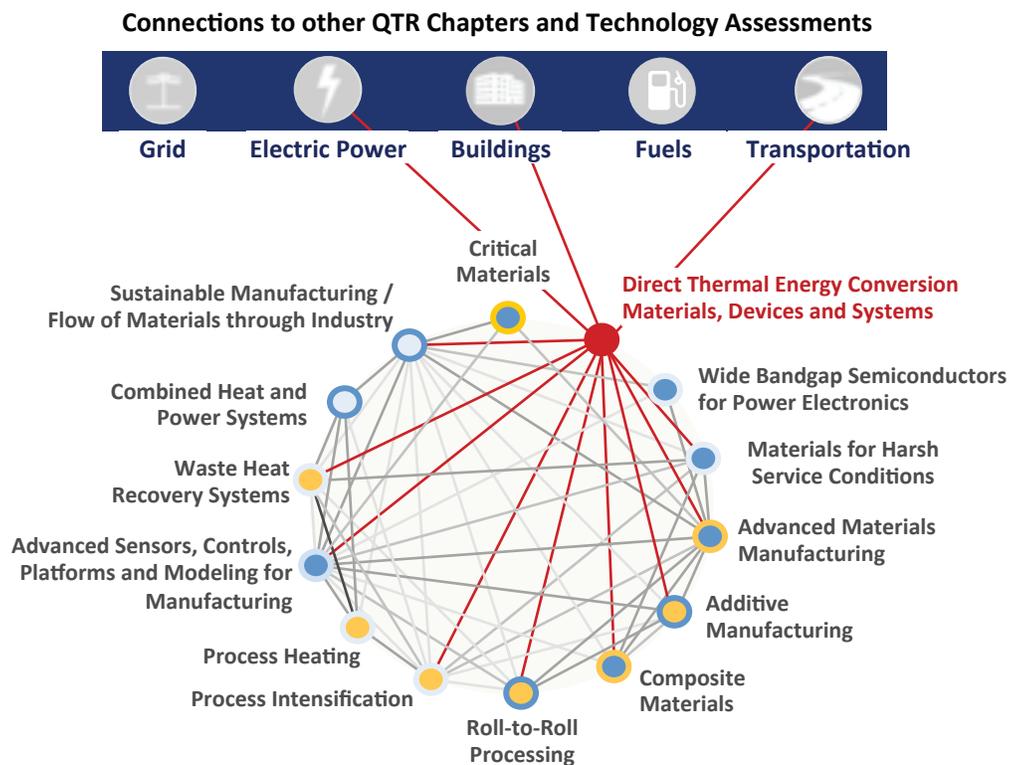
U.S. DEPARTMENT OF
ENERGY



Direct Thermal Energy Conversion Materials, Devices, and Systems

Chapter 6: Technology Assessments

NOTE: This technology assessment is available as an appendix to the 2015 Quadrennial Technology Review (QTR). Direct Thermal Energy Conversion Materials, Devices, and Systems is one of fourteen manufacturing-focused technology assessments prepared in support of Chapter 6: Innovating Clean Energy Technologies in Advanced Manufacturing. For context within the 2015 QTR, key connections between this technology assessment, other QTR technology chapters, and other Chapter 6 technology assessments are illustrated below.



| Representative Intra-Chapter Connections | Representative Extra-Chapter Connections |
|---|---|
| <ul style="list-style-type: none"> ■ Materials for Harsh Service Conditions: thermal conversion materials and devices for high-temperature or corrosive environments ■ Roll-to-Roll Processing: thermoelectric device fabrication via roll-to-roll ■ Waste Heat Recovery Systems: novel energy conversion materials, devices and systems for waste heat to power ■ Additive Manufacturing: additive manufacturing of thermoelectric modules ■ Advanced Sensors, Controls, Platforms and Modeling for Manufacturing: thermal control systems; power for wireless sensor networks | <ul style="list-style-type: none"> ■ Electric Power: water withdrawal for power plant cooling; waste heat recovery in power plants ■ Buildings: thermoelectric heat pumps for HVAC ■ Transportation: direct thermal energy conversion for internal combustion engines |



Introduction to the Technology/System

Advances and maturation in energy conversion technologies followed by their wider implementation will augment the capture and repurposing of readily available waste-energy sources. A number of technologies and prototypes exist for converting heat energy into electrical energy. Conventional technologies for electricity generation from heat recovery rely on boiling liquids to produce steam that drives turbines. The steam Rankine cycle is the most traditional generation method in this category. Water is boiled to produce the steam in this cycle, and the process is the most efficient means of producing electricity from waste heat when exhaust temperatures are around 340°C–370°C. Owing to some fundamental limitations in steam Rankine systems, including low condensation temperatures, low pressure, and high specific volumes,¹ large installations are needed; the space required to accommodate such large footprints can often be unavailable or make such systems undesirable. For lower-temperature waste heat, there are variations on the Rankine cycle that use other fluids and their associated gases. In organic Rankine cycle (ORC) generators, working fluids such as propane or toluene are used and have lower boiling points. A number of candidate fluids and ORC applications are discussed in a review by Tchanche et al.² The ORC has cost and complexity advantages over a typical steam Rankine cycle, including the avoidance of superheating; this comes at the expense of maximum efficiency of 24%, compared to more than 30% efficiency for its water-based counterpart.³ A number of manufacturers produce ORC systems at costs estimated in the \$2–\$3 per watt range compared to \$1.10–\$1.40 per watt for the steam Rankine cycle.⁴

The Kalina cycle is another Rankine-type system that uses a mixture of ammonia and water. This binary working fluid avoids the temperature plateau seen in single fluids during boiling and allows Kalina cycle generators to achieve high efficiencies through better thermal matching of heat sources and sinks.⁴ This effect led to a Kalina cycle efficiency of 25.7% versus an ORC efficiency of 21.5% under the same thermal conditions in a recent study.⁵ Heating and cooling of fluids can also be converted to mechanical energy and then electricity via the Stirling cycle. For example, a 2015 study⁶ described the use of a Stirling engine for exhaust gas heat recovery from an internal combustion engine.

Numerous alternative technologies for energy conversion have been proposed and are at different stages of maturity. Phase change material (PCM) engine generators use the volume changes caused by the melting and solidification of a PCM material such as paraffin wax to drive a hydraulic system. That hydraulic power is used to drive a generator and produce electric power. A study of these systems found they had the potential for higher net present value than ORC systems at very low temperatures (60°C–75°C) over a 20-year life.⁷ Magnetocaloric generators, which harvest energy from temperature-induced changes in a material's magnetic characteristics over time, have high exergy efficiencies and would be useful in industrial waste heat recovery.⁸ However, few magnetocaloric materials with a sufficiently large magnetocaloric effect have been discovered; they are generally expensive and can be difficult to manufacture; they are susceptible to cycling stability problems; and many materials lack the high Curie temperatures (temperature at which a material's permanent magnetism changes to induced magnetism) necessary for most waste heat applications.⁹ Magnetocalorics represent an active research area, and progress is being made to develop magnetocaloric systems for practical applications.¹⁰

A similar effect with time-dependent, temperature-induced electrical polarization changes leading to voltage differences across a material is called the pyroelectric effect. Lee et al.¹¹ discussed the use of pyroelectric materials to generate electricity with the Olsen cycle. Thermal power can also be converted into vibratory mechanical power and then harvested on the macroscale by using a thermoacoustic heat engine¹² or on the microscale by using piezoelectric power generation.¹³ Results for a prototype thermoacoustic-piezoelectric generator indicate a system-generated 0.128 mW with an efficiency of 0.00028%.¹⁴

Heat can also be used to stimulate the emission of photons or electrons. Photons are emitted in thermophotovoltaic generation, as discussed by Arnaud et al.¹⁵ for automotive heat recovery. Thermophotovoltaic generation data from a number of sources was collected in a review by Ferrari et al.,¹⁶ where an experimental result with 66 watts of electrical power generation and 11% efficiency was the most efficient demonstration of this technology. Electron excitation drives thermionic generation, which Melosh and Shen¹⁷ discuss as a means of improving the efficiency of conventional solar photovoltaics. Alkali metal-based thermionic generators with demonstrated efficiency of 15% (and projected to be capable of 22.5% efficiency) in space applications were mentioned in a 2014 review by McCarthy et al.¹⁸ This review also discusses the advances that carbon nanostructures could bring to thermionic generation. These structures in materials such as carbon nanotubes can trap electrons and force them into higher energy states, causing more emission with less input energy. However, all these novel methods are unproven in industrial heat recovery and currently not economically viable.

Thermoelectric waste-energy recovery systems are among the most promising heat-to-electricity energy conversion technologies. They require small footprints when implemented, and the technology is relatively mature. Thermoelectric materials allow for direct electricity generation through the Seebeck effect, wherein a temperature gradient applied to a circuit at the junction of two different conductors produces an electromotive force based on the relation $E_{\text{emf}} = -S\nabla T$, where S is the Seebeck coefficient (or thermopower) and T is the temperature.¹⁹

The use of thermoelectric modules as solid-state heat pumps for heating and cooling applications using the opposite Peltier effect is currently far more common than their use as solid-state generators. Peltier modules, with their ability to heat and cool with great precision, have proven useful in optical equipment, automotive seats, and small consumer refrigerators. Thermoelectric coolers are typically used in aerospace and defense, telecommunications, medical, industrial, automotive, and consumer applications. Other than the fuel-burning generators that utilize thermoelectric technology to produce electricity manufactured by a few companies, Seebeck generation products are not widely used. There are some small products, such as woodstove fans, camp stoves with cell phone charging, and cook pot chargers based on Bi_2Te_3 generators, that are sold in large quantities annually through large retailers and specialty distributors. This report will focus on the unique energy-conversion challenges and opportunities associated with thermoelectric generation, specifically for waste heat recovery.

Thermoelectric Generation

The most common thermoelectric materials today are alloys of chalcogenides (materials with a chalcogen or IUPAC group 16 anion). Specifically, these materials are either based on bismuth telluride (Bi_2Te_3) or lead telluride (PbTe). Bi_2Te_3 can be alloyed with Bi_2Se_3 to form n-type $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ and with Sb_2Te_3 to form p-type $\text{Bi}_x\text{Sb}_{2-x}\text{Te}_3$. PbTe can be alloyed with PbSe to form p-type $\text{PbTe}_{1-x}\text{Se}_x$ and with SnTe to form n-type $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$. PbTe has been used successfully by the National Aeronautics and Space Administration (NASA) as radioisotope thermoelectric generators (RTGs), but has been rejected by all current power generation projects because of the lead content and poor mechanical properties during thermal cycling under variable temperature gradients.

New material classes could allow for waste heat recovery with better efficiency or use with higher-temperature heat sources. These classes include skutterudites, clathrates, half-Heuslers, and oxides, such as cobaltites and perovskites.²⁰ Other material classes such as silicides²¹ and tetrahedrites²² are primarily considered for their relatively low cost. These new classes have been the subject of a great deal of fundamental materials research but have had limited commercial use, owing to cost, reliability, efficiency, and processing issues (in addition to immature device technology) that prevent them from being selected over traditional materials.

A thermoelectric material's efficiency of converting heat to electricity is characterized by the dimensionless figure of merit $ZT = (\sigma S^2 T) / \kappa$, where σ is the electrical conductivity; S is the Seebeck coefficient (or thermopower), as before; T is the temperature; and κ is the thermal conductivity. This figure of merit reflects the fact that less resistance to electric current and increased resistance to thermal flux at higher temperature will lead to greater efficiency, as further illustrated by equation 1 below. However, it also reflects a major challenge for thermoelectric materials research: thermal transport and electrical transport are positively related in most materials according to the Wiedemann-Franz law,¹³ so materials with higher electrical conductivity also tend to have higher thermal conductivity.

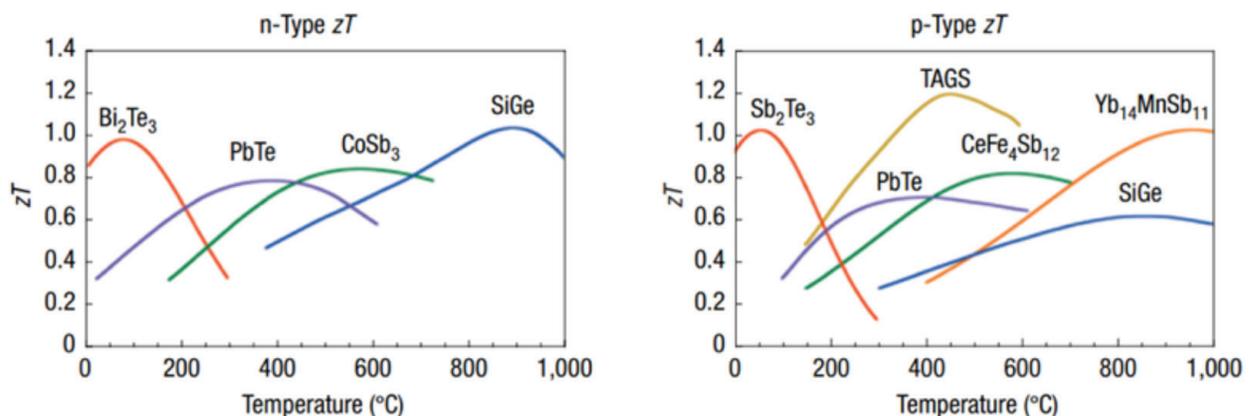
Another challenge in the engineering of thermoelectric devices is the dependence of ZT on temperature. ZT increases with temperature at lower temperatures but decreases with temperature above a certain temperature range, with an increase in thermal conductivity as shown in Figure 6.G.1. Thus, an accurate prediction of thermoelectric performance requires an integral of ZT over the temperature range to which a thermoelectric material is exposed. There is no theoretical limit to ZT , but the best materials in common use today have values around 1.¹⁹ The relationship between ZT and maximum theoretical efficiency for a thermoelectric element is expressed in the equation below, where T_h and T_c are the temperatures on the hot and cold sides of the element, respectively, and T is the average of T_h and T_c .¹⁹

$$\eta = \frac{T_h - T_c}{T_h} \frac{\sqrt{1 + ZT} - 1}{\sqrt{1 + ZT} + T_c/T_h}$$

This equation assumes no irreversible device losses, that ZT for the average temperature is representative of the entire temperature range, and that a higher temperature gradient increases power efficiency. Given hot and cold side temperatures of 250°C and 50°C, respectively, an increase of ZT from 1 to 3 would correspond with an efficiency increase from 11% to 19% for the simplest device architecture (i.e., not cascaded or segmented).

Figure 6.G.1 Relationship Between ZT and Temperature for p-type and n-type Materials²³

Credit: Snyder, G. J., & Toberer, E. S. Complex thermoelectric materials. *Nature Materials*, 7, 105-114 (2008).



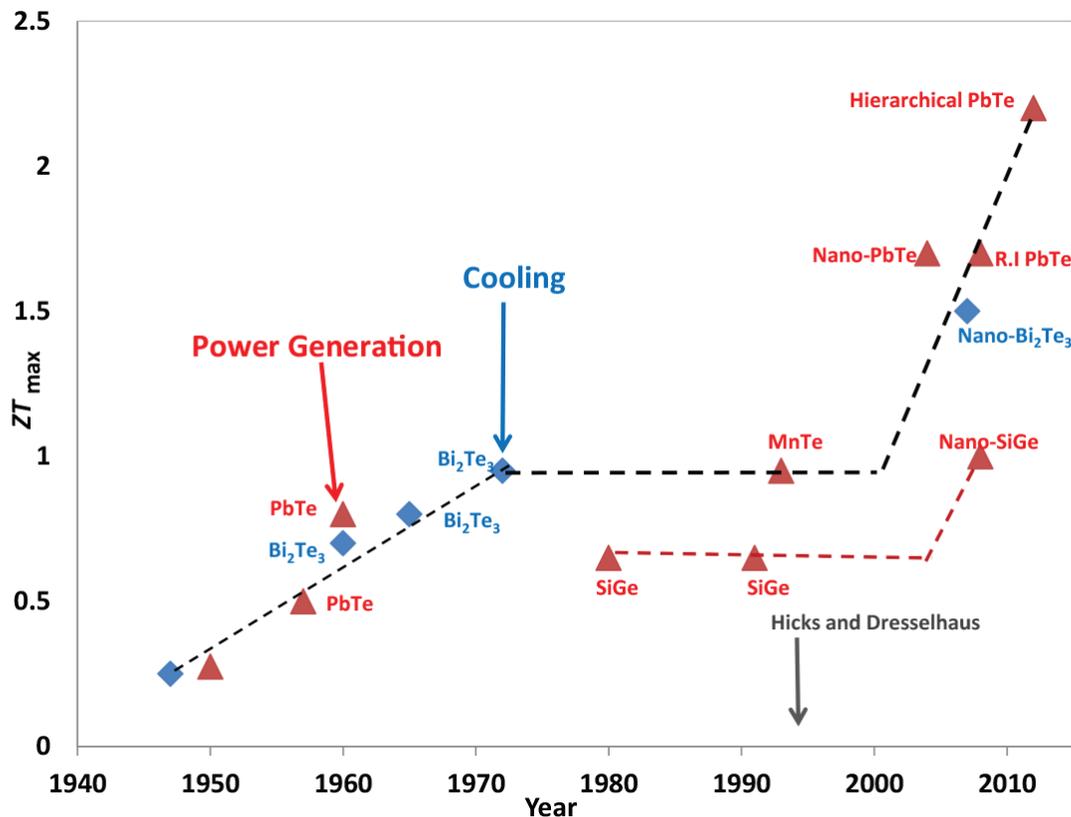
Thermoelectric Technology Assessment and Potential Performance Advances

High ZT Materials

Advances in high ZT (greater than 1) thermoelectric materials research have been made in the last 20 years.²⁴ Among the uniform or bulk materials (materials with no intentional micro- or nanostructuring, including most current commercial thermoelectrics), the highest performing materials display phonon-glass electron-crystal behavior, wherein phonons (an elementary excitation in a material consisting of a quantum of vibrational energy transporting thermal energy) move through the material as though it were a glass—with high resistivity, while electrons move through the material as in a crystal—with low resistivity. The resulting reduction in thermal conductivity while maintaining or increasing electrical conductivity causes an increase in ZT , as discussed earlier. Material features that can lead to this behavior include heavy elements and atoms or molecules in cage-like lattice structures that serve to scatter phonons.²⁰ However, the best compositions for traditional bulk thermoelectric materials had largely been discovered by 1980.²⁴ Further improvements in ZT values were made possible as a result of research published by Hicks and Dresselhaus,²⁵ who found in 1993 that material nanostructure could lead to low dimensional quantum wells and phonon-scattering at grain boundaries that lowered thermal conductivity. Figure 6.G.2 shows that reported ZT results in literature had reached a plateau at the time that Hicks and Dresselhaus published their 1993 paper and that these results began to climb afterward. In actual field applications, the highest ZT bulk material incorporated into thermoelectric devices and used in

Figure 6.G.2 Progress in Reported ZT Values Over Time²⁴

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an actual field application is around 1.3–1.5. No one has been able to produce devices made with $ZT > 2$ bulk materials as noted in Figure 6.G.2. The techniques used to create nanostructure in thermoelectric materials are prohibitively expensive at present; more research is required in order to bring down their cost to fully realize the gains in efficiency they allow.²¹

Potential for Improvement

High ZT Materials

High- ZT materials have been discovered in a number of materials systems in recent years, but high efficiency has only been proven in laboratory settings. Some less commercially established material classes that have shown promising results include skutterudites, clathrates, half-Heuslers, and oxides, such as cobaltites and perovskites.²⁰ Raw material costs vary among these material families, but for each material, lowering the cost of production could lead to more cost-effective high-efficiency thermoelectric waste heat recovery. Continued increases in ZT and other advancements are essential if thermoelectric waste heat recovery is to become common practice in the United States. Low thermal resistance in combination with high electrical resistance, ability to withstand high temperatures and thermal cycling, and ZT limitations are some of the major issues that remain to be addressed.

In addition, lead is toxic and highly regulated, and tellurium could see dramatic changes in demand, depending on the market for CdTe solar cells. Tellurium is a rare earth element with limited production capacity. Historically it has been subject to price volatility due to demand. New, high volume thermoelectric applications that use tellurium-based thermoelectric materials or CdTe solar cells could cause drastic swings in tellurium pricing.²⁶

Alternative material classes provide other benefits as well. Half-Heusler materials can tolerate high temperatures,²⁷ and tetrahedrites²² and magnesium silicides²¹ have cost advantages over traditional materials. Less expensive approaches to creating nanostructure in thermoelectric materials are also required if high ZT materials are to become common. The U.S. Department of Energy (DOE) Vehicle Technologies Office (VTO) is currently funding work to develop, test, and demonstrate advanced TEGs that provide a fuel economy increase of at least 5% by using bulk thermoelectric materials (e.g., skutterudite and half-Heusler). With improved manufacturing technologies such as wafer-based manufacturing and automation to eliminate labor-intensive pick and place methods that are currently in use, commercial viability is possible, especially for production volumes of 100,000 units/year.^{28,29,30} Leveraging technologies for cost reduction and economies of scale may allow for mainstream applications in the future.

Low-Cost Materials

Some thermoelectric materials such as silicides²¹ and tetrahedrites²² are considered promising primarily because of the relatively low cost of the starting raw materials. Average raw material cost of silicides is \$151/kg, compared to the high-end cost of half-Heusler materials at around \$2,000/kg.²¹ It is likely that material prices would fall with economies of scale from a large-scale commercialization. Estimated average and maximum efficiency of various n- and p-type materials based on the data in Figure 6.G.1 are shown in Table 6.G.1. Average ZT (i.e., ZT_{avg}), based on the integrated ZT over the desired temperature range, is lower than the maximum ZT efficiency. Efficiencies are estimated to be around 10%, which is significantly higher than those obtained at the system level in actual applications. In practice, two material types (p and n) are needed for thermoelectric generation, and for most TEG device structures, overall efficiency is significantly reduced owing to dissimilar properties. Oxide materials such as cobalt oxide are not being used today because there are few known n-type oxides with similar structures as p-type cobalt oxide. When an oxide TEG system is attempted, the best ZT values reported are around 0.3. More common use of these materials and improvement of their thermoelectric performance could lead to thermoelectric generation that would be cost-competitive.

Table 6.G.1 Average and Maximum ZT and Efficiency of Thermoelectric Materials²³

| Material | ΔT (°C) | T_{avg} (°C) | ZT_{max} | Efficiency w/ ZT_{max} | ZT_{avg} | Efficiency w/ ZT_{avg} | |
|----------|----------------------------------|----------------|------------|-----------------------------|------------|-----------------------------|-------|
| n-type | Bi_2Te_3 | 290 | 150 | 0.98 | 10.9% | 0.78 | 9.3% |
| | PbTe | 580 | 310 | 0.79 | 13.4% | 0.63 | 11.5% |
| | CoSb_3 | 550 | 450 | 0.85 | 11.1% | 0.66 | 9.3% |
| | SiGe | 610 | 680 | 1.04 | 10.8% | 0.80 | 9.0% |
| p-type | Sb_2Te_3 | 270 | 160 | 1.02 | 10.5% | 0.67 | 7.7% |
| | Te-Ag-Ge-Sb | 440 | 370 | 1.20 | 12.5% | 0.98 | 11.0% |
| | $\text{CeFe}_4\text{Sb}_{12}$ | 540 | 410 | 0.82 | 11.0% | 0.64 | 9.2% |
| | $\text{Yb}_{14}\text{MnSb}_{11}$ | 600 | 690 | 1.03 | 10.2% | 0.73 | 8.0% |
| | SiGe | 690 | 640 | 0.62 | 8.7% | 0.50 | 7.4% |
| | PbTe | 500 | 340 | 0.71 | 10.2% | 0.63 | 9.4% |

When a broader perspective of TEGs is examined, the share of material cost is significant, in the range of 50%–80% of the overall thermoelectric system generation cost.²¹ As shown in Table 6.G.2, the cost of thermoelectric generation is many times greater today than other competing technologies, such as coal, natural gas, geothermal, and photovoltaics. The system cost figures are based on several underlying assumptions, such as equivalent properties in p- and n-type materials, as discussed in LeBlanc et al.²¹ This equivalent properties assumption makes calculations much simpler but disregards a major difficulty of thermoelectric module design.

Due to high costs, the total thermoelectric generation market of \$45 million today has been mostly limited to military and aerospace applications.³¹ An early application of thermoelectric generation was pioneered by the NASA Jet Propulsion Laboratory, which used thermoelectrics with nuclear power sources for spacecraft power systems and thermal control for various space exploration missions. In August 2012, the NASA Mars Science Laboratory—Curiosity Rover,³² powered by a multi-mission radioisotope thermoelectric generator (MMRTG),³³ landed on Mars. One of the future target applications of thermoelectric power generation is to power wireless sensor networks, particularly in buildings, with a total market expected to reach \$25 million by 2016.³⁴

Table 6.G.2 A Cost Comparison of Competing Power Generation Technologies²¹

| Application Temperature | Power Generation Technology | System Cost (\$/W) |
|---|--|--------------------|
| Low Temperature ($T_h \approx 100^\circ\text{C}$) | Geothermal | \$4.14 |
| | Chalcogenide Thermoelectric (Bulk Bi_2Te_3) | \$95.68 |
| Medium Temperature ($T_h \approx 250^\circ\text{C}$) | Organic Rankine Cycle | \$4.00 |
| | Concentrating Solar Power with Thermal Storage | \$3.60 |
| | Photovoltaic Target | \$1.00 |
| | Skutterudite Thermoelectric (Bulk $\text{Yb}_{0.2}\text{In}_{0.2}\text{Co}_4\text{Sb}_{12}$) | \$19.02 |
| | Chalcogenide Thermoelectric (Nanobulk $\text{Bi}_{0.52}\text{Sb}_{1.48}\text{Te}_3$) | \$11.92 |
| High Temperature ($T_h \approx 500^\circ\text{C}$) | Nuclear | \$5.34 |
| | Coal | \$2.84 |
| | Natural Gas | \$0.98 |
| | Silicide Thermoelectric (Bulk $\text{Mg}_2\text{Si}_{0.6}\text{Sn}_{0.4}$) | \$5.56 |
| | Chalcogenide Thermoelectric (Bulk $\text{AgPb}_{18}\text{SbTe}_{20}$) | \$5.06 |
| | Half-Heusler Thermoelectric (Bulk $\text{Zr}_{0.25}\text{Hf}_{0.25}\text{Ti}_{0.5}\text{NiSn}_{0.994}\text{Sb}_{0.006}$) | \$4.48 |

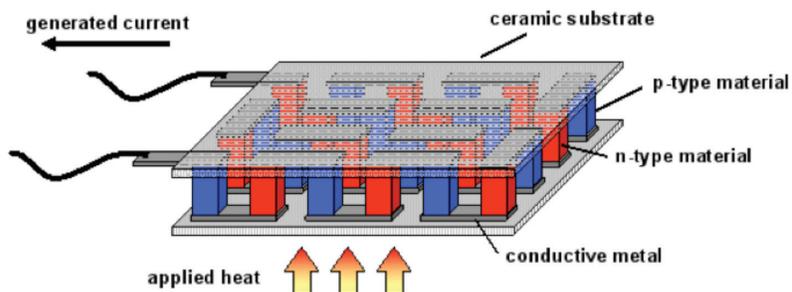
High Temperature Modules

Thermoelectric generation is usually accomplished by means of thermoelectric couples, as shown in Figure 6.G.3. Small legs of p-type (blue) and n-type (red) thermoelectric elements are connected in series and then sandwiched between insulating ceramic substrates. These couples are most often arranged into a planar package called a thermoelectric module. TEG systems are composed of these modules along with additional equipment that moves heat and electricity through the system. Because thermoelectric efficiency increases with the temperature difference, recent advances in high-temperature thermoelectric modules are showing promise. Half-Heusler alloys, which contain varying quantities of nickel, tin, zirconium, titanium, and hafnium,¹⁹ can sustain generation at temperatures higher than the 583°C melting point of bismuth telluride and seem particularly close to a market breakthrough. Evident Thermoelectrics has produced a module by using half-Heusler materials that they claim can operate continuously, exposed to a hot side temperature of 600°C and a cold side temperature of 100°C .³⁵ Under these conditions, the module is advertised to produce 15.3 W of electricity from a 16 cm^2 area. A new n-type Mg_2Sn -based material, $\text{Mg}_2\text{Sn}_{0.75}\text{Ge}_{0.25}$, has been reported with leg efficiency and output power of 10.5% and 6.6 W/cm^2 , respectively, at $T_h = 400^\circ\text{C}$ and $T_c = 50^\circ\text{C}$ under a temperature gradient of 150°C/mm .³⁶ Novus Energy Technologies is developing a competing high-temperature module, also using half-Heuslers, that they project could produce 55 W from the same area and could cost as little as $\$0.10/\text{W}$ with highly automated production at scale.³⁷

Thermoelectric generation systems must address a number of challenges beyond simply maximizing ZT in thermoelectric modules. Typical systems will involve a liquid cooling on the cold side and extracting heat from gaseous exhaust streams on the hot side. The heat exchangers on both sides will necessarily dissipate some of the thermal energy that would produce power in the modules. Thus, heat exchanger design is a particular challenge in thermoelectric generation, especially on the hot side, where techniques to increase heat flux in low-thermal conductivity gases can result in increased cost and pumping power requirements that reduce overall power output. Technologies to improve hot-side performance include heat pipes, microchannels, and jet impingement systems. Corrosion and/or fouling from chemicals in the exhaust stream are additional challenges of hot-side heat exchange. Additionally, materials throughout the generation system must survive varying chemical environments as well as thermal expansion and contraction with changes in temperature. Finally, electrical concerns included the requirement of high voltage power output, matching of module resistance with load resistance, and potential requirements for DC to AC conversion.¹³

Figure 6.G.3 Schematic Diagram of a Typical Thermoelectric Module³⁸

Credit: Sigma-Aldrich



Segmented Modules

In order to maximize the efficiency over a large temperature range, combinations of material may be used so that the integrated average ZT over the operating temperature range is maximized. There are two common ways of combining thermoelectric materials in devices to maximize device efficiency over large temperature ranges: segmenting and cascading. In a segmented module, the thermoelectric legs are composed of a series of materials as opposed to a uniform composition over their length.³⁹ Materials for each segment can be chosen based on which materials have the highest ZT for the temperature in that part of the leg. Figure 6.G.1, which shows the peak ZT occurring at different temperatures for each material, illustrates how this approach could be used to optimize a module. This optimization of ZT over the entire thermal gradient would result in a higher effective ZT for the thermoelectric module and thus higher electrical generation efficiency.

Making thermoelectric legs with different material segments would obviously make module manufacturing more expensive but could be applicable in applications such as remote generation, where efficiency and reliability would be at a premium. For example, NASA's MMRTG segments PbSnTe with nanostructures in Te-Sb/Ge/Ag (TAGS), and Teledyne's RTGs use the same couple for reliability.⁴⁰ Segmented thermoelectric modules are often discussed in literature, but they are not in common use for energy harvesting applications. This module type requires manufacturing techniques that are not currently cost-effective. More research and development (R&D) work could allow segmentation techniques to become cost-effective and lead to commercialization of this high-efficiency technology in a wider range of applications.

Cascading Modules

Cascaded generators are meant to better match thermoelectric materials to their optimum temperature gradients and thereby their highest effective efficiencies by stacking modules with different materials (rather than subdividing the module legs as in segmented modules). One particular advantage of cascaded TEGs not shared by segmented generators is that a separate electric circuit can be implemented at each stage of a cascaded thermoelectric device. Avoiding the inherently serialized circuit in a segmented device allows for higher efficiencies but also leads to greater system complexity.⁴¹ The overall conversion efficiency of cascade-type modules becomes roughly the sum of the efficiencies of the individual modules. Some cascaded thermoelectric modules are commercially available, but their potential can be expanded with more R&D. By using three-stage cascade-type modules consisting of high-end ZT values of $\text{Ca}_3\text{Co}_4\text{O}_9$ for p-type elements and SrTiO_3 for n-type elements, an overall thermoelectric generation efficiency of 20% has been estimated for a heat transfer rate of 400 kW/m^2 .⁴² Better thermoelectric assembly techniques could enable easier construction of cascaded TEGs.

Demonstrations

Demonstrations of high-power thermoelectric waste heat recovery are necessary to prove that such systems can take advantage of economies of scale. Demonstrated power has typically been less than 1 kW, with notable demonstrations of 169 W generation from a cement kiln,⁴³ 250 W generation from glass furnace exhaust,⁴⁴ and 240 W generation from a steel carburizing furnace afterburner.⁴⁵ A 1 kW generator was mounted successfully into the Bradley fighting vehicle by a Department of Defense contractor based on a module from Hi-Z Technology, Inc. Two recent thermoelectric energy harvesting efforts have demonstrated power generation in excess of 1 kW. The first of these involved a high power TEG installed over a continuous casting line. This system contained 896 Komatsu modules, 16 of which were used in the aforementioned carburizing furnace demonstration, and it produced power on the order of 9 kW when exposed to the radiant heat of a 915°C slab.⁴⁶ The other is the first plug-and-play TEG available for purchase, the 25 kW Alphabet Energy™ E1, which was announced in October 2014.⁴⁷

Assembly

Progress must also be made in the area of automated assembly so that thermoelectric devices can be made in a reliable and cost-effective manner. Traditionally, metal interconnects are attached to ceramic insulating plates by using one of several available processes, such as soldering, thin film sputtering, and plating.¹³ The thermoelectric legs are then soldered to these interconnects. More than 90% of the thermoelectric modules assembled today require some manual operations, such as attaching leads and visual inspections.⁴⁸ Some manufacturers have implemented automation systems for the assembly process, but in most cases, price points do not justify straying away from the standard pick and place machines used to assemble electronic components.⁴⁹ Thin film thermoelectric modules offer an alternative to the manufacturing methods of conventional bulk materials because the p- and n-type materials can be sputtered onto separate wafers (using techniques from silicon microelectronics fabrication) that are then fused together.

System Integration Needs

Module and System Level Design

Efficient and cost-effective thermoelectric energy generation systems depend on a number of module- and system-level design factors in addition to the selection of materials with good thermoelectric properties. At the module level, the choice of materials can be complicated by the fact that p- and n-type materials are both typically required. In addition, assembly of thermoelectric materials together with conductive leads



and dielectric plates to form modules at an industrial scale is challenging. The different materials and their interfaces must be robust enough to tolerate thermal expansion and contraction, and modules must be designed to properly conduct heat through thermoelectric materials, maximizing temperature gradients and thus power generation. Module assembly quality requirements are high: a single bad connection makes a module useless due to serial electrical connections between the thermoelectric legs. Automation techniques for module assembly are not widely adopted and most modules are still assembled by hand. At the system level, the challenge of maximizing the temperature difference over the thermoelectric modules to maximize efficiency means that heat exchangers on the hot and cold sides must be well designed to maximize heat flux to the modules. Hot-side heat exchangers are particularly challenging to design in the many cases where they must tolerate high-heat-flux fluids that can be corrosive or contaminated with particulate matter. Electrical design challenges include proper matching of resistance between thermoelectric modules and loads as well as efficiently inverting the DC power for use on the grid.

Thermal Management

More research is needed into heat transfer in TEGs. This includes cost optimization of heat exchangers that transfer source heat to the cold side, but it also would include heat transfer within the module. Additionally, in high-temperature applications, heat exchanger materials and protective coatings impact costs as do the material thermal properties. Costs for electrically insulating plates (usually ceramic) must be reduced while maintaining good thermal conductivity at elevated temperatures. Electrical interconnects and other interfaces must be engineered to minimize electrical and thermal losses and to provide oxidation protection in order to maximize device and system efficiency and reliability. Using more corrosion-resistant heat exchangers would allow thermoelectric heat recovery from a more diverse range of industrial exhaust streams. Studies to co-optimize the thermal and electrical properties of the whole TEG system while maintaining its mechanical integrity are also important.⁵⁰ Heat exchangers can present significant design challenges for applications with modest temperature gradients. Enabling high-heat flux in these regimes requires more complex and highly engineered systems whose cost can significantly impact overall system cost. One set of calculations²¹ estimated that heat exchangers account for roughly 20%–30% of system cost, while calculations described in the Appendix below arrive at an even greater cost contribution of \$4.00/W (based on power output of 625 W/m² and heat exchanger cost of \$2500/m², as shown in Table 6.G.5) for heat exchangers in a \$7.61/W system (about 53%). To reduce these costs will require further R&D, as well as other advances in the technology and manufacturing.

Technology Needs

An overarching technology need is to reduce the cost of power generated by thermoelectric waste heat recovery systems. This need can be met by using lower cost materials as well as by using automated methods of thermoelectric assembly. A commonly discussed cost target in the thermoelectric field is \$1/W for an installed system. This, along with a system life of five years, a discount rate of 7%, a capacity factor of 75%, and an annual cost (for maintenance and operating costs) of \$0.20/W would lead to a levelized cost of electricity (LCOE) of \$0.067/kWh. This is comparable to the 2013 average U.S. industrial electricity price of \$0.068/kWh.⁵¹

Manufacturing Challenges and Opportunities

Labor-intensive pick-and-place hand loading methodology is currently state of the art in TEG production. A recent DOE workshop on manufacturing opportunities for low-cost thermoelectric modules indicated that labor is responsible for a significant portion of the cost of thermoelectric modules.⁵² New manufacturing approaches, such as automation and wafer-based manufacturing, have the potential to reduce thermoelectric module costs. Concepts discussed at the workshop include additive manufacturing of thermoelectric modules



and wafers, among others. The Fraunhofer Institute for Manufacturing Technology and Advanced Materials has demonstrated additive manufacturing of thermoelectrics with embedded sensors.⁵³ More demonstrations with medium- and high-temperature thermoelectric materials are needed to prove that this approach is viable.

Value-Added Applications

Current technology can be cost effective when the thermoelectric system adds value beyond electricity production, as is the case in generation for wireless sensor networks. TEGs combined with wireless sensor network nodes can add value by allowing sensing and automation without the need for wire runs or batteries that require checking and replacement. Additionally, remote industrial facilities with abundant waste heat and expensive electricity—in the oil and gas industry, for example—might benefit from current thermoelectric technology. Examples of these value additions outside of the manufacturing sector include the use of thermoelectrics to drive fans that increase the efficiency of woodstoves⁵⁴ and to power wirelessly controlled radiator valves that do not need batteries. Several companies have demonstrated woodstoves with TEG-powered fans to show the potential of TEGs for self-powered appliances, including BioLite, Hi-Z Technology, Research Triangle Institute, Greenway Grameen, and others.⁵⁵ High-efficiency, low-emission biomass stoves have the potential to significantly reduce the 4 million deaths per year caused by pollution from indoor cooking with biomass in developing countries, as estimated by the World Health Organization; thermoelectric-driven fans offer an important pathway to help achieve this.⁵⁶ The overall effort is being led by the U.S. Department of State and the Global Alliance for Clean Cooking.⁵⁷

Potential Impacts

Thermoelectric Waste Heat Recovery

The lack of moving parts in TEGs holds the promise of reduced operation and maintenance costs and longer intervals between failures. These potential benefits make TEGs important to consider for industrial waste heat recovery applications because they have good reliability. Large-scale TEGs (greater than 1 kW) that generate general-purpose power (i.e., power not meant for a particular dedicated application) from industrial waste heat are not in general use at the time of this report. The largest commercially available TEG systems are remote generators manufactured by Global Thermoelectric, Inc., a Calgary-based company recently acquired by Gentherm, Inc., which has installed over 20,000 TEGs worldwide. These systems are generally fuel burning with a maximum power around 500 W, and they provide electricity along gas pipelines and on offshore oil platforms, among other similar locations.⁵⁸ However, there are a few larger waste heat systems that have been installed and discussed in literature. An extensive study of a TEG in a working glass plant⁴⁴ discussed the difficulty of delivering heat from the exhaust stream to the generator via a heat pipe. The power generation in this study was not cost effective, and the researchers faced great difficulties with degradation of heat flux through the heat pipe, owing to corrosion in the exhaust flue.

The iron and steel industry is a common target for waste heat recovery technology based on its high quality waste heat. As such, the iron and steel industry has been the subject of the most extensive discussion of industrial thermoelectric waste heat applications in literature. One notable study involved a TEG with 16 bismuth telluride modules placed above an afterburner flame in the exhaust system of a carburizing furnace at the Komatsu, Ltd., Awazu steel plant in Japan.⁵⁹ The afterburner flame was estimated to produce up to 20 kW of heat and to induce temperatures between 120°C and 250°C on the heat collection place of the water-cooled TEG. The modules used were developed by a Komatsu subsidiary, had a potential power density of 1 W/cm², and had the highest conversion efficiency of any commercial thermoelectric module when they were announced in 2009.⁶⁰ The modules were very expensive, however, with a price of roughly \$30/W when they were released. A later study at this plant demonstrated power outputs on the order of 240 W for single generators and discussed the installation of power hardware to effectively manage the output of multiple generators.⁶¹

Besides the steel industry, any industry where high-quality waste heat goes unused should be considered as a possible target for thermoelectric waste heat recovery. These potential targets include glass, aluminum, cement, and ethylene manufacturing, all discussed in a 2006 report by Hendricks and Choate.¹³ This report also considered industrial and commercial boilers for their large aggregate waste heat, but these were found to lack high enough temperatures to make thermoelectric energy harvesting with current technology feasible. The most promising source the report found in terms of potential annual electricity generation was aluminum melting, which the authors determined could produce 1.4 TBtu/year by using thermoelectric materials with a ZT of 1.

National Recovery Potential

To obtain an estimate of the amounts of waste heat in each industrial sector, the DOE Advanced Manufacturing Office (AMO) “Manufacturing Energy and Carbon Footprints” data⁶² were used. An initial estimate of the potential of thermoelectric energy harvesting from the waste heat of manufacturing plants can be obtained by estimating the fraction of the heat that can be recovered by generation systems and then assuming an efficiency value for those systems. The choice for the low end of the recoverable heat range was 10%, based on an estimate from Polcyn and Khaleel,⁴⁴ and the high end of 25% was based on heat recovery calculations for boiler exhaust from a study by Hill.⁶³ The results for such an estimate can be seen in Table 6.G.3, with the recoverable heat as a range from 10% to 25% of the sector’s process heating losses and the thermoelectric generation efficiency assumed to be 2.5%. This efficiency figure was chosen because module efficiencies of around 5% are seen in the sales literature of market modules for temperature differences around 200°C–250°C,⁶⁴ and generally only half of the temperature gradient across the TEG system is available for power conversion across the TEG material (while the other half is dissipated across the heat exchangers).⁶⁵ Additionally, this 2.5% figure matches the efficiency implied in early press related to the first large-scale, off-the-shelf, exhaust-based thermoelectric generation system⁶⁶ discussed.

Table 6.G.3 Estimate of Waste Heat That Could Be Recovered with Thermoelectric Generation Technologies for Major Process Industries

| Manufacturing process industry | Process heating energy use (TBtu/yr) ¹⁰⁰ | Process heating energy losses (TBtu/yr) ¹⁰¹ | Estimated recoverable heat range (TBtu/yr) ¹⁰² | Estimated thermoelectric potential (TBtu/yr) ¹⁰³ | Estimated thermoelectric potential (GWh/yr) ¹⁰⁴ |
|--------------------------------|---|--|---|---|--|
| Petroleum refining | 2250 | 397 | 40–99 | 1–2 | 291–727 |
| Chemicals | 1460 | 328 | 33–82 | 1–2 | 240–601 |
| Forest products | 980 | 701 | 70–175 | 2–4 | 513–1280 |
| Iron and steel | 729 | 334 | 33–84 | 1–2 | 245–612 |
| Food and beverage | 518 | 293 | 29–73 | 1–2 | 215–537 |
| Glass | 161 | 88 | 9–22 | 0–1 | 64–161 |
| Other manufacturing | 1110 | 426 | 43–107 | 1–3 | 312–780 |
| All manufacturing | 7200 | 2570 | 257–642 | 6–16 | 1880–4700 |

*Based on the 2010 “Manufacturing Energy and Carbon Footprints.”⁶²

** Low estimate based on 10% recovery of process heating energy losses;⁴⁴ high estimate based on 25% recovery.⁶³

*** Estimated thermoelectric potential is based on a thermoelectric generation efficiency of 2.5%. Conversion factor: 1 TBtu = 293 GWh.



Based on this estimate, the thermoelectric recovery potential for U.S. manufacturing is about 1,880 GWh–4,701 GWh (6 TBtu–16 TBtu). This is a conservative estimate based on the thermoelectric generation efficiencies of existing systems on the market, and does not take into account future technology development. The energy savings opportunity could be considerably enhanced with advanced materials, better coupling through improved heat exchangers and other technology improvements.⁶⁷

Steel Industry Potential and Cost

Results for a modified version of a cost model from LeBlanc et al.²¹ for thermoelectric generation system costs and the resulting LCOE values have been used to evaluate the economics of thermoelectric generation in the steel industry, based on a detailed waste heat breakdown. These results are shown in Table 6.G.4 for both optimistic price calculations (using calculated module cost per watt figures for an ideal thermoelectric material) and pessimistic price calculations (using a module cost per watt based on the prices of modules currently on the market). Casting was assumed to have no exhaust losses (as all losses would be from cast products cooling to room temperature); therefore, estimates have been limited to non-exhaust sources in this case. The shaded sources—castings, basic oxygen furnaces, and blast furnaces/stoves—were deemed the most promising for thermoelectric waste heat recovery and are the non-exhaust waste heat sources with the lowest LCOE values. Non-exhaust waste heat sources are desirable because the corrosive chemicals in steel industry exhaust gases are a great obstacle to thermoelectric waste heat recovery.

Program Considerations to Support Thermoelectric R&D

Research and Development

Discussions with industry leaders indicate that creating and promoting uniform performance standards and metrics by which to measure thermoelectric materials and devices is important for the adoption of thermoelectric waste heat recover systems in manufacturing facilities. Materials standards, standard materials testing, and device testing procedures are critical to the commercialization of thermoelectrics as power generation devices. Better standards would increase manufacturer confidence in the technology, with a resulting higher potential for market growth. Development of objective standards and methods for evaluating material and device performance will improve end-user confidence and help to avoid poor decisions caused by reliance on unconfirmed claims, bad data, or poor measurements. Round-robin testing of thermoelectric materials to develop reliable and confirmed properties would be a positive step in this direction.⁶⁸ As private companies in this space have vested interests, the development of credible metrics, standards, test methods, and common data formats, among others, would benefit from engagement by the public sector, which does not have a vested interest in a particular product.

The establishment of shared use facilities for some of the more expensive nanostructuring technologies used for thermoelectric materials would potentially allow smaller companies with limited manufacturing design capabilities and financial investment resources to develop improved device processing steps, produce devices at lower costs, and enter the market. It could have an impact similar to the “fabless” foundry model in silicon microelectronics, encouraging innovation and decreasing up-front costs. Research facilities and capabilities for such nanostructured technologies may be out-of-reach for many small companies, and so may be a potentially important contribution by the public sector.

There have been numerous incremental improvements in thermoelectric materials over the past 20 years. Technologies and materials solutions to improve interface contact resistance are very important to reduce interfacial losses, thereby maximizing the performance. Breakthroughs in thermoelectric material development

Table 6.G.4 Estimated System Cost and Electricity Price Predictions Based on Cost Model Results for Various Waste Heat Sources Within the Steel Industry*

| Plant type | 2010 U.S. production (Mtons) | Heat source | Average temp (°C) | TEG efficiency (T _c = 35°C)* | TEG output (kBtu/ton) | TEG output technical potential (GWh) | Based on Pessimistic Module Costs ⁷⁸ | | Based on Optimistic Module Costs ⁷⁹ | |
|--------------|------------------------------|-------------|-------------------|---|-----------------------|--------------------------------------|---|-----------------------|--|-----------------------|
| | | | | | | | Initial system cost (\$/W) | 15-5 yr LCOE (\$/kWh) | Initial system cost (\$/W) | 15-5 yr LCOE (\$/kWh) |
| Integrated | 34.3 | Exhaust | 527 | 3% | 4-7 | 37-73 | \$12 | \$0.24-0.44 | \$5 | \$0.11-0.20 |
| | | Non-exhaust | 586 | 2% | 0.4-0.8 | 4-8 | \$28 | \$0.57-1.05 | \$14 | \$0.28-0.52 |
| | | Exhaust | 192 | 1% | 2-4 | 22-43 | \$78 | \$1.59-2.92 | \$40 | \$0.88-1.62 |
| | | Non-exhaust | 1472 | 3% | 6-12 | 61-122 | \$8 | \$0.17-0.31 | \$4 | \$0.08-0.14 |
| Mini-mill | 54.4 | Exhaust | 1341 | 3% | 2-4 | 19-37 | \$7 | \$0.14-0.26 | \$3 | \$0.06-0.11 |
| | | Non-exhaust | 1520 | 4% | 0.6-1.2 | 6-12 | \$8 | \$0.16-0.30 | \$4 | \$0.07-0.14 |
| | | Exhaust | 1110 | 4% | 7-13 | 107-214 | \$7 | \$0.14-0.26 | \$3 | \$0.06-0.11 |
| | | Non-exhaust | 1110 | 3% | 0.5-1.0 | 8-15 | \$11 | \$0.22-0.40 | \$5 | \$0.10-0.18 |
| Cross-sector | 88.7 | Exhaust | - | - | - | - | - | - | - | - |
| | | Non-exhaust | 1600 | 4% | 2-4 | 46-91 | \$8 | \$0.16-0.29 | \$4 | \$0.07-0.13 |
| | | Exhaust | 900 | 4% | 3-6 | 28-56 | \$7 | \$0.15-0.27 | \$3 | \$0.07-0.12 |
| | | Non-exhaust | 900 | 3% | 3-5 | 27-54 | \$14 | \$0.28-0.52 | \$6 | \$0.13-0.24 |
| | | Exhaust | 500 | 3% | 2-3 | 17-34 | \$13 | \$0.26-0.48 | \$6 | \$0.12-0.22 |
| | | Non-exhaust | 500 | 1% | 0.5-1.0 | 5-11 | \$37 | \$0.74-1.37 | \$19 | \$0.38-0.70 |
| | Exhaust total | | | 2.7% | 12-23 | 229-281 | \$15 | \$0.30-0.56 | \$7 | \$0.15-0.28 |
| | Non-exhaust total | | | 2.8% | 8-16 | 157-221 | \$11 | \$0.22-0.40 | \$5 | \$0.10-0.19 |
| | Total | | | 2.7% | 20-39 | 386-772 | \$13 | \$0.27-0.49 | \$6 | \$0.13-0.24 |

*Shaded values indicate the heat sources deemed the most promising for thermoelectric generation.



could lead to substantial improvements in ZT values. System-level development requiring a high level of investment is necessary alongside the material development activities.

Public/Private Research Efforts

There has been a great deal of collaboration on thermoelectric research between public institutions and private companies. An early DOE collaboration with the truck manufacturer PACCAR successfully developed a TEG demonstrator unit using bismuth telluride cells integrated with the muffler of a long-haul truck.⁶⁹ This provided the impetus for continued work to develop advanced TEGs to harvest the energy in the hot engine exhaust (300°C to 600°C) to improve the overall fuel economy and reduce emissions from passenger and commercial vehicles. Subsequent projects successfully completed design, fabrication, and installation of prototype TEGs into production vehicle platforms to demonstrate feasibility.⁷⁰

DOE/VTO also leverages thermoelectric materials expertise in academia through partnership with the National Science Foundation (NSF). DOE and NSF provided grants to selected university teams to develop cost-competitive automotive thermoelectric materials and manufacturing techniques.²⁹ Advances achieved in these projects will help to foster thermoelectric developments for other uses, including industrial applications.^{71,72,73} Many of the public investments have centered on the improvement of thermoelectric efficiency, with only a few projects related to cost reduction in thermoelectric modules and generators. This has left a gap in the development of low-cost generators and more efficient methods of using conventional and proven materials.

Internationally, Japanese applications research has been extensive, involving organizations such as the New Energy and Industrial Technology Development Organization and the National Institute of Advanced Industrial Science and Technology and including trials in working steel plants.^{46,74} European programs Nanoparticle Embedded in Alloy Thermoelectrics (NEAT) and Next Generation Nano-Engineered Thermoelectric Converters (NEXTEC) mention industrial applications as goals. NEAT aims to develop a nano-composite material that can be produced in bulk and achieve a ZT greater than 3. NEXTEC is a demonstration project involving nano-engineered materials.⁷⁵

Applications

While thermoelectric systems could contribute to efficiency gains at manufacturing facilities, demonstration at the levels of prototype and full-scale production is needed, particularly to understand and address the 10%–20% drop in ZT that often occurs for large production volumes due to process defects. There are only a few large-volume thermoelectric material producers in the world today. Collaboration with manufacturers to perform cost-effective, system-level TEG demonstrations in near-term potential applications such as those performed in Japanese steel plants^{46,74} would also be useful for establishing the feasibility of TEG waste heat recovery for commercial applications. Finally, encouragement of more and better wireless sensor network energy data collection without large infrastructure investments would allow manufacturers to develop more efficient processes by identifying which of their systems produce the most sensible and latent heat for waste heat recovery. Encouraging the use of self-power TEG sensor nodes would have the added benefit of increasing the exposure of TEG technology.

Risk, Uncertainty, and Other Considerations Related to the Thermoelectric Technology

Risks involved in encouraging R&D in thermoelectric waste heat recovery include the following three categories: those related to the effectiveness (efficiency, power, and durability) of TEGs; those related to competing technologies; and those related to the amount of waste heat available. The practical potential for waste heat recovery using thermoelectric generation could be limited if TEGs never reach a low enough price point for wide adoption. TEGs might also be found to degrade when exposed to variable temperature environments over multiyear life spans.

Other countries could also have advantages in thermoelectric production due to their extant research base (Japan) or manufacturing infrastructure (China, Vietnam). Other technologies for waste heat recovery (such as low temperature Rankine cycle variants, load preheating, or exotic solutions, such as phase change material [PCM] generators) could see breakthroughs that would cause them to outcompete TEGs. Preheating and Rankine cycle variations are more commercially established than TEGs as industrial waste heat recovery solutions, but thermoelectrics have advantages of low maintenance requirements as well as the option to be installed with minimal downtime and minimal effects to existing systems. Finally, if higher efficiency industrial processes are adopted or value chains change to lower waste heat options (integrated steel mills to mini-mills, for example) then the amount for waste heat available for thermoelectric recovery would decrease, potentially leading to a smaller return on thermoelectric R&D investment.

Case Studies

Nucor Mini-Mill in Jewett, Texas

The possibilities for installing a similar system to the one at the JFE Steel Corporation plant in Japan⁴⁶ at the Nucor mini mill in Jewett, Texas, were explored. At 13–30 cm wide, the five continuous casting lines at the Nucor plant are not as wide as the 1.3–1.7 m slabs at the JFE plant, but assuming that the slab temperatures are the same, a similar amount of heat flux (on the order of $17 \text{ kW}_{\text{thermal}}/\text{m}^2$) could be intercepted by placing 50-cm-wide generators roughly 20 cm from the cast slabs. Assuming that the same level of thermoelectric generation per unit area that Kuroki et al.⁴⁶ discussed ($1.13 \text{ kW}_{\text{electric}}/\text{m}^2$) could be achieved over 14 meters for each strand, $39 \text{ kW}_{\text{electric}}$ of thermoelectric power could be produced by 35 m^2 of generators (based on a $14 \text{ m} \times 0.5 \text{ m}$ generator above each of five strands) at the Nucor plant. Under these conditions, using a nano-bulk $\text{Bi}_{0.52}\text{Sb}_{1.48}\text{Te}_3$ TEG of a higher ZT value of 1 with a 15-year life span and a capacity factor of 60%, a modified version of LeBlanc's cost model²¹ predicts an LCOE of $\$0.31/\text{kWh}$. A complete cost estimate breakdown of this along with a cost comparison using a bulk module $\text{Mg}_2\text{Si}_{0.6}\text{Sn}_{0.4}$ of a lower ZT value of 0.3 are discussed in the Appendix below.

Alphabet Energy

In October 2014, Alphabet Energy, Inc. announced a TEG product called the E1 that fits in a standard shipping container, connects to the exhaust pipe of a generator, and has a modular design so that thermoelectric components can be swapped out as materials improve. The thermoelectric materials used in the E1 are p-type tetrahedrites and n-type magnesium silicide (Mg_2Si), which will provide an average ZT of around 1, similar to that obtained by skutterudite (GM, Gentherm) and half-Heusler (Evident Thermoelectrics) materials used by the DOE Waste Heat 2 (WH2) projects.⁷⁶ Alphabet Energy states that the E1 can produce 25 kW from the exhaust of a 1,000 kW generator,⁶⁶ implying an efficiency of about 2.5% based on the exhaust heat of such a generator.⁷⁷ If running constantly, the generator would produce roughly 219,000 kWh and save 50,000 liters of diesel fuel per year.

APPENDIX: Nucor Mini-Mill, Jewett, Texas: Thermoelectric Generation Potential Economics

A cost model based on LeBlanc et al.²¹ was used to determine potential costs for a thermoelectric generation system in a plant similar to the Nucor mini mill discussed above. Detailed calculations were possible for this case, as the heat flux and temperature difference across the modules were known.⁴⁶ Radiation heat transfer calculations led to heat flux agreement when the exterior temperature of the hot side heat exchanger was 330°C. The temperature of the cooling water was 35°C. For this case, the heat exchanger U-values in the 100–120 W/m²-K range used in LeBlanc et al. and previously in this report would not achieve a module ΔT of 200°C given a system ΔT of 295°C. Thus the U-values for the heat exchangers were increased to 500 W/m²-K to reflect the lower thermal resistance between the heat exchanger boundaries and the thermoelectric material. Given these inputs and set of material properties, various combinations of fill factor and leg length input parameters could be examined until an appropriate heat flux is achieved.

The inputs and outputs for the simulated Nucor continuous casting line facility are shown in Table 6.G.5 for two TE material cases: bulk Mg₂Si_{0.6}Sn_{0.4} and nano-bulk Bi_{0.52}Sb_{1.48}Te₃. As shown in the table, the electricity generation rate for bulk Mg₂Si_{0.6}Sn_{0.4} material was low (625 W/m²) because of its relatively low ZT value of 0.3. However, Mg₂Si_{0.6}Sn_{0.4} still produces one of the lowest theoretical costs per watt because the material is so inexpensive. The 15-year levelized cost of electricity (LCOE) for this material case study was \$0.29/kWh, assuming \$2/W of additional expenses and a known capacity factor of 60%. In comparison, nano-bulk Bi_{0.52}Sb_{1.48}Te₃ has a higher ZT (1 versus 0.3) at the relevant temperatures, and could yield a higher electrical

Table 6.G.5 List of Major Input and Output Parameter Values for Application of Cost Model for the Nucor TEG System with Bulk Mg₂Si_{0.6}Sn_{0.4} Modules*

| Inputs | | |
|---|---|--|
| | Bulk Mg ₂ Si _{0.6} Sn _{0.4} Module | Nano-Bulk Bi _{0.52} Sb _{1.48} Te ₃ Module |
| Thermoelectric module leg length (L) | 11.5 mm | 5.0 mm |
| Thermoelectric module fill factor (F) | 20% | 25% |
| Ratio of load resistance to TE module resistance (m) | 1.0 | 1.0 |
| Hot-side temperature (T _h) | 330°C | 330°C |
| Cold-side temperature (T _c) | 35°C | 35°C |
| Seebeck coefficient (S) | -1.4 × 10 ⁻⁴ V/K | -2.3 × 10 ⁻⁴ V/K |
| Electrical conductivity (σ) | 1.54 × 10 ⁴ S/m | 3.91 × 10 ⁴ S/m |
| Thermal conductivity (κ) | 3.08 W/m ² -K | 0.81 W/m ² -K |
| Density of TE material (ρ) | 4.17 × 10 ³ kg/m ³ | 6.90 × 10 ³ kg/m ³ |
| Cost of bulk TE material (C _B) | \$128/kg | \$829/kg |
| Cost of processing bulk TE material (C _{M,B}) | \$0/kg | \$2/kg |
| Cost of processing TE material by area (C _{M,A}) | \$168/kg | \$168/kg |
| Cost of ceramic plate (C _{HX,ceramic}) | \$2/[W/K] | \$2/[W/K] |
| Cost of external heat exchanger (C _{HX,external}) | \$5/[W/K] | \$5/[W/K] |
| Heat transfer coefficient of heat exchanger, hot side (U _{hot}) | 500 W/m ² -K | 500 W/m ² -K |
| Heat transfer coefficient of heat exchanger, cold side (U _{cold}) | 500 W/m ² -K | 500 W/m ² -K |

Table 6.G.5 List of Major Input and Output Parameter Values for Application of Cost Model²⁰ for the Nucor TEG System with Bulk Mg₂Si_{0.6}Sn_{0.4} Modules* continued

| Outputs | | |
|--|---|--|
| | Bulk Mg ₂ Si _{0.6} Sn _{0.4} Module | Nano-Bulk Bi _{0.52} Sb _{1.48} Te ₃ Module |
| Junction temperature difference (ΔT) | 225°C | 226°C |
| Power | 625 W/m ² | 1,300 W/m ² |
| Heat flux | 17.6 kW/m ² | 17.8 kW/m ² |
| TE material cost | \$1,255/m ² | \$7,210/m ² |
| Ceramic plate cost | \$1,000/m ² | \$1,000/m ² |
| External heat exchanger cost | \$2,500/m ² | \$2,500/m ² |
| Efficiency (η) | 3.6% | 7.3% |
| Cost per watt (G) | \$7.61/W | \$8.27/W |

* Cost model adapted from LeBlanc et al.²¹ Further assumptions are provided in this Appendix.

generation rate and heat flux; however, the material cost is much higher. The 15-year LCOE for this higher cost ZT material (again assuming \$2/W of additional expenses and a capacity factor of 60%) is \$0.31/kWh. This price is still not competitive with the current grid-based electricity price of \$0.08/kWh at the Nucor plant. The detailed economic analysis has thereby further confirmed that significant breakthroughs are needed before electricity produced with thermoelectric generation systems can be competitive with electricity purchased from the grid for this situation.

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⁷⁸ Optimistic initial system costs are based on a cost-per-watt calculation given by ²¹

$$G = \frac{4}{S_{pn}^2 \sigma (T_1 - T_2)^2} \left(\frac{(m+1)^2}{m} \right) \left(C''L^2 + C''L + \frac{C_{HX}UL}{F} \right)$$

where G is the cost per watt for the system, S_{pn} is the couple thermopower (the difference in the Seebeck coefficients of the p- and n-type materials, in volts per degree Celsius), T_1 and T_2 are temperatures on either side of the thermoelectric legs in degrees Celsius (determined by the hot and cold side temperatures and heat transfer calculations for the heat exchangers and thermoelectric module), m is the ratio of the load resistance to the thermoelectric resistance, σ is the electrical resistivity of the thermoelectric material in Siemens per meter, $C'' = (C_B + C_{M,B})\rho$ is the volumetric cost of the thermoelectric legs in $\$/m^3$, C_{HX} is the total heat exchanger cost (including the module's electrically insulating ceramic plates) in $\$/(W/K)$, U is the average heat transfer coefficient of all heat exchangers in the system in W/m^2-K , and $C' = C_{M,A}$ is the areal cost of the thermoelectric legs in $\$/m^2$. Values for these variables are shown in Table 6.G.5 of the Appendix.

⁷⁹ Pessimistic initial system cost results use module cost-per-watt figures extrapolated from publicly available module price data rather than the calculations described in endnote 78.

Acronyms

| | |
|---------------|---|
| AMO | Advanced Manufacturing Office (of the Department of Energy) |
| IUPAC | International Union of Pure and Applied Chemistry |
| LCOE | Levelized cost of electricity |
| MMRTG | Multi-mission radioisotope thermoelectric generator |
| NASA | National Aeronautics and Space Administration |
| NEAT | Nanoparticle Embedded in Alloy Thermoelectrics (R&D project) |
| NEXTEC | Next Generation Nano-Engineered Thermoelectric Converters (demonstration project) |
| ORC | Organic Rankine Cycle |
| PCM | Phase change material |
| RTG | Radioisotope thermoelectric generator |
| TE | Thermoelectric |
| TEG | Thermoelectric generation |
| VTO | Vehicle Technologies Office (of the Department of Energy) |

Glossary

| | |
|--|---|
| Cascaded thermoelectric generator | A generator composed of modules stacked in the direction of heat flow. Different materials and doping are used to tune each module's peak thermoelectric performance to its average temperature. Cascaded generators allow opportunities to parallelize or serialize modules electrically to achieve a desired output voltage or current. |
| Chalcogenides | The group of materials most often seen in thermoelectric modules. They are named after the chalcogen or International Union of Pure and Applied Chemistry (IUPAC) group 16 anion they contain. Thermoelectric chalcogenides include bismuth telluride (Bi_2Te_3) and lead telluride (PbTe). |
| Figure of merit (ZT) | A dimensionless figure used to characterize thermoelectric materials. ZT is given by the expression $ZT = (\sigma S^2 T) / \kappa$, where σ is the electrical conductivity, S is the Seebeck coefficient, T is the temperature, and κ is the thermal conductivity. Higher ZT values indicate better performance. Typical thermoelectric materials in use today have values around 1. |
| N-type material | A thermoelectric material that has a negative Seebeck coefficient so that electric current travels in the opposite direction of heat flow. |
| Peltier effect | A temperature gradient induced by an applied voltage on a thermoelectric material. The Peltier effect is used in thermoelectric heating and refrigeration. |
| P-type material | A thermoelectric material that has a positive Seebeck coefficient so that electric current travels in the same direction as heat flow. |
| Radioisotope thermoelectric generator (RTG) | A thermoelectric generator that produces power from heat due to the decay of radioactive material. A prominent application of RTGs is to provide electric power to deep space probes. |
| Seebeck effect | A voltage difference induced by a temperature gradient in a thermoelectric material. The Seebeck effect is used in thermoelectric generation. |
| Seebeck coefficient | The negative ratio of electromotive force to temperature gradient in a thermoelectric material, $S = -E_{\text{emf}} / \nabla T$. Positive values of S mean that heat and current flow in the same direction, while negative values mean that the flows are opposite each other. The Seebeck coefficient is also called the thermopower. |
| Segmented thermoelectric module | A thermoelectric module in which the thermoelectric legs contain layers of different or differently doped materials. The material for each layer is chosen to optimize thermoelectric performance at that layer's average temperature. |
| Thermoelectric couple | A pair of thermoelectric material columns (legs) wired electrically in series with one p-type leg and one n-type leg. This configuration allows for higher voltage than a single column of equivalent size. Couples are the basic units of a typical thermoelectric module. |
| Thermoelectric generation | Direct conversion of heat to electrical power via the Seebeck effect. |



Thermoelectric generator system

A system composed of thermoelectric modules, power electronics, structural components and heat exchangers. The system conducts the heat provided by a source through thermoelectric modules to a heat sink and outputs the electric power produced by the modules.

Thermoelectric module

A device consisting of thermoelectric elements, electrical interconnections, and insulating structural materials such as ceramic plates. Modules are usually composed of multiple thermoelectric couples, and in turn, multiple modules are used to convert heat to power in a thermoelectric generator system.

Wiedemann-Franz law

An empirical law stating that the ratio of the thermal conductivity (κ) to the electrical conductivity (σ) of a metal is proportional to the temperature. The law is expressed as $\kappa/\sigma = LT$, where L is the proportionality constant (Lorenz number) and T is the temperature.