Kirk-Othmer Encyclopedia of Chemical Technology.
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THERMOELECTRIC ENERGY CONVERSION

Thermoelectric energy conversion is the science of the interchange of thermal and electrical energy in simple solid-state devices, generally heavily doped semiconductors (qv). Figure 1 shows two thermocouples connected in series. If thermal energy is applied at the top of the device from some heat source, and removed at the bottom by a heat sink, an electrical potential appears across the device as indicated by the polarity signs. The size of the ΔT and the basic material properties determine the voltage across the couple. Potential per couple is usually on the order of tenths of a volt. Practical working voltages are obtained by connecting a large number of these thermocouples in series. The amount of current is dependent on the cross-sectional area and length of the legs.

If an electric current were to be passed through the device from an outside source, heat would be absorbed at one junction and released at the other. The device then operates as a solid-state heat pump.

Thermoelectric devices can be used to generate electrical power, to refrigerate, or to transfer large amounts of heat without the use of freons or compressors or any rotating machinery. However, the overall efficiency of these devices is somewhat lower than other systems, and the initial cost is often higher. Mass production, improved design and manufacturing techniques, and an extremely long (decades or more) operating life for many of these solid-state devices should both decrease initial cost and serve to aid in the recovery of the costs over time.

Segmenting of legs (Fig. 2) to take advantage of the higher performance of certain materials in a given temperature range has been used to increase conversion efficiency. However, this technique is limited because all of the thermal and electrical currents must flow through each segment. Every material has its own optimum current-to-charge (I/q) ratio. Thus in a given segmented couple it is normally impossible to have each segment operating at its own optimum efficiency unless the couple is used at precisely the design hot-and-cold junction temperatures.

In thermoelectric cooling applications, extensive use has been made of cascaded systems to attain very low temperatures, but because the final stage is so small compared to the others, the thermal flux is limited (Fig. 3). The relative sizes of the stages are adjusted to obtain the maximum ΔT. Thus, for higher cooling capacity, the size of each stage is increased while the area ratios are maintained.

A number of good references have been published on thermoelectric energy conversion, the first in 1957 (1). A thorough survey of the field, together with information on materials properties, is also available (2), as are works on the various approaches to the analysis, design, and construction of thermoelectric devices (3–6). The most current materials research and device design work is presented annually in two conferences: the International Conference on Thermoelectrics, sponsored by the International Thermoelectric Society, and the Intersociety Energy Conversion Engineering Conference. Work on thermoelectricity takes only a few sessions of this latter conference, which is hosted on a rotating basis by seven cooperating technical societies: ACS, American Institute of Aeronautics and Astronautics (AIAA), AIChE, American Nuclear Society (ANS), ASME, Institute of Electrical and Electronics Engineers (IEEE), and SAE.

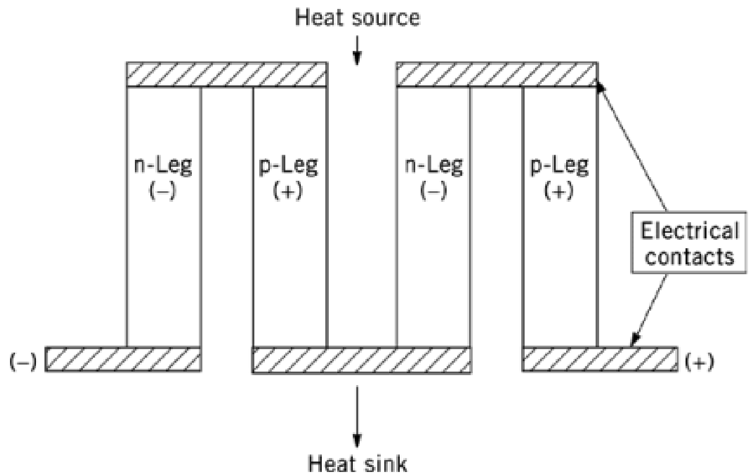

Fig. 1. Schematic of a simple thermoelectric device having two thermocouples in series.

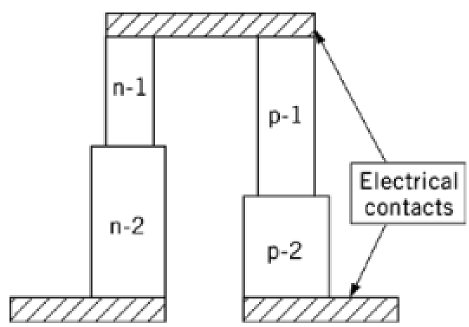

Fig. 2. Schematic of a segmented thermocouple. Each segment of each leg must be optimized in size for the design temperatures.

1. Historical Background

The basic ideas of thermoelectricity have been known for nearly two centuries, but until well after the Second World War the primary use was for temperature measurement (qv) using metallic wires. Then, upon improvements in semiconductor technology, thermoelectric power generation and refrigeration came under serious consideration.

In 1822 Seebeck began to study the magnetic polarization of metals and ores produced by a temperature difference. His goal was to prove that the earth's magnetic field arose from temperature differences between the equator and the poles. The extensive data collected laid the foundation for later development, even though Seebeck himself had steadfastly refused to believe that the magnetic fields observed in the experiments came from the electric current flowing as a result of the electrical potentials generated by the temperature differences in the circuits of dissimilar materials.

The second principal thermoelectric effect was discovered by Peltier in 1834, who reported the production or absorption of heat at the interface of two dissimilar conductors when an electric current was passed through them. The significance of this discovery was misinterpreted, however. Peltier thought that Joule heating (I^2R) only occurred with strong electrical currents. It was not until 1838 that Lentz finally gave the correct

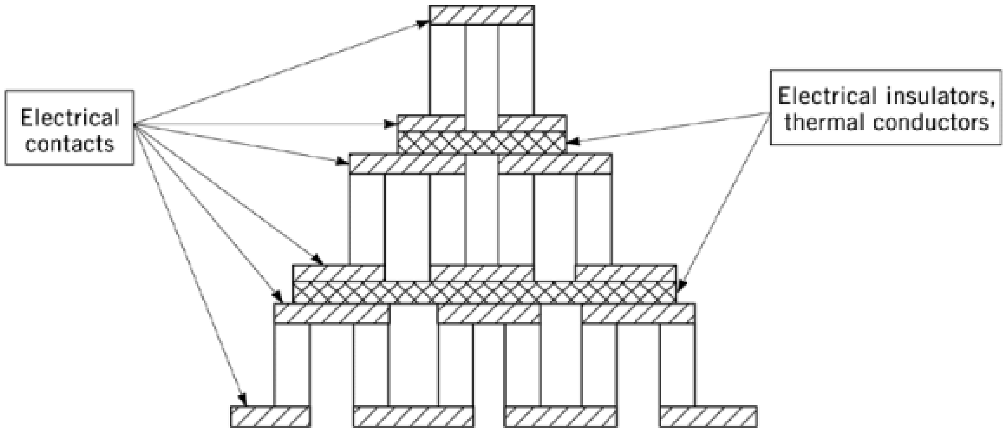

Fig. 3. Three-stage cascaded thermopile. The relative sizes of the stages must be adjusted to obtain the maximum ΔT.

interpretation of the Peltier effect. He provided a phenomenological demonstration by placing a drop of water at the junction of bismuth and antimony rods and caused it to freeze or melt, depending on which direction an electrical current was made to flow through the rods.

In 1857, Thomson (Lord Kelvin) placed the whole field on firmer footing by using the newly developing field of thermodynamics (qv) to clarify the relationship between the Seebeck and the Peltier effects. He also discovered what is subsequently known as the Thomson effect, a much weaker thermoelectric phenomenon that causes the generation or absorption of heat, other than Joule heat, along a current-carrying conductor in a temperature gradient.

In 1919, electrical power generators using these effects were attempted. Metallic components were used, which caused the efficiencies to fall well below one percent. These generators were not economically justifiable. However, the rapid growth of semiconductor theory brought a renewed interest in these devices. Practical power generators having from 6 to 11% efficiency were developed, which were especially useful for remote terrestrial and space applications. Indeed, radioisotope thermoelectric generators proved to be an enabling technology for deep-space exploration programs to the outer planets and beyond.

2. Thermoelectric Effects

The primary thermoelectric phenomena considered in practical devices are the reversible Seebeck, Peltier, and, to a lesser extent, Thomson effects, and the irreversible Fourier conduction and Joule heating. The Seebeck effect causes a voltage to appear between the ends of a conductor in a temperature gradient. The Seebeck coefficient, S, is given by

$$S = \frac{\delta V}{\delta T}$$

For metals, S generally varies between about 0 and 40 μV/K; low conductivity semiconductors and insulators have values of S up to 1000 μV/K and higher.

The Seebeck voltage is often referred to as being generated only at the junction of dissimilar conductors in an electrical circuit. Consideration of the Thomson effect, however, leads to the conclusion that the Seebeck voltage is generated along the entire thermoelectric element in a temperature gradient. The Thomson effect is the generation or absorption of heat, q_τ, other than I^2R heat, in a current-carrying conductor subjected to a thermal gradient:

$$q_\tau = \tau I$$

The Thomson coefficient, τ, is given by

$$\tau = -T\frac{\delta S}{\delta T}$$

Because the third law of thermodynamics requires $S = 0$ at absolute zero, the following equation is derived, which enables the determination of the absolute value of the Seebeck coefficient for a material without the added complication of a second conductor:

$$S = -\int_0^T \frac{\tau}{T}\,dT$$

Voltage measurement have been made at very low temperatures using a superconductor as one leg of a thermocouple. For a superconductor, S is zero, so the output of the couple is entirely from the active leg. The Thomson heat is then measured at higher temperatures to extend the absolute values of the Seebeck coefficients (7, 8). The Thomson heat is generally an order of magnitude less than the Peltier heat and is often neglected in device design calculations.

The other primary thermoelectric phenomenon is the Peltier effect, which is the generation or absorption of heat at the junction of two different conductors when a current flows in the circuit. Whether the heat is evolved or absorbed is determined by the direction of the current flow. The amount of heat involved is determined by the magnitude of the current, I, and the Peltier coefficients, π, of the materials:

$$q_p = \pi_{A,B} I$$

Kelvin showed the interdependence of these phenomena by thermodynamic analysis, assuming that the irreversible processes were independent of the reversible ones. This approach was later proved theoretically sound using Onsager's concepts of irreversible thermodynamics (9).

$$\pi_{A,B} = S_{A,B} T$$

$$\tau_A - \tau_B = S_{A,B} - \frac{2\pi_{AB}}{2T}$$

The irreversible phenomena represent entropy gain through irrecoverable heat losses as follows, where λ is the thermal conductivity and l is the length:

$$\textit{electrical (Joule heating)} \qquad q = I^2 R$$

$$\textit{heat flow (Fourier conduction)} \qquad q = \lambda\frac{A}{l}\Delta T$$

Taking all of the above into account, it can be shown that the efficiency, η, of a thermoelectric power generator, neglecting Thomson heat, is given by

$$\eta = \frac{P_{out}}{Q_{in}} = \frac{I^2 R_0}{K\Delta T + ST_H I - \frac{1}{2}I^2 R}$$

Optimizing for both leg geometry and load resistance and using average values for S, ρ, and λ, the following equation is derived:

$$\eta = \frac{\Delta T}{T_H}\left(\frac{(1 + ZT_{\mathrm{av}})^{1/2} - 1}{(1 + ZT_{\mathrm{av}})^{1/2} + \frac{T_c}{T_H}}\right)$$

where

$$Z = \frac{(|S_A| + |S_B|)^2}{\left((\lambda_A \rho_A)^{1/2} + (\lambda_B \rho_B)^{1/2}\right)^2}\ \mathrm{deg}^{-1}$$

The first term in the efficiency is simply the Carnot efficiency for a reversible heat engine and the second term is the reduction in efficiency owing to the irreversible effects. The important factors can easily be seen to be Z (the figure of merit) and ΔT. Increasing Z or T_{H} or decreasing T_{c} can increase the efficiency in general. However, because S, ρ, and λ are all temperature-dependent, changing T also changes the value of these properties, thus making the prediction of the overall effect less easy to estimate without detailed calculations using actual material properties.

For insulators, Z is very small because ρ is very high, ie, there is little electrical conduction; for metals, Z is very small because S is very low. Z peaks for semiconductors at $\sim 10^{19}$ cm^{-3} charge carrier concentration, which is about three orders of magnitude less than for free electrons in metals. Thus for electrical power production or heat pump operation the optimum materials are heavily doped semiconductors.

As indicated in Figure 4, the basic thermoelectric parameters are all functions of carrier concentration. Thus adjusting the dopant level to increase the output voltage generally also increases the electrical resistance. In addition, it affects the electronic component of the thermal conductivity. However, there are limitations on what can be accomplished by simply varying the carrier concentration in any given material.

The lattice contribution to the thermal conductivity can be varied by other means, such as differences in the atoms of the crystal. Alloy disorder, resonance (impurity) scattering, charge carrier scattering, and grain boundary scattering are all aimed at reducing the phonon mean free path. Unfortunately, modifying the crystal structure to reduce the thermal conductivity also causes changes in the carrier mobilities and effective masses, which also influences S and P.

Theoretical calculations can only point to promising types of materials. Because the interactions between the various parameters are too complex for direct calculation, it is necessary to rely on experimental data to confirm that proposed materials really perform as predicted.

Operating in the opposite mode, ie, causing an electric current to flow through the device from an outside source rather than impressing a thermal gradient on it, can result in a cooling or heating system. In thermoelectric cooling applications, the effectiveness of a device is measured in terms of the coefficient of performance, β, rather than efficiency. This is the ratio of the heat removed from the cold reservoir to the electrical power input.

$$\beta = \frac{q_c}{P_e} = \frac{ST_c I - \frac{1}{2}I^2 R - \lambda \Delta T}{SI\Delta T + I^2 R}$$

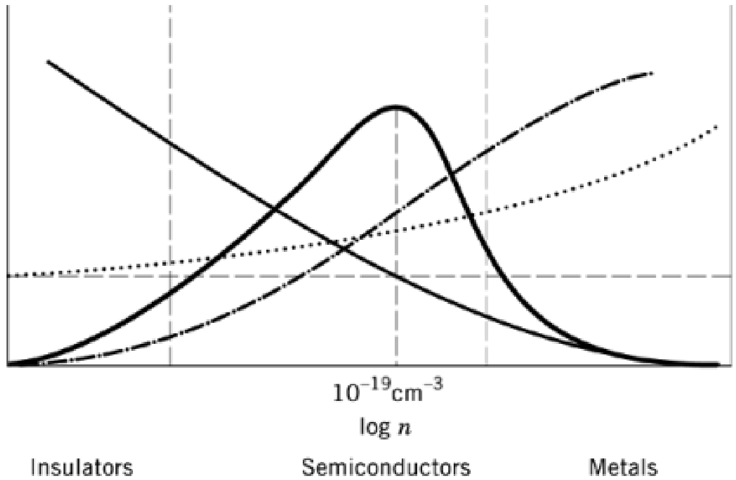

Fig. 4. Dependence of thermoelectric parameters on carrier concentration, where (—) is the Seebek coefficient (S); (▬▬▬), the figure of merit (Z); (_._.), reciprocal of electrical resistivity, $\sigma = 1/\rho$; (...), thermal conductivity (λ); and (_), (λ_1).

When optimized for geometry and current this becomes

$$\beta = \frac{T_c}{\Delta T} = \left(\frac{(1 + ZT_{\text{av}})^{1/2} - \frac{T_H}{T_c}}{(1 + ZT_{\text{av}})^{1/2} + 1} \right)$$

Under these conditions the maximum heat pumping rate, c_{cmax}; the maximum temperature difference across the module, ΔT_{max}; and the minimum temperature attainable on the cold side, T_{cmin}, are given by the following relations:

$$q_{c_{\max}} = \frac{S^2 T_c^2}{2R} - \lambda \Delta T$$

$$\Delta T_{\max} = \frac{S^2 T^2}{\left((\rho_n \lambda_n)^{1/2} + \left(\rho_p \lambda_p\right)^{1/2} \right)^2} = T_c^2 Z$$

$$T_{c_{\min}} = \frac{(1 + 2ZT_H)^{1/2}}{Z}$$

As of the mid-1990s, devices are generally capable of cooling rates of 2–3 W/cm^2 using electrical current densities of 1 A/mm^2. Typical temperature drops are about 30°C across a single stage, but much larger ΔT_{s} can be obtained by cascading.

Table 1. Operating Modes and Temperatures of Thermoelectric Materials

Temperature, °C			
Hot	Cold	Predominant materials	Operating mode
200	−130	bismuth telluride; bismuth antimony telluride	cooling or power
600	100	lead telluride; silver antimony germanium telluride	power
1000	300	silicon germanium	power

3. Technology

3.1. Materials

Because the Seebeck coefficient, the electrical resistivity, and the thermal conductivity of thermoelectric materials all vary with temperature, no single material can function well over the entire temperature range in which thermoelectric devices are used. Table 1 indicates the generally accepted operating range categories and the primary thermoelectric materials used in each range. Many other materials have been or are being developed to obtain either higher conversion efficiencies or less expensive manufacturing (2).

More recently the idea of using materials having various properties along the legs have been revived. Adjustment of dopant levels changes the carrier concentration along the thermoelement and allows each small segment of the leg to operate at optimum power conversion levels along the entire thermal gradient (10). However, this results in only incremental improvement over existing thermocouples.

In order to obtain a step function increase in conversion efficiency, new materials are needed. One promising class of compounds being investigated is the skutterudites, which have very good electrical properties, but rather high thermal conductivities in their simplest form. Work is proceeding on ways to reduce the thermal conductivity through the use of ternary alloys, and also by filling vacancies in the skutterudite structure with rare earth elements. As of this writing (1997), the most promising filled structure found is $CeFe_4Sb_{12}$, which has a figure of merit of $1.6 \times 10^{-3}\ \mathrm{K}^{-1}$ at 600°C (11).

An interesting and promising method of obtaining significant improvement in thermoelectric properties is by fabricating materials of good thermoelectricity in two-dimensional quantum well structures of very thin (<2.5 nm) layers, separated by large (>40 nm) band gap barrier layers in one sample. This multiple quantum well structure, fabricated by molecular beam epitaxy, gave an increase of a factor of three in S, but showing little effect on the other thermoelectric properties. Although this would be expected to lead to a five-fold increase in Z, the heat loss through the relatively thick barrier layers negates much of that increase. It is possible that barrier materials having a higher band gap would result in thinner barrier layers and real gains in Z (12).

The physical form of the thermocouples varies significantly according to applications. Most spacecraft power supplies utilize separate thermocouples that can be checked for performance at successive stages of manufacturing and be replaced if necessary. This approach fits in very well with the extremely high reliability requirements imposed on such systems. In terrestrial systems where such individualized attention is not economically feasible, modular assemblies are generally used, which can contain tens to hundreds of couples in a single unit.

One approach to improving the performance of existing materials through novel manufacturing techniques is the use of the mechanical alloying of extremely fine powders of germanium silicide and its dopants through high energy ball milling. This method has resulted in an increase of the integrated figure of merit from 0.7×10^{-3} to $0.9 \times 10^{-3}\ \mathrm{K}^{-1}$ for n-type SiGe alloys (13).

Because most thermoelectric materials are very strong in compression but rather weak in tension and shear, most low and moderate temperature devices are either spring-loaded or made integral with the heat exchangers to avoid stress problems and to ensure good thermal contact for conductive coupling with the heat

Table 2. Summary of Radioisotope Thermoelectric Generators Successfully Launched by the United States from 1961 to 1990

Power source	Initial average power, W	Spacecraft	Mission type[a]	Launch date	Orbital lifetime, yr
SNAP-3B7	2.7	Transit 4A	N	June 29, 1961	500
SNAP-3B8	2.7	Transit 4B	N	Nov. 15, 1961	1200
SNAP-9A	>25.2	Transit 5BN-1	N	Sept. 28, 1963	1900
SNAP-9A	26.8	Transit 5BN-2	N	Dec. 5, 1963	1800
SNAP-19B3	56.4	Nimbus III	M	Apr. 14, 1969	3600
SNAP-27	73.6	Apollo 12	L	Nov. 14, 1969	on lunar surface
SNAP-27	72.5	Apollo 14	L	Jan. 31, 1971	on lunar surface
SNAP-27	74.7	Apollo 15	L	July 26, 1971	on lunar surface
SNAP-19	162.8	Pioneer 10	P	Mar. 2, 1972	beyond solar system
SNAP-27	70.9	Apollo 16	L	Apr. 16, 1972	on lunar surface
Transit-RTG	35.6	Triad	N	Sept. 2, 1972	137
SNAP-27	75.4	Apollo 17	L	Dec. 7, 1972	on lunar surface
SNAP-19	159.6	Pioneer 11	P	Apr. 5, 1973	out of solar system
SNAP-19	84.6	Viking 1	ML	Aug. 20, 1973	on Martian surface
SNAP-19	84.2	Viking 2	ML	Sept. 9, 1975	on Martian surface
MHW-RTG	307.4	Les-8	C	Mar. 14, 1976	1,000,000
MHW-RTG	308.4	Les-9	C	Mar. 14, 1976	1,000,000
MHW-RTG	477.6	Voyager 2	P	Aug. 20, 1977	out of solar system
MHW-RTG	470.1	Voyager 1	P	Sept. 5, 1977	out of solar system
GPHS-RTG	576.8	Galileo	P	Oct. 18, 1989	second earth flyby
GPHS-RTG	~288	Ulysses	P	Oct. 6, 1990	solar–polar orbit

[a] C = communications; L = lunar; M = meteorological; ML = Mars landers; N = navigational; P = planetary.

source and sink. The high operating temperature of silicon germanium devices and the physical ruggedness of these materials have allowed cantilever mounting of the thermocouples from the cold surface of the generator housing and the use of radiant heating to supply heat to the hot shoes.

4. Thermoelectric Power Generation

Thermoelectric devices represent niche markets, but as economic and environmental conditions continue to change, they appear poised to advance into more common use. Thermoelectric power generators are in use in many areas, including satellites, deep-space probes, remote-area weather stations, undersea navigational devices, military and remote-area communications, and cathodic protection.

Undoubtedly, the most exciting application of thermoelectric power has been in the radioisotope thermoelectric generators (RTG) of the U.S. space programs. These began very modestly. Two SNAP-3B three-watt demonstration units were flown as proof-of-principle tests on the mainly solar-powered Transit 4A and 4B navigational satellites in 1961. These were followed by the 27-watt SNAP-9A design on the Transit 5BN-1 and 5BN-2 satellites in 1963, the first spacecraft to be fully powered by radioisotope power sources. The U.S. RTG-powered missions are summarized in Table 2. The power levels have steadily increased up to the 850 watts scheduled for use on the Cassini mission, which is to send a probe into the atmosphere of Saturn's moon Titan and then spend four years orbiting Saturn, making multiple encounters with its other moons. The launch for this spacecraft is scheduled for October 1997.

Thermoelectric generators have made extended spacecraft missions possible for exploration of the giant outer planets and the regions beyond the far reaches of the solar system, eg, the two Pioneer and the two Voyager missions. As of this writing (1997), the Pioneer spacecrafts have been operating over twenty-five years in the frigid reaches of outer space, surviving extremely high radiation fields on very close flybys of Jupiter and sending back data from $>9.6 \times 10^9$ km away from the sun. None of these missions has encountered any failures in the thermoelectric power systems (14, 15).

For terrestrial applications, 77 radioisotope-powered thermoelectric generators were put into operation between the years 1961 and 1995. Their electrical power outputs range from one to 500 watts. They have been used in a wide range of applications, mostly involving remote locations where supply and servicing is difficult and long-term unattended operation is of primary importance. Among the uses of these generators have been arctic weather stations, navigational light buoys, undersea acoustic beacons, oceanographic data collection, Federal Aviation Administration (FAA) communications relay stations, seismic sensors, and offshore oil well beacon lights and foghorn (16).

Because normal radioisotopic decay lowers the thermal output by about 2.5%/yr in these units, they are purposefully overdesigned for beginning of life conditions. Several of these generators have successfully operated for as long as 28 years. This is approximately equal to the half-life of the strontium-90 isotope used in the heat sources. The original SNAP-7 series immobilized the strontium-90 as the titanate, but the more recent ones have used it in the form of the fluoride, which is also very stable. A number of tiny nuclear-powered cardiac pacemaker batteries were developed, which have electrical power outputs of 33–600 μW and have been proven in use (17).

More mundane but, in the long run, much more important economically and environmentally are the terrestrial systems for power generation and cooling. The primary focus of the power-generating devices is to recapture some of the waste heat dumped by commercial processes and vehicle engines, or to make use of the heat from geothermal sources (see Geothermal energy). In cooling devices the emphasis is on eliminating the use of refrigerant gases that could be environmentally harmful, and in providing very small systems for specialized uses.

The California Energy Commission, Energy Technology Advancement Program, and the U.S. Departmant of Energy jointly sponsored a project for reducing diesel engine fuel use and NO_x particulates (18). An engine-driven electrical generator uses up to 2200–3700 W (3–5 hp) from the engine drive shaft, whereas a thermoelectric generator uses only exhaust heat and coolant from the radiator. In the latter instance there is very little degradation of the engine power output. The unit is about 1-meter long and 25-cm in diameter, and uses bismuth telluride thermoelectric modules. Initially more expensive than the engine driver alternator, at 1997 fuel costs, however, the device could recover this cost differential in two years in the United States or 6–8 months in Europe. It is believed that on-board electrical usage in trucks for powering computer NO_x reduction systems, particulate trapping, etc, is only to increase in the future, making the gains from the thermoelectric system even better.

The U.S. Coast Guard has been experiencing very high fuel and maintenance costs on their diesel motor-generator-powered major aids to navigation's systems, and are therefore sponsoring work on such systems as photovoltaics, wind, or wave power generators to float-charge large battery packs. Because each of these new power supplies is subject to significant down time owing to adverse weather conditions, a very reliable low maintenance backup power supply is required. A 1.5-W thermoelectric generator burning diesel fuel is being investigated, which uses a segmented lead telluride–bismuth telluride module.

As an offshoot of the Saudi–German HYSOLAR program that uses photovoltaics to produce hydrogen by electrolysis of water, giving in effect storable solar energy, the hydrogen can later be burned at 200–700°C using catalytic combustion (19). This provides the heat to a modified Teledyne Energy Systems thermoelectric converter that was originally designed for natural gas, propane, or butane fuels. The H_2 is both storable and transportable and the combustion product is water.

Osaka University and the University of Wales are collaborating on a research project aimed at the recovery of electrical power from waste heat from commercial processes (20). This is a low (80°C) temperature low (~60°C) ΔT process that makes use of very thin thermoelements and very large area heat exchange devices. The initial costs could be quite high, but the low temperature operation should result in extremely long life times to depreciate the costs effectively. Because this system is using only waste heat from another process, electrical power is gained without additional pollution of any sort. The efficiency of these systems is rather low compared to other devices operating over wider temperature ranges, but because it is piggybacking on other processes that take care of the economic investment, it is a promising approach to alleviating any energy crunch in the future.

Cold climate electrical heaters for trucks in far northern areas of the United States, Canada, Northern Europe, and the CIS are very important. These are used when the trucks are idle and provide heat to the engine coolant and the cab without idling the engine for extended periods (21). This not only minimizes engine wear and reduces pollution but also provides significant economic savings. Many jurisdictions now prohibit extended idling of engines. In extremely cold environments, engines can quickly become difficult, sometimes nearly impossible, to start. If ordinary gasoline- or diesel-oil-fired heaters are used, the coolant circulation pump, air fan, etc, must be powered from the vehicle's batteries, thus curtailing the time the system can be used, especially at very low temperatures when it is needed the most. By adding PbTe thermoelectrics to such heater systems, about 2% of their thermal output can be turned into electricity to run the heater's electronics, fuel pump, combustion fan, and coolant circulation pump, with still sufficient power left over to keep the vehicle's battery fully charged. The market for such units is in the hundreds of thousands if manufacturing costs can be reduced.

5. Thermoelectric Cooling

In the 1960s there were a number of attempts to make thermoelectric cooling a significant industry. Although all of the systems worked very well, they could not compete economically with the low fuel costs of those years. Nevertheless, the groundwork was laid. A corporate headquarters building in Wisconsin was fitted with a thermoelectric air conditioning system by Carrier Corporation. It consisted of 30 decentralized units that were still operating well over 10 years later (22). However, Carrier has since withdrawn from the business.

Small refrigerators were developed by several companies and some were even installed in hotel rooms in Chicago. Borg-Warner and other companies produced many compact systems for laboratory uses (23). Air-Industry in France built an air conditioning system for a passenger railway coach that was still in daily use after 10 years of operations without a single thermoelectric failure (24).

With the international agreements concluded in the 1990s on banning chlorofluorocarbons by the year 2000, the efficiency of refrigeration systems using substitute working fluids has moved much closer to that of the thermoelectric cooling systems. Considering the economics of scale, it now seems possible to market thermoelectric refrigerators at only 10 to 20% above the cost of similar sized compressor units. The quieter operation and much longer life of thermoelectric units could make these competitive in the near future (25).

The U.S. Army is sponsoring work on a modular device to be used in protecting personnel in severe conditions. This is a thermoelectric cooling device, designed for mounting in a two-person army vehicle, which is to provide a controlled working atmosphere for two personnel wearing nuclear, biological, and chemical (NBC) protective clothing (26). The device consists of a thermoelectric cooling unit, a multiple-filter pack, and a blower assembly. The unit can supply 0.67 m^3/min (24 ft^3/min) of cooled, filtered air with 250 watts of cooling to each person. The unit operates off of the vehicle's 28-volt electrical system and can easily maintain an effective working climate inside the suits over an external ambient range from 35°C/85% rh to 51.5°C/3% rh.

By far the most important applications for thermoelectric devices as of the mid-1990s are the fields of small laboratory and medical devices and recreational coolers. These range in cooling capacity from fractions of a watt to 600 watts and minimum temperatures as low as -100°C up to reverse-mode heating temperatures of $+100^\circ$C (27). Such devices range from simple laboratory measurement devices, uses in biotechnology and medical and surgical devices, to rugged coolers for photodetectors and lasers and portable

NOMENCLATURE OF THERMOELECTRIC ENERGY CONVERSION

Symbols	Definition	Units
A	area	cm^2
I	electric current	A
K	device thermal conductivity	
l	length	cm
η	efficiency	
P	electrical power out	W
q	heat	W
Q	heat in	W
R	electrical resistance	Ω
S	Seebeck coefficient	V/K
T	temperature	K
V	electrical voltage	V
Z	figure of merit	K^{-1}
β	coefficient of performance	
λ	thermal conductivity	W/(cm·K)
π	Peltier coefficient	W/A
ρ	electrical resistivity	ohm·cm
τ	Thomson coefficient	V/K

coolers for boats and autos. The market is in the hundreds of thousands of thermoelectric modules per year.

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