Novel thermoelectric materials development, existing and potential applications, and commercialization routes

by

Philippe Bertreau

Ingénieur Ecole Centrale Paris, 2006
Licencié ès sciences-économiques, Université Paris Dauphine, 2005

MASSACHUSETTS INSTITUTE
OF TECHNOLOGY
OCT 0 2 2006
LIBRARIES

Submitted to the Department of Materials Science and Engineering
in partial fulfillment of the requirements for the degree of

Master of Engineering in Materials Science and Engineering at the
Massachusetts Institute of Technology

September 2006

©2006 Massachusetts Institute of Technology
All rights reserved.

Author..
Department of Materials Science & Engineering,
August 7, 2006

Certified by..
Eugene A. Fitzgerald
Merton C. Flemings-SMA Professor of Materials Science and Engineering
Thesis Supervisor

Accepted by..
Samuel M. Allen
POSCO Professor of Physical Metallurgy
Chair, Departmental Committee on Graduate Students

ARCHIVES

Novel thermoelectric materials development, existing and potential applications, and commercialization routes

By

Philippe Bertreau

Submitted to the Department of Materials Science and Engineering
on August 7, 2006 in partial fulfillment of the requirements for the degree of
Master of Engineering in Materials Science and Engineering

ABSTRACT

Thermoelectrics (TE) are devices which can convert heat in the form of a temperature gradient into electricity, or alternatively generate and absorb heat when an electrical current is run through them.

It was established in the 1950's that the effectiveness of a thermoelectric could approximately be described in terms of a dimensionless figure of merit, $ZT = \frac{\alpha^2 T}{\lambda\rho}$, with α, ρ and λ being respectively the Seebeck coefficient, the electrical resistivity and the thermal conductivity of the material. Until recently, $ZT \approx 1$ was the best performance these materials could achieve. However, the field of thermoelectrics advanced rapidly in the five last years, leading to the first significant breakthroughs in this area in the past fifty years, with materials with ZT up to 3 being reported. It is therefore interesting to wonder what new applications and markets these improvements at the material level could lead to.

The first section of this thesis is a review of the principles of TE technology, the current materials and their level of performance. The recent materials developments are also described. The commercialization of TE is then discussed, along with the requirements in terms of performance and costs which would have to be achieved to make TE a further commercial success. Eventually, a business model for one of the applications is developed.

A special focus on the PbTe/PbTeSe quantum dot superlattice structure developed by the MIT Lincoln Laboratory is adopted in this paper.

Thesis Advisor: Eugene A. Fitzgerald
Title: Merton C. Flemings-SMA Professor of Materials Science and Engineering

Table of Content

I Acknowledgements 4
II Background on technology 5
  II.1 Principles of thermoelectrics 5
    A Peltier effect 5
    B Seebeck effect 9
  II.2 Performance of TE materials 10
    A COP=f(ZT) 10
    B The TE figure of merit ZT: evolutions and temperature dependence 12
  II.3 Modules designs 15
    A Cascaded modules 17
    B Segmented legs couples 17
  II.4 Advantages offered by thermoelectric compared to alternative technologies 19
  II.5 Current standard TE materials 20
    A Materials review 20
    B Production of the previously cited materials 22
III Link between theoretical coefficient of performance determined by material performance and actual performance of the overall device 23
IV Patent search 24
V Review of applications of thermoelectrics and assessment of their economic value 28
  V.1 Applications of the Seebeck effect: power generation 28
    A High-power generation 28
    B Low-power generation 41
  V.2 Applications of the Peltier effect 46
    A Cooling and heating applications 46
    B Cooling applications 51
    C Electronics cooling 57
  V.3 Applications as thermal sensors 70
  V.4 Summary of key decision factors 71
VI Commercialization of thermoelectric technology 72
  VI.1 Walk-down the learning curve and niche markets 72
  VI.2 Materials' place and role in the value and commercial chains 75
  VI.3 Business model for industrial waste heat recovery 77
VII Conclusion 80
VIII References 82
IX Appendix: Economic model for industrial waste heat recovery 83

Acknowledgements

First, I would like to thank my advisor, Eugene A. Fitzgerald, for allowing me the opportunity to work on this subject.

I would also like to acknowledge the people outside of MIT who took some of their time to answer my questions which enabled me to have a better understanding of the field: Professor Ali Shakouri (UCSB), Dr. Chris Wilson (Novartis), Dr. Lon Bell (BSST), Dave Wanat (Conair), Dan Midea (Global Thermoelectric Inc), A. Ajupudi (Melcor), and my friend Martin Beauvais (Arcelor Research).

I would like to give a special thanks to Dr. Mayank Buslara for his insights on the topic and his careful reading of this thesis. I would also like to acknowledge John Maloney, who proof-read this work.

Finally, I would like to thank my MEng colleagues and all the people I met this year who contributed to making my time at MIT such a rich personal experience.

II Background on technology

II.1 Principles of thermoelectrics

A Peltier effect

a. Principle

Thermoelectric devices can convert electricity into a temperature gradient. This effect was discovered by Peltier in 1834 and is known as the Peltier effect. This heat transfer is achieved when a direct current is passed through a pair of n-type and p-type semiconductor materials. The electrons go from a low energy level in the p-type material to a higher energy level in the n-type semiconductor leg. They gain energy by absorbing heat at the conductor interconnect between the two legs (heat is absorbed from the lattice) thereby reducing the temperature, T_C, of this interconnect. Heat is rejected at the other end of the legs when the electrons return to a lower energy level and dissipated in a heat sink. The temperature T_H of this other junction is increased. (See Fig 1 and Fig 2)

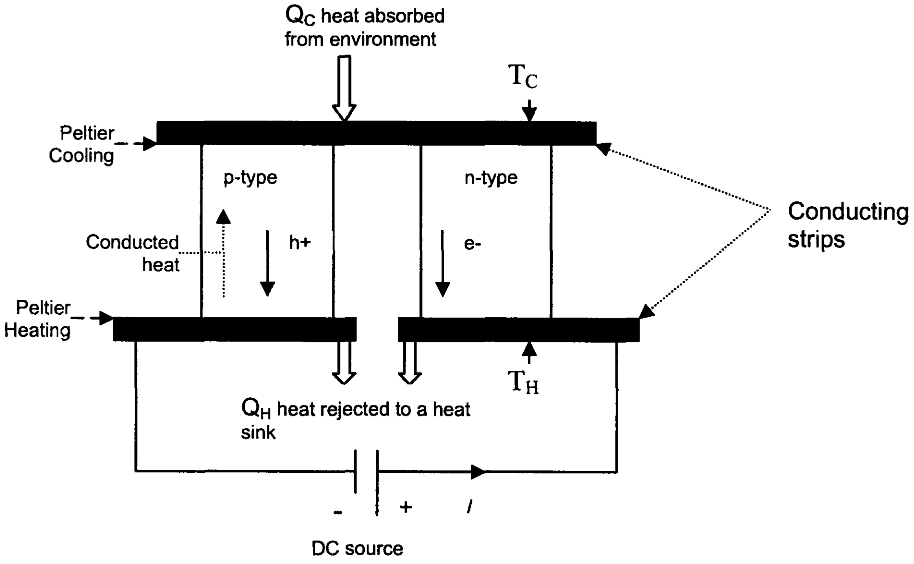


Fig 1: Peltier cooling

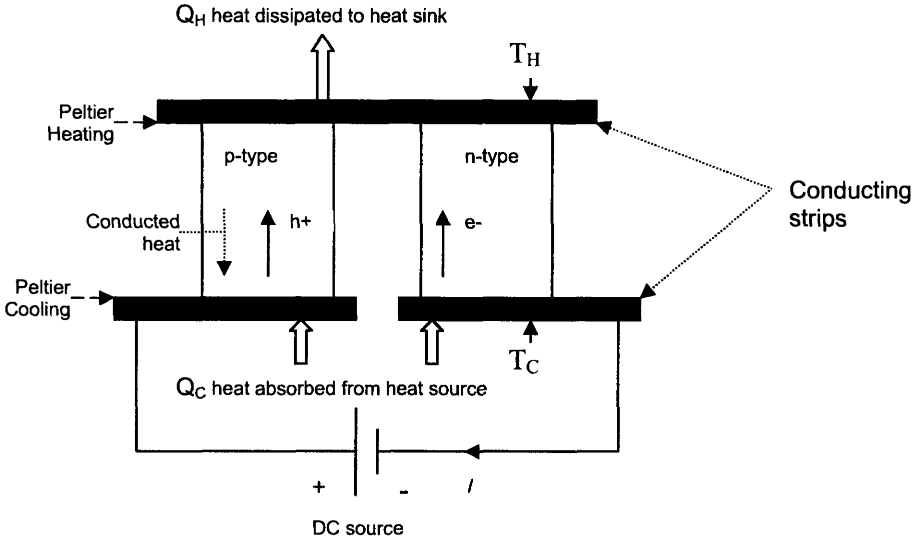


Fig 2: Peltier Heating

Thermoelectrics powered with electricity can thus be used for cooling or heating applications. It only takes a change the direction of the current to go from one mode to the other. (Fig 2) Ideally, the heat absorbed at the cold junction is related to the current by the Peltier coefficient: $j = Q_{p-n} \times I$ with Q_{p-n} the Peltier coefficient, and the amount of heat absorbed at the cold end would equal the heat rejected at the hot end. However, two effects reduce the efficiency of this heat transfer: conducted heat in the legs and Joule heating. Because of the temperature difference between the two sides of the semiconductor, heat diffuses from the hot side to the cold side, according to the equation: $j = -\lambda \frac{\partial T}{\partial s}$. The other loss, Joule heating, occurs as current is run through the material and energy is dissipated at a rate that is proportional to the square of the current. This phenomenon can eventually become the dominant factor; as current is increased, a point is reached at which an increase in current results in less net cooling.

b. Cooling rate, Heating rate and the TE figure of merit

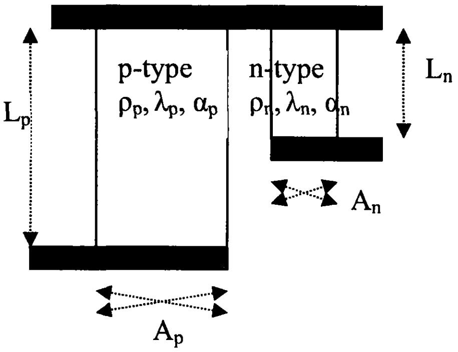


Fig 3: Single-couple refrigerator

The derivation of the following formulae can be found in different textbooks. The interested reader can go over the derivations in the book given in reference [1] (section 1.3).

The net pumping rate Q_C (J.s^{-1}) is given by

$Q_C = (\alpha_p - \alpha_n)IT_C - K\Delta T - \frac{1}{2}I^2R$ with:

- α_p the Seebeck coefficient of the p-leg material
- α_n the Seebeck coefficient of the n-leg material
- I the current
- T_C the temperature of the cold junction
- T_H the temperature of the hot junction
- $\Delta T = T_H - T_C$
- $K = \frac{\lambda_p A_p}{L_p} + \frac{\lambda_n A_n}{L_n}$ (thermal resistances in parallel) with λ_p and λ_n the thermal conductivities of the p-leg and n-leg respectively, L_p and L_n the lengths of each leg and A_p and A_n the cross-sectional areas of each leg.
- $R = \frac{L_p \rho_p}{A_p} + \frac{L_n \rho_n}{A_n}$ (electrical resistances in series) with ρ_p, ρ_n the electrical resistivities.

The electrical power consumed by the thermocouple is given by the sum of Joule losses and the work against the Seebeck voltage: $W = I\left[\left(\alpha_p - \alpha_n\right)\Delta T + IR\right]$

The efficiency of the TE couple can be maximized by running the current which gives the maximum efficiency ϕ. $\phi = \frac{T_C}{T_H - T_C} \times \frac{\sqrt{1+Z_C T_{av}} - \frac{T_H}{T_C}}{\sqrt{1+Z_C T_{av}} + 1}$ with $Z_C = \frac{(\alpha_p - \alpha_n)^2}{R \times K}$ (Note: the Seebeck coefficient of an n-type material is negative). For an optimized geometry for which Z_C, the Z of the couple, is maximized, $Z_C = \frac{(\alpha_p - \alpha_n)^2}{\left[(\lambda_p \rho_p)^{1/2} + (\lambda_n \rho_n)^{1/2}\right]^2}$. The dimension of this figure Z is the inverse of a temperature. $ZT = Z \times \frac{T_C + T_H}{2}$ is a dimensionless figure that is a good indicator of material performance.

When materials improvements will be discussed, it will be referred to the figure of merit Z of a material, defined by $Z = \frac{\alpha^2}{\lambda \rho}$ not to the Z of a couple. However, as n-type and p-type materials have very close properties, the structure, composition and processing method of a high-performance n-type material are usually reproducible to build a similarly performing p-type material. The efficiency does not change when a number of couples are linked together in a device, whereas the cooling power Q_c is proportional to the number of couples, all other things equal.

It is important to notice that thermoelectrics do not remove heat in the overall system. On the contrary, they add heat because of the Joule heating which occurs when a current is run through the material. Instead, thermoelectric coolers move heat from one extremity to the other. In the 1D two-legs model, the heat removed is given by:

$$Q_C = \underset{\uparrow}{(\alpha_p - \alpha_n) I T_2} - \underset{\uparrow}{K \Delta T} - \underset{\uparrow}{\frac{1}{2} I^2 R}$$

Heat removed by the e- gas

Heat flow due to thermal conduction

Joule heating. The extremity to be cooled receives ½ this heat in most models, sometimes a fraction χ ($0<\chi<1$) replaces the factor ½

Therefore:

- The higher the Seebeck coefficients, α, the higher the pumping rate.

- The higher the electrical conductivities, σ, the lower the Joule heating and thus the better the cooling.
- If the side to cool is actually at a higher temperature than the other side, (ie. $\Delta T<0$) and therefore, the higher the thermal conductivities, λ, the more heat is dissipated by conduction and the better the cooling. It must be noted that this model fails at low dimensions (see section on electronics cooling).

B Seebeck effect

When a temperature difference is established between the hot and cold ends of a thermoelectric material, a voltage is generated; this voltage is the Seebeck voltage, and this effect is known as the Seebeck effect (discovered in 1821). Electrons and holes will thermally diffuse from the hot side to the cold side and carry their charge with them, creating an electric field. The electric field leads to a drift that actually balances the diffusion of the charges. The Seebeck coefficient is the ratio of the electric field and the temperature gradient. It is therefore given by: $\alpha = \frac{dV}{dT}$, with V the voltage. The sign of the Seebeck coefficient is the same as the sign of the majority charge carriers (positive for a p-type material and negative for an n-type material).

The Seebeck effect is actually the inverse of the Peltier effect. As a consequence, a thermoelectric couple can convert thermal energy from a temperature gradient into electricity.

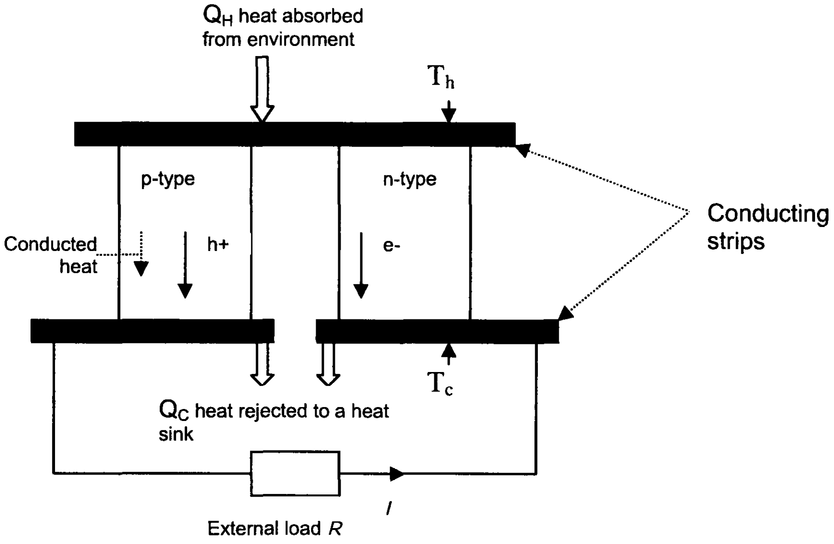


Fig 4:Seebeck effect

In practice, a large number of couples are connected thermally in parallel and electrically in series, therefore forming a "module", to deliver a higher power.

The net heat pumping rate is given by: $Q_H = K\Delta T + (\alpha_p - \alpha_n) I T_H - \frac{1}{2} I^2 R$ The optimized design efficiency is then given by: $\eta = \frac{T_H - T_C}{T_H} \times \frac{\sqrt{1 + Z_C T_{av}} - 1}{\sqrt{1 + Z_C T_{av}} + \frac{T_C}{T_H}}$, in which the reader will have identified the Carnot limit $\frac{T_H - T_C}{T_H}$, as the highest efficiency permitted by thermodynamics, as for any heat engine.

II.2 Performance of TE materials

A COP=f(ZT)

We already reported that the coefficient of performance of a TE device is a function of *ZT*:

Power generation mode:

$$COP = \frac{T_H - T_C}{T_H} \times \frac{\sqrt{1 + ZT_{av}} - 1}{\sqrt{1 + ZT_{av}} + \frac{T_C}{T_H}}$$

Cooling mode:

$$COP = \frac{T_C}{T_H - T_C} \times \frac{\sqrt{1 + ZT_{av}} - \frac{T_H}{T_C}}{\sqrt{1 + ZT_{av}} + 1}$$

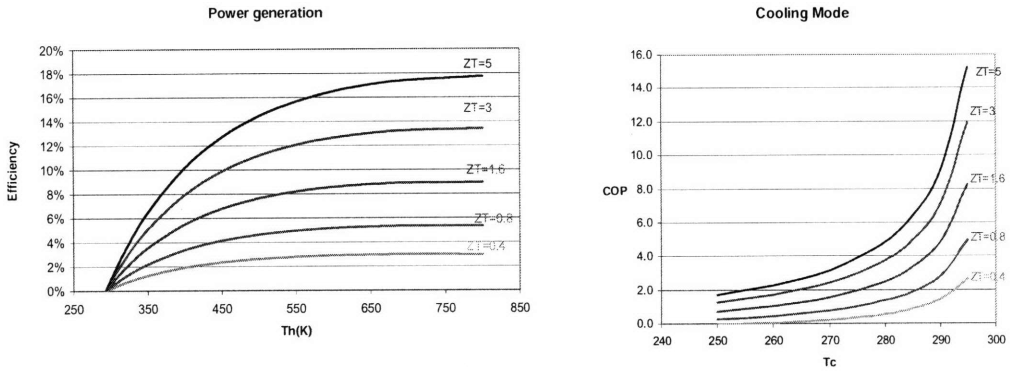


Fig 5: Theoretical TE systems COP function of ZT and ΔT. For the power generation case, T_C=20°C; for the cooling case T_H=30°C.

It is clear that large *ZT* are required to achieve high heat-to-electricity conversion efficiencies, or high cooling efficiencies.

An outlook at the figure $Z = \frac{\alpha^2\sigma}{\lambda}$ makes us realize how difficult it is to optimize a good thermoelectric material. While having a good electrical conductivity, the material must have a low thermal conductivity, which is clearly intuitively unlikely. The ideal material would have the electrical conductivity of a metal while having the thermal conductivity of a glass! It is therefore necessary to look for a compromise in the semiconductor class. To minimize the thermal conductivity λ without affecting σ, only the effect of the phonons (lattice conductivity λ_L) must be diminished, not the carriers contribution. Several techniques can be used, and they are described in the following section. In addition, the Seebeck coefficient α and the electrical conductivity σ are not independent. α decreases when the concentration in charge carriers (electrons or holes) is increased, whereas σ increases with the charge carrier concentration. The figure, $\alpha^2\sigma$, which is called the power factor, has to be optimized when adjusting the carrier concentration.

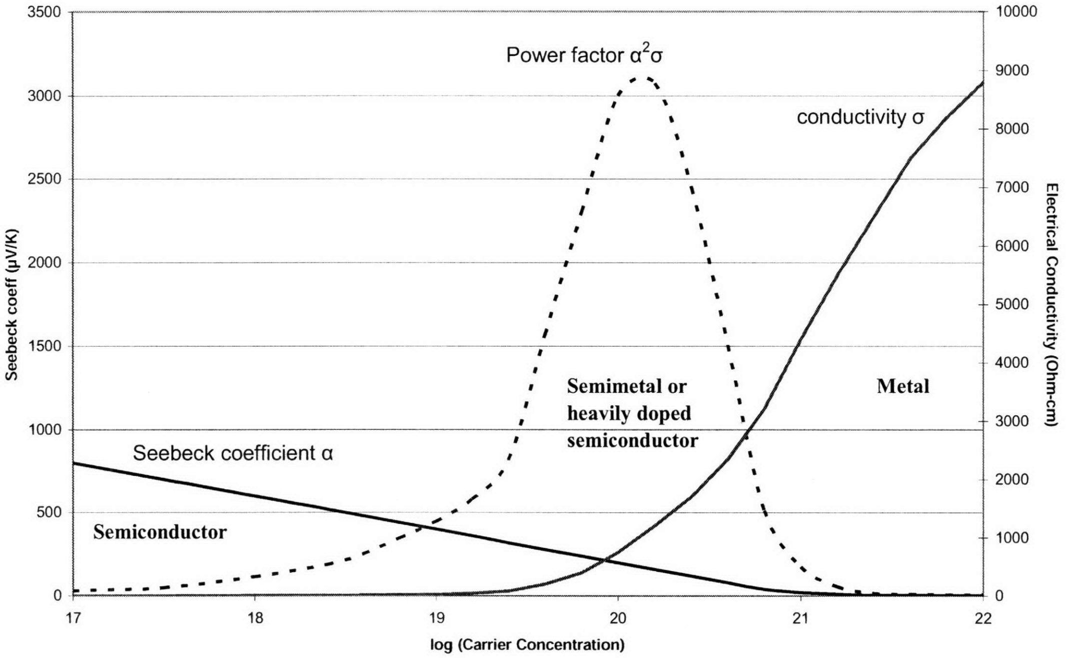
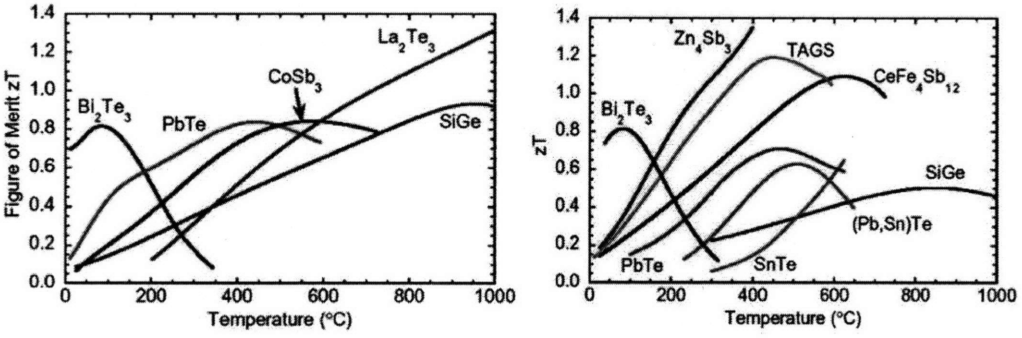


Fig 6: Power factor: a balancing act

B The TE figure of merit ZT: evolutions and temperature dependence

Temperature dependence

The thermoelectric properties of semiconductor materials, namely the thermal conductivity λ, the electrical resistivity ρ and the Seebeck coefficient α are temperature dependent. The figure of merit *ZT* is thus temperature dependent (see Fig 7).



from: http://www.its.caltech.edu/~jsnyder/thermoelectrics/

Fig 7: ZT=f(T) for n-type materials (left) and p-type materials (right)

Recent materials developments

Until recently, thermoelectric material could only be used in niche applications because of their low efficiency, with $ZT<1$. Bismuth Telluride (Bi_2Te_3) was the most efficient material at room temperature, and is thus the most widely used for current commercial applications. However, in recent years, new materials with increased figures of merit up to 3 have been obtained in various laboratories. These research breakthroughs pave the way for new applications and markets.

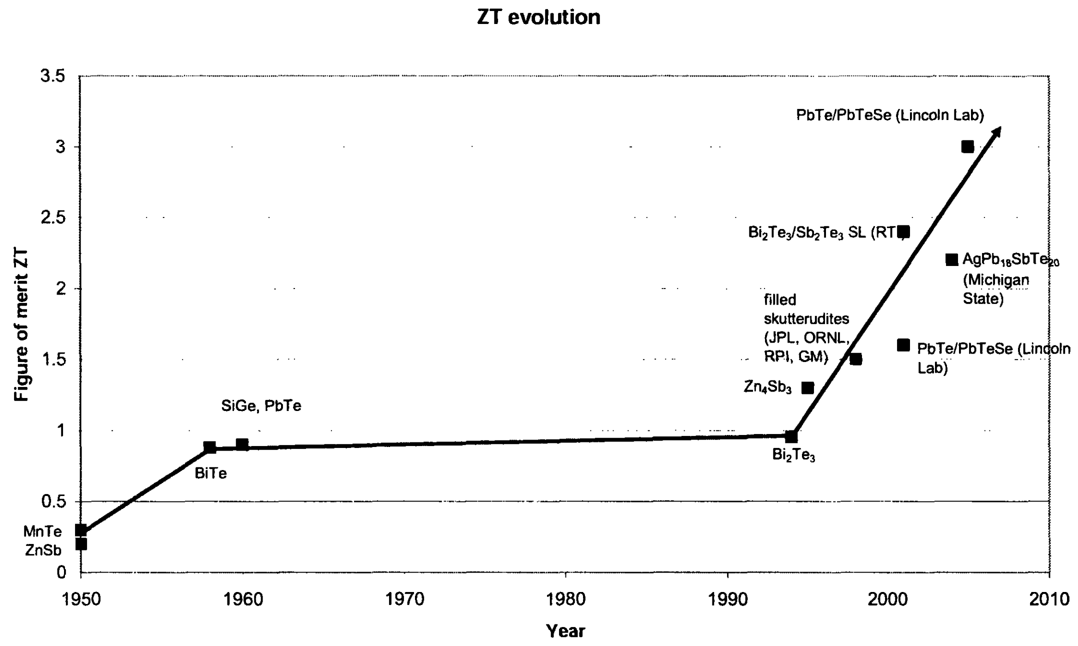


Fig 8: ZT evolution in the last 60 years.

Methods to lower the thermal conductivity

Two methods to lower the thermal conductivity in a material are:

- The use of complex crystalline structures: Most of the heat is conducted by the acoustic modes of phonons. When a crystal has N atoms per cell, it has 3 acoustic modes and 3(N-1) optic modes. Therefore, the greater N is, the more optic modes there are and the less heat is transported in this crystal.
- To have atoms with weak bonds inside the crystal (e.g. small atoms in a big cage) or atoms whose position is not very well defined. Such atoms induce an important disorder, which contributes to phonon scattering and thus lowers thermal conductivity.

Most promising materials and recent breakthroughs

The materials which are the more promising at present are:

- Semi-Heusler compounds, whose general formula is XYZ, with X and Y transition metals, and Z a metalloid or metal (e.g. ZrNiSn). The power factor for such structures can be very high, but their thermal conductivities are still too high.
- Clathrates compounds, which are chemical substances consisting of a lattice of one type of molecule, usually Si, GaGe or GaSn, forming large cages trapping and containing a second type of molecule, such as heavy lanthanides or alkalines. Their thermal conductivity is low.
- Skutterudites, which have a cubic structure with an MX_3 type lattice, where M is a transition metal and X=As, P or Sb, at the center of which can be inserted a large cage in which can be inserted heavy atoms, such as lanthanides. These compounds have a high Seebeck coefficient, a good electrical conductivity, but still too high a thermal conductivity.

The main recent breakthroughs in the field of thermoelectric materials are:

- PbTe/PbTeSe quantum dot superlattice alloy developed by the MIT Lincoln Laboratory. PbSe nano-particles are grown in a PbTe matrix. This structure has a decreased thermal conductivity because of the large interface area per unit volume; with little effect on the Seebeck coefficient and electrical conductivity (Selenium and Tellurium are very close in the periodic table). ZT=1.6 was achieved at room temperature [2]. ZT=3 was achieved at 550K [3].
- Bi_2Te_3/Sb_2Te_3 superlattice developed by the Research Triangle Institute (RTI) (North Carolina, USA). ZT=2.4 was achieved at 300K [4]. Nextreme Thermal, which is a spin-off of RTI, is a start-up company which aims at commercializing this technology.
- Cubic $AgPb_mSbTe_{2+m}$ bulk materials with ZT=2.2 at 800K developed at Michigan State University [5].
- Other high performance materials have been demonstrated by H Böttner and co-workers at the Fraunhofer Institute in Freiburg, Germany.

It must also be noted that the new materials with improved thermoelectric properties were processed in the form of thin-films (except for the work at MSU). (The currently commercialized materials are bulk materials). For commercialization, this basically means that:

- Either applications have to be found for these thin-films, most likely in electronics cooling
- Or, techniques have to be found to process the same compositions and structures in the form of bulk materials.

II.3 Modules designs

A typical thermoelectric device is composed of two ceramics or alumina substrates which serve as electrical insulators, between which p-type and n-type legs (each pair of p-type & n-type leg forming a "couple") are connected electrically in series and thermally in parallel.

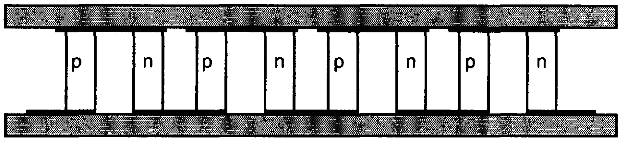


Fig 9: TE module: couples connected electrically in series and thermally in parallel

Such a "module" is sandwiched between a heat source and a heat sink. Thermoelectric devices are usually not used independently, but with heat exchangers which dissipate heat. The system design has a strong impact on the overall device efficiency.

The efficiency does not change when a number of couples are linked together in a device, whereas the cooling power, heating power and power generated are proportional to the number of couples.

The main problems invariably encountered in practice with thermoelectric modules are related to heat transfer. There is always some transfer of heat from the hot to the cold junctions through the space between and around the legs. Besides, there is thermal resistance between the module junctions and the heat sources and sink at the substrate level. Models taking into account these phenomena have been developed and can be found in the section 5.5 of "Thermo-electrics: Basic principles and new materials development" [1].

A comment on packing density

It is apparent from the equations developed in III.1 that the geometry of the legs affects the performance of the couple only through the ratio *A/L*. When the load is matched to obtain the maximum efficiency, the power output of a couple is $W=\frac{\sqrt{1+ZT_{av}}\alpha^2\Delta T^2}{R(1+\sqrt{1+ZT_{av}})^2}$ with $\alpha=\alpha_p-\alpha_n$, $R=\frac{L}{A}(\rho_p+\rho_n)$; or the cooling power is given by $Q_C=K\Delta T\left[ZT_C-\frac{\Delta T(\sqrt{1+ZT_{av}}+1)}{2T_{av}}-1\right]$ with $K=(\lambda_p+\lambda_n)\frac{A}{L}$. It is interesting to note that the wattage depends on the geometry through the electrical resistance in the power generation case, and of the geometry through the thermal conductivity in the cooling case, which is intuitive. For N couples, the power output is thus $W_T=N\frac{A}{L}\frac{\sqrt{1+ZT_{av}}\alpha^2\Delta T^2}{\rho(1+\sqrt{1+ZT_{av}})^2}$ with $\rho=\rho_p+\rho_n$ in the power generation mode and the cooling power becomes $Q_{cT}=N\frac{A}{L}\lambda\Delta T\left[ZT_C-\frac{\Delta T(\sqrt{1+ZT_{av}}+1)}{2T_{av}}-1\right]$ in the cooling mode ($\lambda=\lambda_p+\lambda_n$). It is apparent that all other things equal, the shorter L, the better the performance, as long as the temperature gradient is maintained (which might be difficult in practice because of heat losses). *2NA* is the footprint area of all the couples which is obviously bounded by the total area of the TE module. We can refer to the ratio of the footprint area of the elements to the footprint area of the module as the packing density. For a given packing density and a fixed L, changing the *A/L ratio* (ie: changing A) to keep the product *NA* constant would not affect the power output or the cooling density. While maintaining a fixed packing density, changing *A/L* to keep *N* constant or changing *N* to keep *A/L* constant only changes the I versus V relationship of the thermoelectric generator or cooler. The product *V*I*, which is the power input to the cooler (power output of the generator) is unaffected. For a fixed packing density (typically 80%), the choice of number of elements and cross section can be used to ensure that the voltage requirements of the TE module are within the limits of the chassis power supply taps. A large number of small cross section elements results in low current but high voltage, and small number of large cross section elements results in high current but low voltage. This provides a design envelope which may allow for some specific TE module design to meet the thermal requirements while requiring a voltage that the chassis power supply is capable of supplying.

A Cascaded modules

Simple stage refrigerators allow a maximum temperature difference of $ZT^2/2$. Multistage (or cascaded) thermoelectrics have been developed for this reason. To allow for greater cooling, the operation of modules in a thermal-series arrangement is a solution. Another reason why cascaded TE have been developed is the temperature dependence of the thermoelectric properties: α, ρ and λ and therefore Z. The use of a single material in a module operated over a wide range of temperature (>100°C) seriously affects the efficiency of the device. To meet the requirement of large temperature difference in the power generation mode, cascaded modules with a different material at each stage offer a significant improvement. At each stage a material with optimized efficiency with respect to the range of temperature between which it operates is used.

The first stage of cascade provides a heat sink at a lower temperature for the second level, which, in turn, provides an even lower temperature sink for the following stage. (See Fig 10)

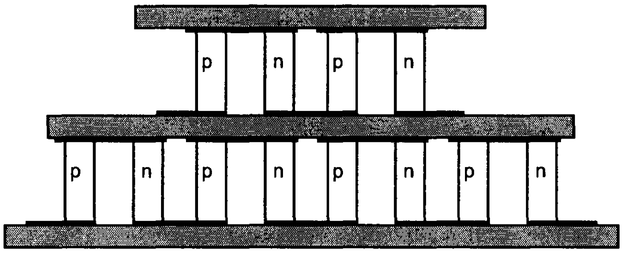
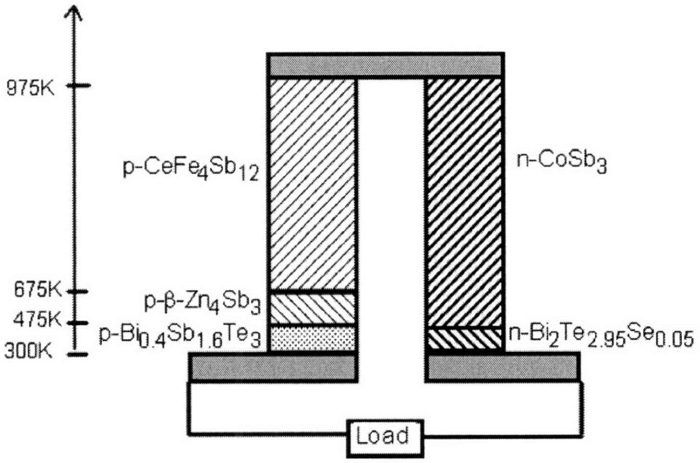


Fig 10: 2-stage cascaded thermoelectric module, in the case when each stage consists of a separate module

B Segmented legs couples

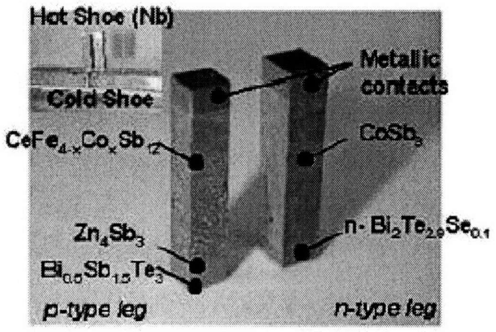
As already mentioned, to achieve high efficiencies, high ZT materials are required. When one operates over a wide range of temperature, the use of one single material will not give satisfying efficiency and is therefore not desirable. One way to get around this problem is the use of cascaded generators. Another solution is to build modules with legs made of different materials, i.e. segmented legs. A material with high efficiency at high temperature is placed in contact with the hot ceramic plate, whereas a material efficient at around the cold side temperature is placed in contact with this cold side. This way, each material is only operating in its most efficient temperature range.



from: http://www.its.caltech.edu/~jsnyder/thermoelectrics/

Fig 11: Principle of a segmented legs generator

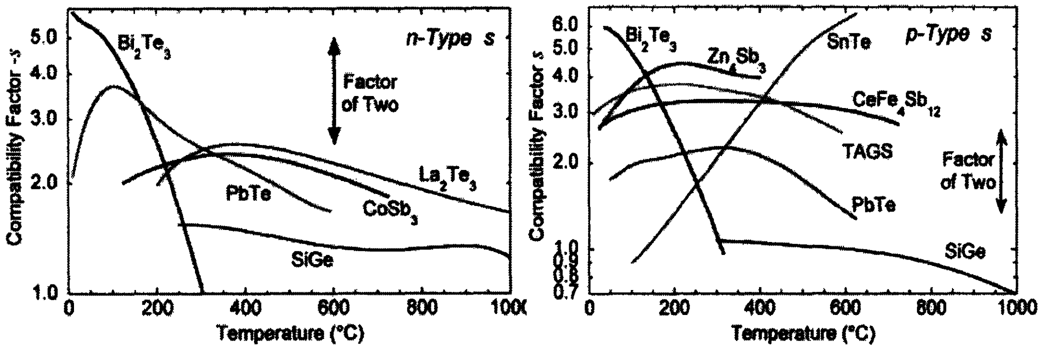
Jeff Snyder *et al.* from the Jet Propulsion Laboratory at Caltech have grown such segmented-legs materials. They were able to achieve 14% efficiency in power generation between 975K and 300K with traditional and skutterudite materials, which translates to an average ZT of 0.77.



from: http://www.its.caltech.edu/~jsnyder/thermoelectrics/

Fig 12: Example of a segmented leg couple generator produced by the JPL group at Caltech

The JPL group further explored this idea by proposing a way to assess the compatibility of materials which can be mounted on top of one another with improved efficiency. They defined a figure $s = \dfrac{\sqrt{1+ZT}-1}{\alpha T}$, which they called the compatibility factor [6]. It is a measure of the compatibility of two materials in a segmented configuration. The goal is to select high figure of merit materials which have similar compatibility factors. If the compatibility factor differ by a factor of two or more, segmentation will not be efficient.



from:http://www.its.caltech.edu/~jsnyder/thermoelectrics/

Fig 13: Temperature dependence of compatibility factors for different materials

II.4 Advantages offered by thermoelectric compared to alternative technologies

- Thermoelectrics have no moving parts. They therefore require little or no maintenance and do not generate mechanical vibrations. TE devices are also silent.
- Life testing has shown the capability of TE devices to exceed 100,000 hrs of steady state operation.
- The same thermoelectric system can perform both cooling and heating: only the polarity of the power supply needs to be changed to go from the cooling mode to the heating mode.
- Precise temperature control up to ±0.1°C can be achieved when a TE device is mounted with the appropriate electronic circuitry.
- They contain no chlorofluocarbons (compared to most compressor-based refrigerators) or other materials which are environmentally harmful and may require periodic replenishment[1].
- They are not position-dependent.
- TE devices can functions in environments that are too severe or too confined to allow the use of conventional refrigeration systems.

---

[1] The chlorofluocarbons (CFCs) which are the most commonly used in refrigerant cycles are the halomethanes R-12 and R-22, with R-12 being more common in automotive air conditioning and small refrigerators, and R-22 being used for residential and light commercial air conditioning, refrigerators, and freezers. However, it has been discovered that, because of their good stability, these compounds severely damage the ozone layer, and their use has been tremendously restricted. Alternatives (HCFC) have been developed but are still environmentally harmful. In addition, because the only available CFC gases in countries adhering to the Montreal Protocol come from recycling, their prices have gone up considerably.

II.5 Current standard TE materials

A Materials review

a. Bismuth Telluride

The best elemental or simple compound TE material at ordinary temperature is bismuth telluride: Bi_2Te_3 (V_2VI_3). Its main properties can be found in the table below:

Property	Symbol	Value	Temp
Hexagonal unit	a	$(4.3835\pm0.0005)\times10^{-10}$m	293K
Cell dimensions	c	$(30.487\pm0.001)\times10^{-10}$m	293K
Density	ρ	$(7.8587\pm0.001)\times10^{3}$ kg m^{-3}	293K
Elastic constants	c_{11}	6.847×10^{10} N m^{-2}	300K
	c_{66}	2.335×10^{10} N m^{-2}	300K
	c_{33}	4.768×10^{10} N m^{-2}	300K
	c_{44}	2.738×10^{10} N m^{-2}	300K
	c_{13}	2.704×10^{10} N m^{-2}	300K
	c_{14}	1.325×10^{10} N m^{-2}	300K
Specific heat		$1.507\times104+54.4T-0.130T^2$ J K^{-1} kg mol^{-1}	up to 823K
Latent heat of fusion		$(1.21\pm0.04)\times10^{8}$ J kg mol^{-1}	
Carrier mobility (perpendicular to c axis):			
Electrons	μ_n	0.120 m^{2}V^{-1}s^{-1}	293K
Holes	μ_p	0.051 m^{2}V^{-1}s^{-2}	293K
Temperature depence of mobility:			
Electrons		$\mu_n \alpha T^{-1.68}$	
Holes		$\mu_{p\alpha} T^{-1.95}$	
Lattice thermal conductivity	λ_L		
Perpendicular to c axis		1.5 Wm^{-1}K^{-1}	300K
Parallel to c axis		0.7 Wm^{-1}K^{-2}	300K

Table 1: Properties of bismuth telluride, values from [1] p112 & 118

Alloys based on Bismuth Telluride

Although neither antimony telluride (Sb_2Te_3) nor bismuth selenide (Bi_2Se_3) have very good thermoelectric properties at room temperature, the alloying of Bi_2Te_3 with one or both improves ZT mainly by reducing the lattice thermal conductivity. As Sb_2Te_3 is invariably strongly p-type and undoped Bi_2Se_3 is n-type, the majority carrier type in each alloy will vary accordingly. Within the Bi_2Te_3 based alloys improved with Sb_2Te_3 and Bi_2Se_3, the optimal composition for thermoelectric cooling is $Bi_2Te_{2.7}Se_{0.3}$ for the n-type leg and $Bi_{0.5}Sb_{1.5}Te_3$ for the p-type leg.

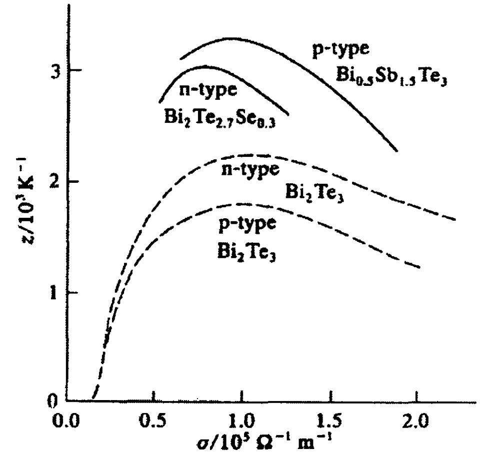


Fig 14: Variation of Z for Bi_2Te_3 and selected pseudobinary alloys at 20°C [1]

b. Lead Telluride and related compounds

PbTe melts at a higher temperature (923°C) than Bi_2Te_3 (585°C) and is therefore applicable for high temperature systems for which bismuth telluride could not be used. These applications include many power generation applications, since thermodynamic considerations underline the advantage of operating at high temperature.

PbTe has a cubic structure. Its thermoelectric properties are therefore isotropic, and a randomly oriented polycrystalline material is as good as a single crystal. It has a low lattice thermal conductivity and its relatively small bandgap (0.32eV) allows for high Seebeck coefficients (>300µV/K at 300K with suitable doping).

The acronym TAGS is frequently used in the thermoelectric literature. It stands for alloys containing Te, Ag, Ge and Sb. They are generally compounds between $AgSbTe_2$ and GeTe and are closely related to PbTe because part of the solid solution range has the same NaCl crystal structure.

c. SiGe compounds

Neither Si nor Ge has a particularly high Z at any temperature. Both materials indeed have high carrier mobilities, but they also have very large lattice thermal conductivities λ_L. However, λ_L is considerably reduced when solid solutions between the elements are formed.

	at 300K		
Material	Si	Ge	$Si_{0.7}Ge_{0.3}$
λ_L (W/m/K)	113	63	10

Table 2: Compared lattice thermal conductivity of Si-Ge compounds

The preferred composition is $Si_{0.7}Ge_{0.3}$.

It must be noted that silicon and germanium have been widely studied in view of the importance of these materials for the electronics industry.

B Production of the previously cited materials

a. Growth from a melt

The best thermoelectric materials are usually grown from a melt. The typical temperature gradients range from 2.5 to 25 $K.mm^{-1}$ and growth rates range from 2.10^{-4} to 4.10^{-2} $mm.s^{-1}$. At high growth rate and low temperature gradients, the thermal conductivity becomes undesirably high.

b. Powder metallurgy

Although the best TE materials are obtained by growth from a melt, there is a certain number of advantages in using a powder metallurgy technique:

- Sintered materials are more robust than those melt-grown
- Precautions to establish homogeneity are not required
- It is possible to reduce the lattice thermal conductivity through scattering of phonons on the grain boundaries.

III Link between theoretical coefficient of performance determined by material performance and actual performance of the overall device

It has been explained how the theoretical performance of a thermoelectric can be expressed as a function of materials properties and module geometry. The simplified COP (with optimized geometry) are given below:

Power generation mode

$$COP = \frac{T_H - T_C}{T_H} \times \frac{\sqrt{1+ZT_{av}} - 1}{\sqrt{1+ZT_{av}} + \frac{T_C}{T_H}}$$

Cooling mode

$$COP = \frac{T_C}{T_H - T_C} \times \frac{\sqrt{1+ZT_{av}} - \frac{T_H}{T_C}}{\sqrt{1+ZT_{av}} + 1}$$

However, these levels of performance can never be achieved practically. We have indeed already mentioned the heat transfer that occurs between the hot and cold junction in the space between the legs and around the modules. Other losses can result from electrical resistances and imperfect thermal or electrical contacts.

For any engineering application, we are interested in the performance of the device in which the thermoelectric material is used. It is therefore necessary to know how the overall device efficiency is linked to the theoretical performance. This information is very useful since it is a crucial indication to assess how materials improvement will lead to improved thermoelectric systems.

From data points which could be found, the overall device performance was linked to the theoretical COP calculated from the material ZT. The results are shown in the chart below.

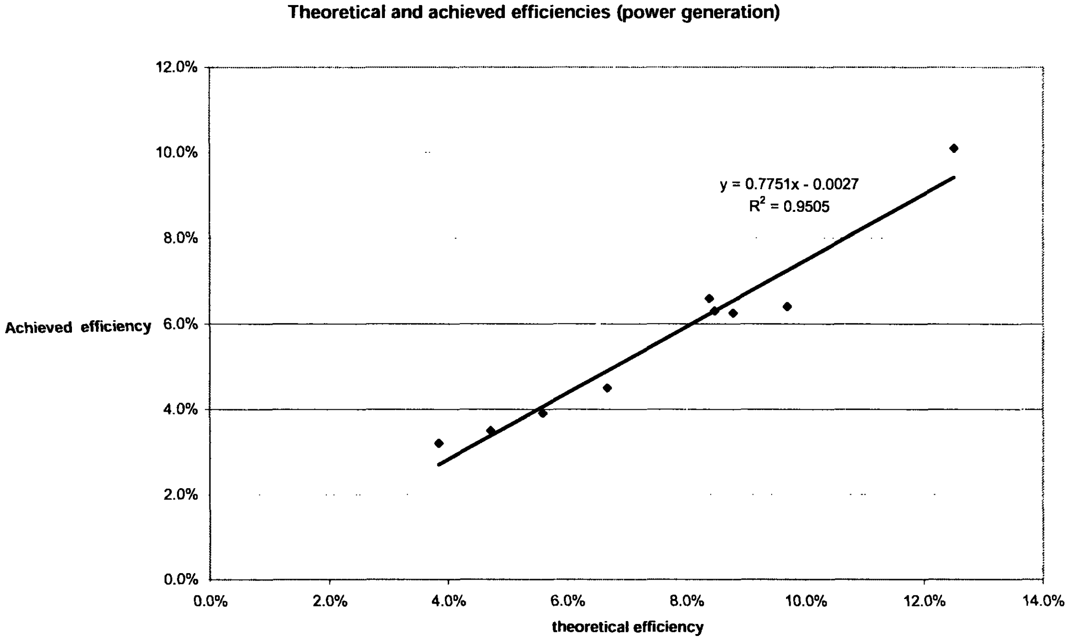


Fig 15: Link between measured achievable efficiency and theoretical efficiency as given by the figure of merit ZT in the case of power generation.

In first approximation, we can take the actually achieved COP to be 78% of the theoretical COP.

This result is consistent with an interview of an industry specialist, Dr. Lon Bell, from BSST. He claims that the performance they currently achieve is 80% to 85% of the theoretical figure. In older commercial activities, they achieved between 70% and 80%, depending on the conditions.

In my estimations of target costs for TE modules, I will assume that thermoelectric systems will commonly achieve 85% of the theoretical efficiency in a few years.

IV Patent search

More than 11,100 patents (issued or pending) are related to thermoelectrics worldwide, out of which close to 3,000 are related to material composition, structure or processing technique. The claims can be separated into different categories:

- Claims on material composition and structure
- Claims on material processing techniques
- Claims on thermoelectric device configuration
- Claims on thermoelectric device manufacturing processes

MIT Lincoln Laboratory

9 filed patent applications could be found by the group working on TE at the MIT Lincoln Laboratory.

Patent Number	Date	Title
WO03100444	12/04/2003	A THERMOELECTRIC DEVICE TEST STRUCTURE
WO03096438	11/20/2003	SELF-ASSEMBLED QUANTUM DOT SUPERLATTICE THERMOELECTRIC MATERIALS AND DEVICES
WO0193343	12/06/2001	NANOSTRUCTURED THERMOELECTRIC MATERIALS AND DEVICES
US2002053359	*05/09/2002*	*Nanostructured thermoelectric materials and devices*
WO0117035	03/08/2001	QUANTUM DOT THERMOELECTRIC MATERIALS AND DEVICES
US6444896	*09/03/2002*	*Quantum dot thermoelectric materials and devices*
WO9842034	09/24/1998	SUPERLATTICE STRUCTURES FOR USE IN A THERMOELECTRIC DEVICE
WO9842033	09/24/1998	Si/SiGe SUPERLATTICE STRUCTURES FOR USE IN THERMOELECTRIC DEVICES
US6452206	09/17/2002	Superlattice structures for use in thermoelectric devices
US5900071	05/04/1999	Superlattice structures particularly suitable for use as thermoelectric materials
WO9416465	07/21/1994	SUPERLATTICE STRUCTURES PARTICULARLY SUITABLE FOR USE AS THERMOELECTRIC COOLIN

Most of the claims relate to the material composition and structure elements (e.g. periodicity and thickness).

The most important patents are:

- QUANTUM DOT THERMOELECTRIC MATERIALS AND DEVICES (WO0117035): This patent protects the QDSL structure for a thermoelectric material made of a selection of metal and semiconductor elements. The patents claims innovation on structure: “A quantum dot superlattice (QDSL) structure comprising: a first plurality of layers formed from material L D_xJ_{1-x}; a second plurality of layers formed from material L J; and wherein: D is a Group VI non-metal selected from the group consisting of Te, Se, and S; J is a group VI non-metal selected from the group consisting of Te, Se, and S; L is a group IV metal selected from the group consisting of Pb, Sn, and Ge; D is not the same as J, L is not the same as J, $0<=x<=1$”. The patents intends to be as broad as possible, with a claim on the substrate used (BaF_2) and a claim on the thickness of the plurality of layers. There is also a claim on the density of quantum dots. The molecular beam epitaxy technique used to obtain the material is claimed in this patent.

- SELF-ASSEMBLED QUANTUM DOT SUPERLATTICE THERMOELECTRIC MATERIALS AND DEVICES (WO03096438). This patent reinforces the previous one. The originality of the structure: alternating layers of a quantum dot material and a matrix material is described. The composition of the material is protected, and the patent aims at being as broad as possible: any material of that structure in which the quantum dot material is selected from the group including a pseudobinary alloy and a pseudoternary alloy and used for TE applications should infringe this patent. The exact composition which enabled a high ZT is also described. There is a claim on the value of the ratio E_g/kT in this patent. A claim on the lattice constant mismatch value between quantum dot material and said matrix material is also present.

- NANOSTRUCTURED THERMOELECTRIC MATERIALS AND DEVICES (WO0193343 and US 2,002,053,359). This patent is more a description of the structure and the resulting properties, namely which maximum temperature difference is obtained for which value of the direct current in cooling mode.

This patent search reveals how difficult it is to protect material structure and composition, especially if the link between structure and properties is not well established or understood. Therefore, IP based upon links between structure and properties may be more valuable.

It must be noted that, as the MIT Lincoln Laboratory has not developed an economical method to process the material, only one claim was reported on the processing technique (claim 8 of WO0117035).

Other Patents

Nextreme, which is the start-up company that is a spin-off of the RTI holds patents on the original structure of its material and fabrication method (US 6,300,150 "Thin-film thermoelectric device and fabrication method of same" and US 6,071,351: "Low temperature chemical vapor deposition and etching apparatus and method")

The patents by RTI/Nextreme differ significantly from the patents that are held by the MIT Lincoln Laboratory in the sense that very few claims concern the material composition.

RTI and Nextreme also hold patents or have pending applications which are more application-oriented: US2006086118 - 2006-04-27; WO2005074463 - 2005-08-18; WO2004049463 - 2004-06-10; WO02081981 - 2002-10-17; US2002174660 - 2002-11-28. It is also interesting to note a chronological shift in the core subjects of the patents deposited by RTI/Nextreme: from patents on materials and fabrication techniques (1999), they filed patents on thermoelectric for applications on DNA genomic and proteomic chips (2002); then they moved to modules configuration (2003) and eventually electronics cooling applications oriented patents (2004-2005).

It is also interesting to look at the patents which are held by BSST, which is currently a big player in the industry. BSST is a subsidiary of Amerigon, which manufactures TE module for heating and cooling car seats. They use conventional TE material (Bi_2Te_3). BSST's main innovations are on the thermal transfer aspects of the device and device configuration. Innovations include:

- (US 6,812,395) The inclusion of agents that improve structural strength, allow current to pass in a preferred direction and minimize or reduce adverse affects, such as shear stresses.
- (US 6,672,076) The association of thermoelectrics in arrays parallel of which pass a convective medium with configurations for increased efficiency. The principle is to place the most suitable couple (that is: made of the most suitable material) for the range of temperature at which this couple will operate in the array (with high ZT at that temperature).
- (US 6,637,210) The powering of thermoelectrics for predefined periods of time to obtain increased efficiency.
- (US 6,539,725) The embodiment of TE legs for reduced thermal losses. As the temperature difference between the hot and cold junctions increases, the length of the TE legs is increased to maintain a constant temperature gradient and thus avoid losses due to heat convection.

The innovations are clearly on the heat transfer management of thermoelectric modules using smart configurations.

This survey on patents reveals that it is certainly harder to infringe patents on processing techniques than on material composition and structure. Innovations on material structure must therefore be protected with their processing technique. Patents on device configuration for better heat transfer management are vital since they enable the full potential of materials.

As thermoelectrics have been confined to niche applications and received relatively little attention up-to-now, there are still relatively few patents protecting the use of thermoelectric technologies for precisely named applications. There is therefore room for patents linking thermoelectric technology to applications no one has thought of yet. Discoveries at the material scale should thus trigger numerous patent applications for the new usage of thermoelectric technology enabled by these breakthroughs.

V Review of applications of thermoelectrics and assessment of their economic value

V.1 Applications of the Seebeck effect: power generation

A High-power generation

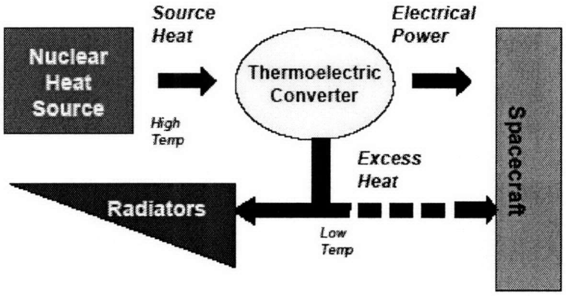
The low efficiency of thermoelectrics-based generators constitutes a main drawback for high power applications. Currently available TE systems can achieve typically 4% to 8% heat-to-electricity conversion efficiency, which compares unfavorably with a standard internal combustion engine (35%) or the best-performing thermodynamic cycles (up to 58% for combined cycles). TE are not economically viable to provide high power level and therefore have been confined to niche applications.

a. Space missions power generation

Thermoelectrics have decisive competitive advantages for powering space missions:

- Missions are long and thermoelectrics have demonstrated reliability and a very long lifetime
- Thermoelectrics do not generate any mechanical vibrations
- They can power a satellite for remote missions where solar irradiance might not be sufficient.

For space missions power applications, thermoelectrics are coupled with a nuclear heat source and convert this energy into electricity. 44 radioisotope thermoelectric generators (RTG) have been used in 25 missions by NASA since 1961. These generators operate between a large temperature differential, typically 300K-1000K. Thermoelectrics for power generation on space missions are currently being developed by the Jet Propulsion Laboratory at Caltech, CA, USA.



From a presentation given by T. Caillat (JPL, Caltech) for the 2005 MRS Symposium

Fig 16: Principles of Radioisotope Thermoelectric Generators

b. Remote instrumentation, automation and communication power systems

Thermoelectric generators are used for diverse remote applications such as providing current to prevent corrosion in oil and gas wells, powering supervisory control and acquisition systems for monitoring, measuring and controlling equipment (e.g.: telemetry units, gas analyzers) in the field. They are also used to power telecom bases in remote locations. They typically serve in remote environments applications for which reliability is key (back-up for remote railways road-crossing). The systems typically function with a heat source obtained from fuel combustion. The thermoelectric technology serves here to convert fossil energy into electricity. The power outputs delivered by these installations typically range from 100W to 5000W. The most powerful commercially available generator is manufactured by Global Thermoelectric, Inc. and provides 550W.

Global Thermoelectrics, Inc. is the only company that still works in this niche market[2]. Their technology is still a technology developed by 3M and NASA in the 1960's. Their thermocouples are PbSnTe couples, which are hand made. Indeed, the company builds its units from scratch: the thermocouples, the combustion chambers, the box which will then be hermetically sealed. Because the power units burn fuel, this application would benefit from

---

[2] Their only "competitor" is PGI which is a spin-off of Teledyne: Teledyne's technology was based on chambers that could create up to 10W of power; typically for a 40W generator, they had to have 4 chambers burning in the meantime. But their catalyst tended to gum-up, it did not burn very well and they could basically never keep all their chambers burning at the same time. Teledyne decided they wanted to go out of this business and PGI bought the smallest generator (up to 8W power). The material used by PGI is Bi_2Te_3.

efficiency increases due to materials improvements. However, they do not make R&D efforts at the material level[3]. Mr Dan Midea, who was contacted, recognizes that Global Thermoelectrics' core technology has evolved little from the technology developed by NASA. Improvements they have made include better controls, new techniques for ignition, and better electronics converters. Because fuel savings is more and more crucial, this technology is moving towards hybrid systems, that is thermoelectrics combined with wind turbine or solar panels. Other developments include the installation of a small motor in adjunction to a liquid-cooled heat sink to force convection and therefore have a more compact system, which is useful on oil platforms (However because of the moving parts, the system is less reliable).

Their application would benefit from efficiency increases due to materials improvements (i.e. higher ZT). This application could constitute a good entry-point for new materials, since it is a company already using thermoelectrics and for them, a new material would constitute a technology improvement, not a technology rupture.

c. Heat recovery from engine exhaust in the transportation sector

A very interesting application of thermoelectrics is waste heat recovery from engine exhaust for power generation. Transportation vehicle such as cars, trucks, motorcycle, submarines and ships are candidates for the installations of TE modules to recover heat wasted by their propulsion systems. Aircrafts are not good candidates because weight is a key performance factor for such applications, and the energy density of oil is higher than that of thermoelectrics. Motorcycles are not as good candidates as cars, ships or submarines because there are not as many electronics that need to be powered. Because the voltage that is delivered by thermoelectrics is typically 12V-16V, it is easily compatible with electronics in a car or any vehicle electronic network in general. In addition to increasing the energy efficiency of the vehicle, special features of TE such as confined space fitting, absence of mechanical vibrations and high reliability are major advantages. It is difficult to know to which extent thermoelectric systems are already in use on military ships and submarines. Nevertheless, the US Office of Naval Research is funding the MIT Lincoln Laboratory to develop thermoelectric materials for applications in submarines. It is obvious that military vehicles (submarines, ships, tanks) are likely to be among the first to receive this technology, since cost is not a decision factor for the army, and technology mastery is a key national security issue.

---

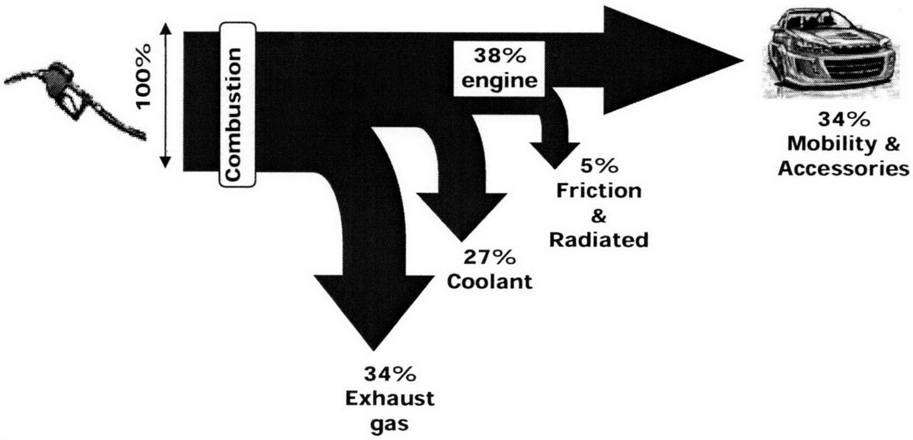
[3] Informations about Global TE Inc. : phone interview, Dan Midea, Salesman

Waste heat recovery from car exhaust

Waste heat recovery from car exhaust has been deeply studied.

- Roughly 1/3 of gas combustion energy goes to the car exhaust. Typical exhaust output at normal running speed for a family car is 10 kW.
- The limited space around a car engine and its exhaust favor the use of thermoelectric technology to recover these losses.
- Increasing oil prices and rising environmental concerns have driven car manufacturers to develop more efficient propulsion technologies.
- TE technologies can be used for other purposes in automobiles. Some car manufacturers already have partnerships with companies working in TE and expertise in implementing thermoelectrics.
- The automotive market is huge, still growing and very diverse. It is also very competitive. All these factors favor the implementation of new technologies.

Nevertheless, waste heat recovery from car exhaust is a high volume, low profit market and thus apparently not a good entry-point for a new technology. However, there are markets inside the car market, and thermoelectrics could be successfully introduced in certain segments such as luxury vehicles, "green" vehicles and commercial vehicles before spreading to consumer automobiles.



from a presentation given at the MRS Symposium by John W. Fairbanks, Dec 2005

Fig 17: Energy losses in a car

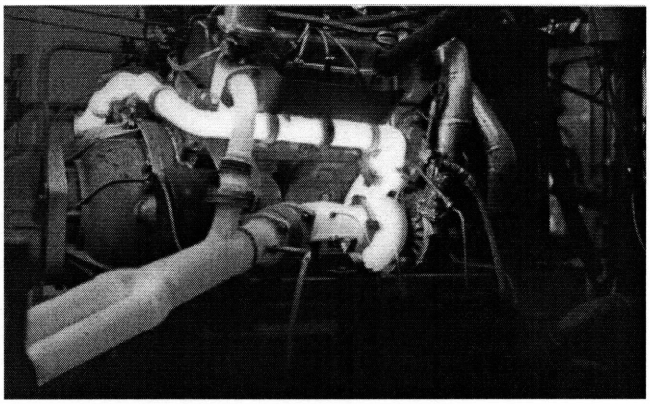


Fig 18: Confined space around car exhaust makes TE technology a good candidate for waste heat recovery

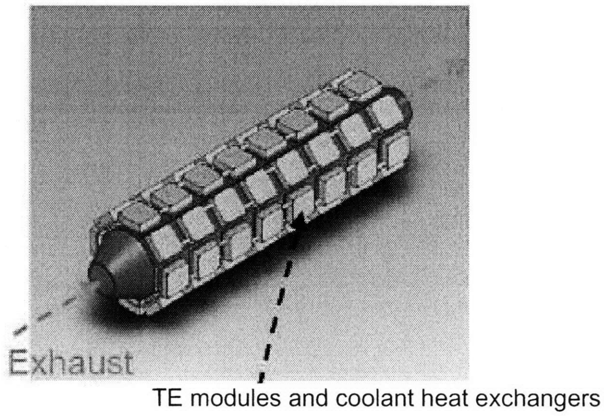


Fig 19: TE modules associated to a car exhaust pipe

An estimation of an upper price bound for thermoelectric modules used in high volume US automotive applications can be made using the monetary value of the fuel saved by the use of this technology. The estimate which follows is largely inspired from a presentation Mr Francis Stabler gave during the 2005 MRS Symposium and from further exchanges I had with him.

Estimation of the monetary value of fuel saved through the use of TE

We assume a typical US driver who drives 15,000 miles (average driving distance in the US) per year, gets about 25 mpg, pays $3 per gallon for gas (close to current gas prices in the US), and looks for a payback for a fuel economy feature in 3 years (Different values could be used. This is just a point estimate. A sensitivity analysis was conducted [7]). Assume the TE technology enables a 10% fuel economy- discussed below, this is a very aggressive target not achievable with currently available materials. This technology would enable him/her to save $180 per year and $540 in an expected 3 year payback period. Note that we did not make any assumption on the costs associated with changing current standards equipment. Nor did we consider government incentives to encourage the purchase of fuel economy technologies.

Our string of assumptions leads us to a value of $540 to the US consumer for a complete thermoelectric generator integrated into a vehicle. Based on a rule of thumb for automotive system design, it is assumed that the thermoelectric modules have to be less than 25% of the total subsystem cost[4]. We therefore come down to a target cost of $135 for the TE power generating modules which could lead to 10% fuel economy.

Required material performance for TE enabling a 10% fuel economy

According to the federal test procedure (FTP) used to measure emissions and fuel consumption by the EPA, the typical vehicle road load is in the 12 to 14 horsepower range or 8.9 to 10.4 kW. If we take a rounded figure of 10kW, a quick analysis leads us to a desired TE efficiency η=17% to achieve an output of 1kW[5]. If we assume the module would operate between 975K (exhaust temperature) and 300K (ambient air), that the TE system efficiency would be 85% of the theoretical efficiency, then a ZT=1.4 is needed to achieve this level of performance.

This rough analysis sets a target cost of 13.5cts/W generated, with a TE module of efficiency 17%, which transforms to an 'average' ZT of 1.4.

While many other factors must be considered, this sets a possible upper price bound for thermoelectric modules used in high volume US automotive applications.

---

[4] This is a rough carryover from F. Stabler's experience with conversion of mechanical systems to electronic controlled systems. The thermoelectric modules have to remain a relatively low portion of the cost (possibly even less than 25%), because of the many other costs to install a thermoelectric generator into a vehicle. Some of these costs are the packaging of the thermoelectric modules and the related components.

[5] If we could generate an average of 1kW of electric power using thermoelectric technology, the next big issue to overcome would be to determine how to use the power to best reduce energy consumption. Eliminating the generator on the FTP is only a 3 or 4% fuel economy gain because of the low electric power requirements on the FTP (about 350W). Converting some mechanical loads to electrical can also reduce fuel use, such as an electric coolant pump. The reduced parasitic losses are greater than the lower efficiency of the electrical pump and can provide 0.5 to 2% fuel economy gains. Other areas to investigate are electric oil pumps, electric power steering, etc. With all these possibilities, to get to 10% fuel economy gain on the FTP (CAFE fuel economy numbers), a way to use part of the power to turn the wheels is almost certain to be needed.

It must also be noted that:

- We do not take into account customer perceived value or image: for instance some customers may be willing to pay more, assuming longer term payback, to help the environment, or for additional features enabled by increased electric power but the value is not estimated here. It is interesting here to look at the commercial success of the Toyota Prius, which is a hybrid electric vehicle. A recent survey among Prius owners showed that the first reason why people bought this car is the status it conveys as an environmentally friendly person[6]. The Prius has the words "GasElectricHybrid"[7] written under its license plates. Professor Ceder of MIT jokes that people are willing to pay a premium of $3,000 to $4,000 for the three words "GasElectricHybrid"[8]. Even with increasing gas prices and the gaining economic value of this technology, the perceived value to consumers is still higher. Could this perceived value exist for TE technology? I am not sure. Firstly because the fuel savings enabled by the Prius are definitely higher (about 33%)[9]. Secondly, because the HEV is a technology disrupter, whereas thermoelectrics are no more than a fuel saver. Could Toyota have built such a commercial success with a better engine enabling 33% fuel economy? Nothing is less certain.
- There are many locations in the world (Japan and Europe) with much higher fuel prices ($6/gallon in some European countries). Carefully selecting the region of the world to introduce thermoelectric technology can allow higher initial prices for systems.
- Waste heat recovery could also be used in association with fuel cells if fuel cells were to become a credible way to power cars.

Requirements for automotive TE systems

- The system must operate in extreme environments: must operate over a wide range of temperatures (-40 to 150° F system ambient), must resist mechanical vibrations and shocks and must resist thermal shocks (locations changes and because exhaust gases go from ambient to 500°C in less than a minute with occasional peaks of near 1000°C)

---

[6] Source : Pr. Gerbrand Ceder, MIT & http://dadahead.blogspot.com/2005/10/hybrids-as-status-symbols.html

[7] The next branding step for HEV is believed to write visible somewhere on the frame of the car the performance, both in terms of fuel savings and acceleration capacity of the automobile.

[8] Prius owners include celebrities such as Tom Hanks and Sting. The Lexus RX400 Hybrid is a 4 wheel drive (!) hybrid car which is a huge commercial success (owners include Prince Albert of Monaco) in spite of a poor mpg performance.

[9] 45mpg for the Prius if driven around town compared to a standard car giving 30mpg.

- The system must be durable: long life with limited or no maintenance. The average car in the US is 10 years old.

To be successful, the TE system will have to operate consistently in a wide variety of conditions and with aging. Nevertheless, given the nature of the technology and its demonstrated durability in space and remote power applications, these constraints will be achievable.

Current state of development

BMW, which is one of the contributors to the "DOE 10% fuel economy" program, should be the first automobile manufacturer incorporating a TE waste heat recovery system in the 5 Series 3L (model year 2010).

Market estimates for TE use in the automotive industry (from F. Stabler's analysis)

The annual new vehicle volume is over 60 Million cars and light trucks manufactured annually (2005) and will approach 70 million per year by 2010. If we assume an average 1kW of electric power needed per vehicle (conservative), 60 Giga-watts of generating capacity would be needed per year. Even if only 10% of vehicles get thermoelectric generators, a quantity of modules with 6 Giga-watts capability will be needed.

Competing technology

Any technology that improves a vehicle's fuel efficiency is a competitor for thermoelectric systems and the key decision factor is fuel efficiency gain per dollar.

d. Waste heat recovery in industrial applications

The industrial sector consumes 31% of the energy consumed in the world[10]. Losses are numerous: 60% of the energy converted in power generation is wasted[11]. For example, it is estimated that 20% of the fuel input in a gas turbine could be used as input in power generation from TE modules [8]. A study of the potential of waste heat TE power generation for diesel cycle and gas turbine in the manufacturing industrial sector demonstrated that the potential net power generation of a country like Thailand could be about 100MW [8]. With

---

[10] IEA Key World Energy Satistics 2005

[11] The Economist (US), 378 (8469): 76US, March 18, 2006

increasing energy prices and TE technology developments, thermoelectrics could become competitive for some industrial waste heat recovery applications.
However, it must be noted for effective energy management, that before investing in heat recovery equipment, other more effective steps such as process control, maintenance improvement or adjustment of excess air rate must be considered.

Few advantages can be drawn from the specifics of TE technology for this application:

- Mills and plants are generally not located in places where space is an expensive resource. Therefore the fact that TE can fit in a confined space is not readily advantageous.
- There are little advantages from the fact that thermoelectrics have no moving parts: plants are noisy and thus there is no point in paying for a premium for the quietness of TE technology. In addition, the main competitor of TE for waste heat recovery is cogeneration, which is also not noisy). Most of the equipments in the factories have moving parts, and therefore the inconvenience caused by mechanical vibrations is already existing, although the high reliability and absence of maintenance is a good selling point for TE. While the absence of required maintenance is a selling point, the presence of employees working on other equipments but easy to train to the maintenance of a waste heat recovery system might eliminate this advantage.
- TE modules used for industrial waste heat recovery are likely to be subject to large temperature variations, which would induce thermal stresses and therefore make the use of thermoelectrics difficult in practice.

In addition, in order to get a high enough power output, the modules have to be operated between two sides with a significant temperature difference. In most existing industrial processes, the heat is rejected into the environment around the equipment, and it would be very costly to isolate the two sides of thermoelectric modules. Thermoelectric technology could only be competitive for closed systems with a cooled part and a heat source. It is shown that a vacuum environment favors the heat flux penetration (under 30 Pa between the legs is desirable) [10].

The key decision factor for this application is the energy savings expressed in \$/yr enabled by the adjunction of a TE generator to the industrial installation. This will have to be compared to the annualized lifetime cost of the thermoelectrics (mainly cost of TE system plus installation, since there should be little maintenance) in $/yr. This is likely to vary a lot from one industry to another, and even inside a given type of industrial installation, from one plant to another.

A survey of the economics of thermoelectric technology in the industrial sector in Thailand was conducted [8]. Using typical installation and maintenance costs of TE systems in a plant, the 2002 electricity prices in Thailand, and the efficiency of conventional bismuth telluride modules operating between a typical temperature range, it was reported that the break even point for the installation of TE was 17 years. A sensitivity analysis was conducted, and even in the most favorable case, the break even point would be at least 9 years, which is a long period of time for an industrial installation.

A model was developed to find the cost of electricity produced by thermoelectrics from industrial waste heat recovery as a function of industrial parameters, materials properties, operations conditions and economic data (Fig 20). See appendix for a detailed explanation on the model.

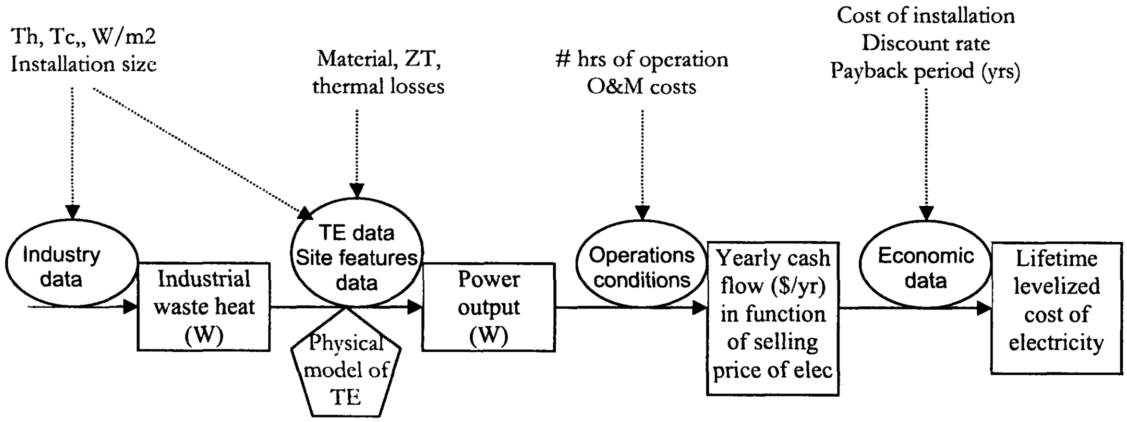


Fig 20: Economic model for industrial waste heat recovery using TE technology

These calculations were based on a per area basis, and the cost of installation of thermoelectric modules was taken on a per area basis.

When reading the charts and results of this model, it must be recalled that the price paid by the industrial sector for electricity in the US averaged 5.76 cts/kWh in March 2006 with large disparities (13.64 cts/kWh in New Hampshire and 3.64 cts/kWh in West Virginia). This price also fluctuated highly in the last years. TE may thus be economically viable in certain regions of the world and at certain periods but not in others.

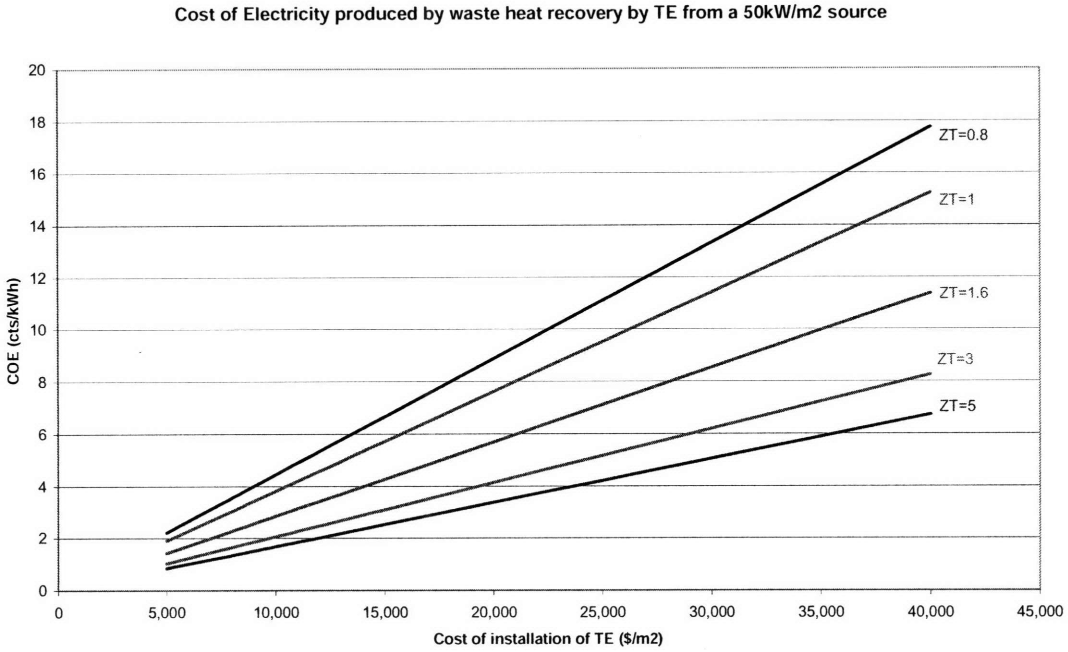


Fig 21: Cost of electricity depending on cost of installation. T_H=673K, T_C=323K, f=75%, N (Payback period)=10yrs, o&m=$0/m^2, r=7%, Heat Input=50kW/m^2

It appears that, for the considered installation costs, thermoelectric technology could be competitive and should be considered in the regions where the price of electricity is high. For an installation cost of $20,000/m^2 to $30,000/m^2 (which is the most likely range), a materials improvement from ZT=0.8 (currently commercialized Bi_2Te_3) to ZT=1.6 would make this technology competitive in certain regions of the world. However, it must be noted that the results given by this model are very sensitive to the parameters.

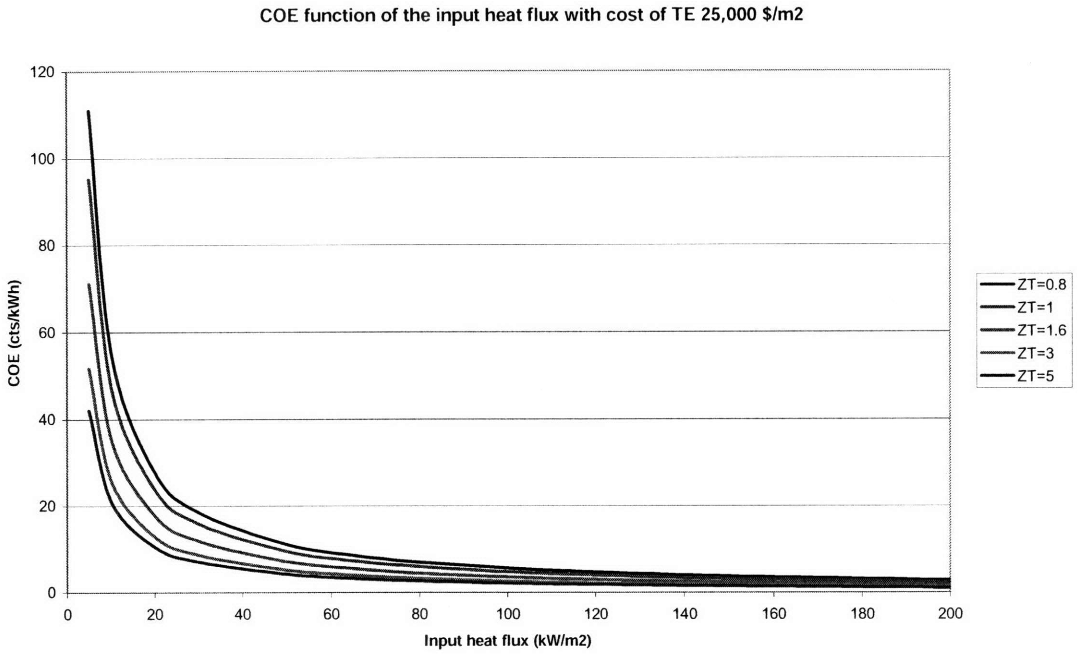

COE function of the input heat flux with cost of TE 25,000 $/m2

Fig 22 Cost of electricity depending on input heat flux. T_H=673K, T_C=323K, f=75%, N (Payback period)=10yrs, o&m=$0/m^2, r=7%, cost of install.=$25,000/m^2

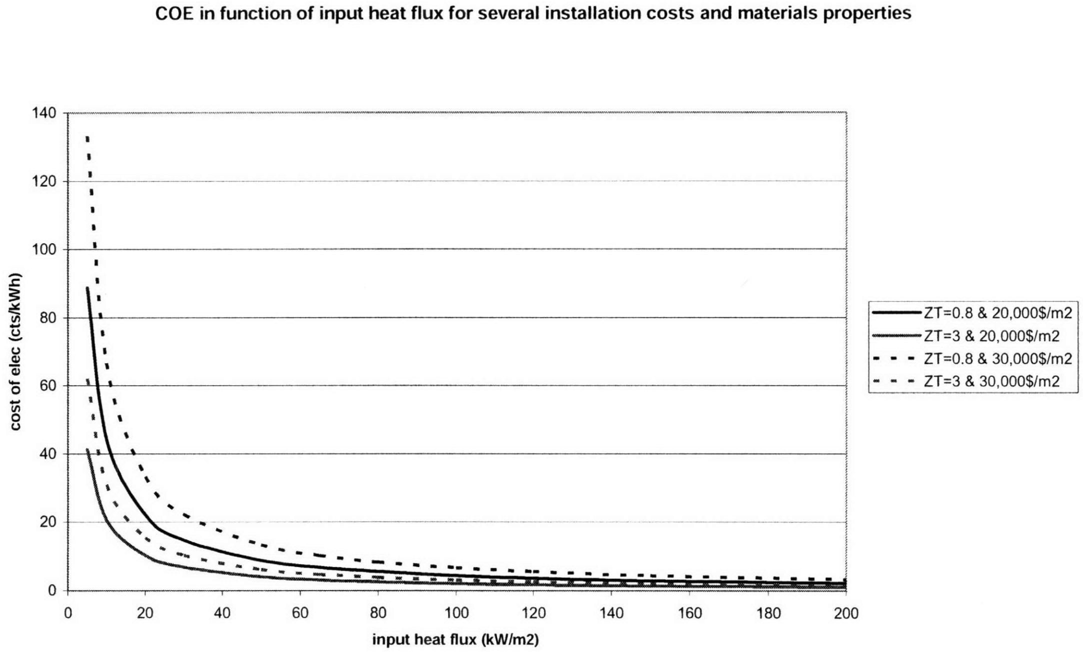

COE in function of input heat flux for several installation costs and materials properties

Fig 23: COE function of input heat flux for several installation costs and ZT. T_H=673K, T_C=323K, f=75%, N (Payback period)=10yrs, o&m=$0/m^2, r=7%

It is also important to consider the scale of the system when proposing the implementation of thermoelectric technology to recover waste heat from the industry: first, because it obviously reduces the cost of installation (economies of scale); and second, because installing a critical size is necessary to make it worth the time and effort devoted to these investments. As a matter of fact, if the electricity produced is to be sold to the grid at a rate of 5cts/kWh, the typical yearly revenue generated is ~\$1,600/yr/m^2, and therefore installing 5m^2 of useful area may not generate an high enough revenue stream at the scale of the budget of a plant to be considered a worthwhile investment (especially considering the potential difficulties and uncertainties).

Competition

The most common way to recover waste energy is to heat water, either for central heating application (cogeneration) or, if the water can be vaporized easily, to run a steam turbine. The economic comparison would be the net present value of each project (installation of thermoelectrics to sell the electricity generated the grid or to be used internally vs. cogeneration)

The economic value of this technology is also highly dependent upon the price of electricity, which can experience large variations[12]. Because the energy sector is cyclic and because thermoelectric technology requires a quite high original investment compared to other technologies, TE projects generally do not offer a high Net Present Value.

The recent material improvements are not sufficient to enable large utilization of TE for industrial waste heat recovery. However, intelligent use of modules in some configurations could prove viable in some cases [9] or in some regions where electricity is very expensive. Some companies are currently investigating the usage of TE conversion systems to recover heat from industrial furnaces [10].

An example: waste heat recovery from aluminum manufacturing process

The use of aluminum in car body could result in weight reduction and therefore fuel savings. Currently, only luxury cars use an aluminum frame and body because of high costs. For these cars, the use of this lighter material instead of steel enables up to 600 lbs weight reduction. As a rule of thumb, a 10% weight reduction provides 6% to 7% improvement in fuel economy[13].

---

[12] http://www.solarbuzz.com/SolarpricesUSA.htm

[13] Source : John W. Fairbanks, DOE

The aluminum manufacturing process consumes much electricity. As a data point, the Pechiney (now Alcan) plant in Voreppe, France, consumes as much electricity as the city of Lyon, France (465,000 inhabitants). The losses in the aluminum manufacturing process in the form of Joule heating are huge. The heat losses from the site of Voreppe (France) are estimated to be ~33MW[14]. However, the use of thermoelectrics to recover heat from the aluminum baths is complex. In Voreppe, heat is recovered above the batch by heat exchangers. Heat losses from the walls (wall temperature=352°C) of the bath which emit and radiate in the surroundings are not recovered. The main issue if thermoelectric technology were to be used to recover these losses would be to isolate the cold side of the module to maintain a high enough temperature gradient.

B Low-power generation

a. TE use in low power generation

The use of thermoelectrics for low power generation applications has been reported. Microwatt or milliwatt power could be generated by TE devices converting the body heat flow or the external side of a water pipe into electricity. This is a form of waste heat recovery, with free energy supply and for which performance is generally not measured in terms of COP=Electrical Energy Output/Waste Heat Input. The decision criteria here will be the cost of supplying energy to the device considered over its lifetime.

Energy supply for small, independent and wireless systems is mostly provided by batteries. In other special cases, alternatives power sources are used. However, thermoelectrics do not constitute a plausible alternative to batteries for several reasons. First, it has been mentioned that low voltage-low power TE generators could be an environment-friendly alternative to batteries [11]. However, the disposal of low-voltage batteries is well-established and controlled (in developed countries at least) and their impact on the environment is relatively small compared to other technologies. Thus, they are far from being the primary concern in terms of environmental impact for the general public. Second, the environmental cost of the

---

[14] Phone Interview, M. Beauvais, ex-Alcan. 200 baths with a tension of 4.5V each receive between 180 and 300kA. Out of these 4.5V, 1.2V is the useful emf, 0.7V are power surges at the electrodes and 2.6V are losses (from which 1V is recovered to heat up the batch).

production of thermoelectric generators, although not established in this paper, is not negligible; and perhaps higher than the beneficial impact of the replacement of a battery by an equivalent thermoelectric generator. People would be unlikely to pay a premium to replace their cheap batteries with a thermoelectric system. The decision criterion to replace batteries by thermoelectrics is and will remain the lifetime cost of energy supply to the device considered.

Operation between body temperature and ambient

One idea is to use the difference between the temperature of the human body and the ambient air to power systems such as a wristwatch, hearing aids or a pacemaker. However, this presents a series of challenges. In some rare cases, the ambient temperature (air or water) can be too close to the skin temperature of ~30°C. For these cases, a back-up power system has to be inserted, which adds complexity (and thus cost) to the system.

Technical feasibility of powering devices from temperature difference between body and ambient temperature

The typical current drain for wrist watches is 10 to 40μA [12], coupled to an operating voltage of 1.5V. The needed power is thus in the range 15μW to 60μW. Wristwatches can typically need up to 100μW.

Leonov *et al*, from the IMEC in Leuven measured the heat flux on a wrist, on the radial artery, along with the psychological reaction to the presence of a thermoelectric generator placed on the skin [13]. They were able to determine the heat flow at a watch position on a wrist. They reported a range of 8.9 to 35.8mW/cm^2 heat flow on a wrist, with an average of 18.8mW/cm^2. The average skin temperature was 30°C at an ambient room temperature of 22.3°C. Their experiments were carried out inside a building. In the case of forced convection, which could be due to walking, presence of wind or a working fan in the room, the heat flow through the skin might deviate significantly from their results. However, for the application to power wristwatches, hearings aids or pacemakers, we have to be conservative and assume that a minimum heat flux is available, and this would be without forced convection. In our hypothesis, we will thus take their minimum measured value of a round number of 10 mW/cm^2, which is at the low end of their measure range.

It is also important to note that the results described here must be taken carefully if to be extrapolated for applications to hearing aids or pacemakers. The body has a non-uniform temperature distribution, not only due to the clothing covering most of the body surface, but also because of anatomy and the cardiovascular system. For example, Leonov and co-workers reported that the heat flow is about three times higher on the other side of the wrist, where the watchstrap usually is, than on the side of the watch typical placement. The heat flux achievable by the ears might be significantly different.

It is possible to calculate what power output we could get from a TE generator to power a wristwatch using different materials:

Assumptions:

- The system must work on the 'least powerful' persons, i.e. emitting 10mW/cm^2 at the back of the wrist (i.e. the area of watch placement.)
- Assume a contact area of 1cm^2 (conservative).
- Take the actual COP of the device to be 85% of the theoretical COP as given by the material figure of merit ZT
- Take T_H=30°C and T_C=22°C

We get:

T_H (K)= 303 T_C (K)= 295 η(Carnot)= 2.6%		Input(mW)= 10					
"ZT"	0.6	0.8	1	1.6	2	3	5
Actual COP	0.27%	0.33%	0.39%	0.53%	0.61%	0.75%	0.95%
Output (μW)	27	33	39	53	61	75	95

Table 3: Power output from human body heat-case 1

The same analysis can be conducted with a more optimistic assumption regarding the body heat flow: 18.8mW/cm^2 and the same temperatures:

T_H (K)= 303 T_C (K)= 295 η(Carnot)= 2.6%		Input(mW)= 18.8					
"ZT"	0.6	0.8	1	1.6	2	3	5
Actual COP	0.27%	0.33%	0.39%	0.53%	0.61%	0.75%	0.95%
Output (μW)	50	62	73	100	114	142	179

Table 4: Power output from human body heat-case 2

In a unfavorable scenario of a high ambient air temperature T_C=27°C and a higher value of the skin temperature (T_H=31°C):

T_H (K)= 304 T_C (K)= 300 η(Carnot)= 1.3%		Input(mW)= 10					
"ZT"	0.6	0.8	1	1.6	2	3	5
Actual COP	0.13%	0.16%	0.19%	0.26%	0.30%	0.37%	0.47%
Output (μW)	13	16	19	26	30	37	47

Table 5: Power output from human body heat-case 3

It is therefore viewed that using only 1cm^2 of skin area to generate electricity will not enable to power a wristwatch in some scenarios, even with TE materials not-already available. The technological feasibility of such devices is not proven. Nevertheless, Citizen Watch Co. has developed a thermoelectric-powered wristwatch as part of its Eco Drive series. It is powered by 1,242 thermocouples. However, problems arise when the watch is not being worn (a power save functions first makes the second hand moves at two-seconds intervals (with the help of a small rechargeable battery); if the watch is not worn for a few hours, it stops and the time has to be reset when being worn again. It must be noted this Citizen watch is not water resistant for sports practice, but it is not known whether it is because of the use of thermoelectric technology. This device is no longer commercially available for reasons unknown.

Issue on comfort

Another interesting result of the IMEC study is the fact that, on a sample of 158 persons on whom the survey was performed, 54.5% claimed that the device on their wrist was too cold and thus non-acceptable. Although the heat flow and body temperature of these "unhappy" subjects were similar to those of the "happy" ones, this psychological reaction to a wrist TE generator might constitute a severe drawback to commercializing a thermoelectrically powered wristwatch.

Competition

Wristwatches can be battery-powered, solar powered, kinetically powered or use other less common power sources. Kinetic powered quartz watches make use of the motion of the wearer's arm turning a rotating weight, which in turn, turns a generator to supply power. However, the most common power source is the battery, the most common of which is the silver oxide and lithium battery. A watch button cell battery typically costs $2; the lifetime cost of powering a watch using a battery is therefore around $4, potentially $50 if the impermeability of the watch must be redone. Thermoelectrics are far from being competitive for these low power generation applications, mainly because of the low production volumes.

In most cases, these systems will not have to operate under extreme conditions (withstandable by the human body) and the replacement of the battery is easy, thus the competitive advantages of TE will not be sufficient to drive adoption.

Potentially interesting products to be developed

For portable devices, an ethanol powered thermoelectric could be a candidate for battery replacement. Initial costs might be similar, but refueling instead of recharging might be a selling point for early adopters.

Another idea is a thermoelectric generator which could be coupled to a battery, recharging the battery when the device is being worn or the temperature difference between body and ambient is high enough. Such a system would enable complete autonomy from an external power source. This kind of application, which could for example replace the charger of a cell phone, would become common if it were to be technically feasible. We can study the feasibility of such a TE-powered battery from temperature between body and ambient:

- Take the heat flow from the palm to be 90 mW/cm^2 instead of 10 mW/cm^2: the capillarity on the palm is much better than on the wrist, and the steady state flow that can be drawn out of the wrist artery was estimated to be 90 mW/cm^2 [13]
- Take the hot temperature to be 35°C
- Assume a contact area between palm and cell phone of 3 cm x 2 cm=6 cm^2. The heat flow from the body is thus estimated to be 540mW.

T_H (K)= 308 T_C (K)= 295 η(Carnot)= 4.2%		Input(mW)= 540 (=3*2*90)					
"ZT"	0.6	0.8	1	1.6	2	3	5
Actual COP	0.43%	0.53%	0.63%	0.85%	0.98%	1.21%	1.53%
Output (mW)	2	3	3	5	5	7	8

Table 6: Power output from human body heat for rechargeable portable devices

Assuming the new generation of thermoelectric materials would be fully developed, we could get ~5mW of power. The features of a typical cell phone battery are: 3.6V and 800mA-hr capacity. A full cell phone battery thus stores ~2.8Whr. 560 hours would be needed to recharge the cell phone battery by holding the phone in one's hands. These applications are thus not realistic at present.

V.2 Applications of the Peltier effect

A Cooling and heating applications

a. Car seat heating/cooling

Methods to use thermoelectrics for car seat cooling and heating are already available. Although this is potentially a high volume application, it is still a luxury, and therefore this market segment still allows relatively high prices. The price for the end-consumer of such a system in his/her car is estimated between $5,000 and $12,000 per car.

This application is nevertheless an interesting illustration of the numerous competitive advantages of TE technology. First, the same system is used to heat and cool the seat, depending on the passenger requirement. Second, the absence of moving parts and of mechanical vibration and the system's high reliability are key arguments over compressor-based technologies. In addition, the thermal management system has to fit in a confined space and must not be position dependent (since the seat must be allowed to recline). It is therefore easy to understand why thermoelectrics are the perfect candidates for such an application. The idea behind the seat thermal management is to offer direct thermal management to the occupant. As a matter of fact, the typical air-conditioning system in a car typically pulls 3kW to 4kW, but 40W of cooling directly on the passenger's back bring a notable additional comfort.

Amerigon is the main player in this market segment. They sell their technology to the seat manufacturers who, in turn, insert them into the seats and sell them to the car manufacturer. Modifications must be made to a classic automobile seat, since a diffusion layer must be added to the cushion so that the cold or warm upcoming air flow is not unpleasant: the air coming through the seat is diffused by a reticulated film which distributes the flow uniformly. Amerigon's technology is made of two TE systems per seat, with a cooling power up to twice 30W of cooling (10W to 20W per module in typical use). Reversing the current, the system functions in heating mode and can offer up to 120W of heating (100W in typical use).

Amerigon uses conventional Bi_2Te_3 material. Even though they are working on segmented material in R&D, Dr Lon Bell do not expect the main improvements of their products to come from materials development, but from better heat transfer management and the reduction in the number of parts. Besides, it must be noted that the thermoelectric material costs in this system represent 12% to 15% of the system cost[15].

In the long term, thermoelectric systems might also replace the main air-conditioning system in cars.

Competition

The competition to such an active heating/cooling is a system that would bring air from the car HVAC to the seat at the same temperature as the temperature required for the HVAC system, or an independent, mechanical HVAC system for the seat. Response time is longer (it is necessary to wait for the car engine to warm up to get a good heating) but it is also probably not cheaper because of the low power required. A heating system for car seats (air heated by contact with heat losses from engine) is already widely available (eg: Peugeot 607 or Renault VelSatis offer this option for a few hundreds of dollars). It is for cooling and response time that thermoelectric technology is actually a superior offer over commercially available technologies.

Market estimates for the use of thermoelectric technology in the automotive industry for passenger cooling

The annual new vehicle volume is over 60 millions cars and light trucks manufactured annually (2005) worldwide and will approach 70 million per year by 2010. For vehicle passenger cooling: If we assume 60% of vehicles get cooling features (air conditioning) and 4kW of cooling is required per vehicle, then 144 GW of cooling capability will be needed.
For the seat thermal management market, assuming 30% of the cars adopt it worldwide by 2010, 5 GW of cooling capability would be needed per year. Amerigon shipped one million TE modules of its Climate Control Seat (CCS^{TM}) system in 2005.

b. Automobile beverage heater/cooler

Most new cars are equipped with beverages racks. It is natural to think of controlling the temperature of these holders by thermoelectrics and thus heat or cool the passengers' drinks on demand. For such a small power, small scale application in a confined space, thermoelectrics are definitely good candidates. They would enable large heating or cooling,

---

[15] Phone interview, Dr. Lon Bell, BSST, April 20, 2006

and fast response time. However, the real interest and value of such an application is questionable: for hot drinks, the good isolation properties of the paper cup associated with the holder (which somehow prevents air-flow around the cup and thus reduces convection) lessen the need for a drink heater. Hot drinks remain hot long enough when consumed in a "standard" time lag. The same comments apply to cold drinks, although there is a need to cool cans containers that are at ambient temperature.

An internet search indicates that it is possible to find a 12V mini cooler/warmer box, which uses thermoelectric technology, that plugs into the cigarette lighter outlet for $50. An individual cup holder cooler/warmer can be purchased for $30[16]. This potentially sets an upper bond to the price people would be willing to pay for such an option. Once again, the thermoelectric modules have to remain < 25% of the total cost of the subsystem. New thermoelectric materials would not bring any additional value to the system, since the currently available materials allow the design of a small cup holder; a large enough temperature shift and a fast enough response time.

c. Motorcycle helmet and clothing

Motorcycle helmets are potentially good candidates to receive a Peltier cooling/heating system. It is actually one of the applications claimed by several thermoelectric modules manufacturers, even though I could not find a single helmet incorporating a thermoelectric cooling system. Only eight patents or applications worldwide could be found for "helmet+thermoelectric(s)" on the European patent office database, which leads me to believe no helmet incorporating this technology is currently commercially available.

Because motorcycle operator's head emits heat, this can cause discomfort or even unsafe conditions. For example, heat which is trapped within the helmet interior can cause the visor to fog and obscure vision. Sweat dripping down in the operator's face can also be distracting and obstruct vision. To solve this problem, helmet manufacturers have tended to provide vents or air intake openings in the helmets, typically in the front portion of the helmet facing the oncoming air flow while driving. But thermoelectrics could bring a better solution to this issue. The required cooling power is estimated to 5 to 20W, most likely around 15W[17]. This value is not clearly defined and could be higher because the helmet foam is not a very good heat conductor, and no system to force convection can really be imagined in that case (fan).

---

[16] http://www.autosportcatalog.com/

[17] From the numbers used for the « low-power generation » section: if the human head emits~10mW/cm^2 (when protected), with a radius of ~10cm, the heat emitted is 12W. It is also the estimate that could be made from [11] knowing that they used a 40mmx40mm Bi_2Te_3 TE element to achieve comfort in their helmet experiment.

Weight should not be an issue, since the weight of the overall system (TE+battery) could be in the range 100g-150g [11] for helmets weighting 1.5 kg or higher. Safety is definitely an issue, since the newly design helmet must pass the conformity tests before being commercialized. It could even be imagined to power the TEC by a photovoltaic cell incorporated on top of the helmet but probably not as an entry offer.

The price costumers might be willing to pay depends on several parameters: the level of additional comfort such a system brings to the operator, the location where the motorcyclist rides and the market segment to which he/she belongs. The motorcyclists' spirit and utility for such a system varies between the races enthusiasts and the person for whom the motorcycle is simply a means of transportation. The former will be more sensitive to marketing ("what top competitors wear") than the latter, who would see it as a good feature to avoid to be sweating when arriving at work. Helmet prices vary from $70 to $700, and the value of a TE cooler incorporated in the helmet would probably be ~$100[18].

Clothing

The military is investigating the use of thermoelectrics for thermal management of the soldier of tomorrow (lightweight system of cooling and heating on-demand) and for portable power (however, as we already mentioned, the power that can be drawn out of the human body is certainly too low). Such a system could be available to the public several years later (motorcycle jackets, mountaineering or sailing jackets, gloves).

BSST is currently working on the incorporation of TE in helmets and clothing (jackets and gloves).

d. Laboratory Cold plates

The Peltier effect has been used in laboratory cold plates systems for the last 10 or 15 years. One of the most common applications of these apparatus is PCR (Polymerase Chain Reaction).

PCR is a molecular biology technique invented in 1985 by Kary B. Mullis (Nobel Prize in Chemistry) for enzymatically replicating DNA. PCR is now commonly used in medical and biological research laboratories for a variety of tasks, such as the detection of hereditary diseases, the identification of genetic fingerprints, the diagnosis of infectious diseases, the cloning of genes, paternity testing, and DNA computing. The PCR process usually consists of a series of 15 to 30 cycles, each of which consist of three steps: denaturating (separating the

---

[18] From the prices of additional options

strands in the double-strand DNA), annealing (attachment of the primers) and elongation (copy of the DNA strands by the DNA polymerase). The two first steps require different temperatures, and therefore a shift is needed from a high temperature of 94°C-98°C (depending on the polymerases used) to a low temperature of 45°C-65°C (depending on the primers used), and then back to the high temperature for the following cycle. The first step can last anywhere from 10 seconds to a few minutes (usually 1 to 2 minutes) and the second and third steps last for a few minutes. A Peltier system provides a practical way to change temperature, which is why they were adopted in PCR thermal cyclers.

There are two types of PCR thermal cyclers: either the apparatus is a tube rack, the temperature of the tube holder being controlled by the thermocouples (old version) or it is a plate with ~100 wells and the wells (depressions) are filled directly with the medium.

from: http://www.bio-rad.com/amplification/

Fig 24: PCR thermal cycler by MJ Research.

The Peltier effect is definitely a good candidate for this application, because it enables both cooling and heating, fast switching times and good temperature control. The absence of mechanical vibrations is also a plus and the apparatus directly cools the content. The alternative before such equipment was available was to carry test tubes between water batches at different temperatures. Peltier effect thermal cyclers enable faster and more precise operations with less manual intervention. In addition, some apparatus have a gradient function, which allows different temperatures in different parts of the block (see Fig 25). This is particularly useful when testing suitable annealing temperatures for primers.

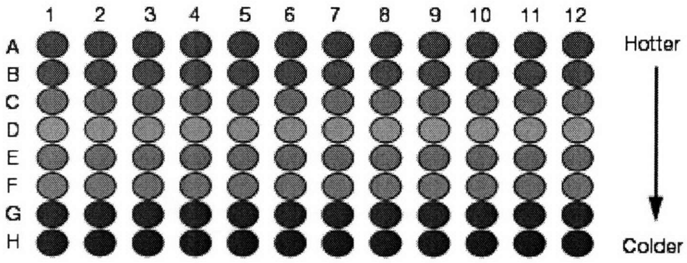


Fig 25: Gradient function of the PCR thermal cycler. Each dot is a well which is filled with the medium.

It must be noted that these apparatus are expensive ($2,500-$6,000) and would theoretically be a good entry-point for a new technology, because the complexity of the equipment and the software they incorporate justify high prices. This can therefore buffer the cost of implementing a new technology. The research and medical sectors are also flexible and welcomes technology improvements.

However, the apparatus usually achieve a temperature precision control of ±0.2°C, whereas a precision of ±1°C is usually needed. The time response of currently available bulk thermoelectrics, in the order of the tenth of a second, is good enough. No improvement in terms of the size of the TE part is really needed. Improvement at the thermoelectric material level would not bring any additional value to the apparatus. Most of the recent and upcoming improvements come from software, graphical display, memory, USB or wireless communications for printing of protocols and reports, sleep mode to save power, etc.

B Cooling applications

Because of the low efficiency that they currently achieve and their relatively high costs, thermoelectrics have been confined to low cooling power applications (under 50W) where their low COP is not an apparent disadvantage. Commercial cooling applications include portable cooling boxes or wine cellars[19].

Competition

A conventional "mechanical" cooling system is composed of a condenser, an expansion valve, an evaporator and a compressor. In the evaporator, the fluid is allowed to expand and evaporate: heat is absorbed from the environment when the fluid goes from liquid to gas. The compressor recompresses the gas into a fluid and work has to be provided. The condenser

---

[19] http://www.crateandbarrel.com/

expels the heat absorbed in the evaporator and the extra-heat added by the compressor out in the environment.

It is important to note that, for both refrigerators and AC systems, a fan is needed in addition to the thermoelectric part. It is necessary to force convection and enhance the cooling process. Even in small cooling boxes, a fan must be used[20]. There is therefore a moving part in the refrigerant system, even when thermoelectrics are used instead of a compressor-based refrigerant cycle. Even though the compressor generates most of the vibrations and noise of a room AC or a family fridge, the use of TE instead of a classic compressor-based system will not enable a completely vibrationless and silent system. It is also clear that these applications do not require the refrigerant system to fit in a confined space nor to be position independent. Therefore, these advantages of thermoelectric technology over the current mechanical system have little or no economic value. Nevertheless, a TE system does not require the use of chlorofluocarbons, which are environmentally harmful. This is the main advantage offered by thermoelectric systems over the current systems, and its economic value is dependent upon legislation regarding CFCs.

a. Room Air-conditioning

The actual purchasing price for current air-conditioning systems is around 25cts per Watt of cooling power[21]. The only current TE-based air-conditioning systems are sold at a rate of $4 per Watt of cooling power, which is 8 times more expensive. This probably explains why only one company (Melcor) currently sells TE air-conditioning systems.

Residential air conditioners sell on the basis of first cost as installed. It makes perfect sense when one realizes that, despite their very low efficiency, the cost of operating a room AC unit is less than $100/yr, typically $60/yr[22]. The rigorous comparison between a compressor-based system and a thermoelectric technology for cooling must be made on the basis of lifetime levelized cost of the unit (aggregated cost of purchase + cost of operation). Nevertheless, because the annual cost of operating the unit is really low, few people think in terms of savings on the electricity bill when they purchase a room AC (even though some people might think in terms of environmental impact). It is thus important to note that, if the overall

---

[20] Phone interview, Dave Wanat, Director of Engineering of Conair: a fan is used in the Cuisinart Wine Cellar

[21] http://www.friedrich.com/

[22] Calculation based on a 5,500 BTU AC with EER= 11 operated 1,200hrs/yr and cost of electricity 10cts/kWh

efficiency of the overall TE-based system does not differ too much from the currently achieved COPs (say between 2.5 and 5), then the target to achieve in order to impose TE-based ACs is a selling price close to that of currently available mechanical systems.

Because little or no economic value is brought by the specific features of thermoelectrics, and because an increase in efficiency around the current level of performance is hardly a selling point, room AC systems do not constitute a good entry point for thermoelectric technology.

Comparison based on lifetime cost of a unit:

We can however try to walk through a method to compare the technologies. Even though many parameters will be estimated, the method developed here is a rigorous way to assess the economic value of thermoelectrics for use in air-conditioning.

It is possible to calculate the cost of operating a currently available compressor-based AC system using the EER ratio[23] which is given by the manufacturer. The EER includes the losses associated with the refrigeration cycle, compressor motor losses, fan motor power, condensing heat exchanger temperature differences and flow losses, evaporator heat exchanger temperature differences and flow losses, temperature rise in outside cooling air and temperature over-cooling of inside air that results in an unnecessary temperature decrease for the inside air. In addition, the EER includes the effect of the heat load due to condensation of the moisture from the inside air[24]. The thermoelectric part would replace only the refrigerant cycle (compressor, condenser, an expansion valve, an evaporator and a compressor). Because a fan is still needed and the inside of the box will still be overcooled (even though a more efficient design could be envisioned for use with TE technology), the efficiency corresponding to the ZT of the thermoelectric material is not the efficiency to take into account.

We can make the following assumptions for room air-conditioning:

- Required cooling power: 5,500BTU/hr (1613W)

---

[23] The EER was originated in response to political pressure to try to make air conditioner energy consumption more comprehensible to the average consumer. It relates overall electric consumption to effective cooling rate for a standard operating condition that is representative of normal average operation.

[24] Informations on EER from Professor Joseph L. Smith Jr, MIT

- System operates 1,200hrs/yr (10hrs/day during 3months+5hrs/day during 2 months), between the temperatures of 27°C and 20°C ("typical" temperatures)
- Lifetime: 10yrs (DOE takes 15yrs)
- COE: 10cts/kWh[25]
- Real discount rate: 4% (DOE takes 4.1% in its energy savings calculations)
- Retail price for current AC system: $400[26]
- EER=11 (overall COP=0.293*EER)
- For TE module: operation between 20°C and 27°C
- Actual COP of TE system is 85% of theoretical COP given by ZT. Overall system efficiency is 17% of thermoelectric part efficiency[27]. Eventually, efficiency of overall system is 0.85x0.17~15% of efficiency given by ZT.
- Cost of TE module should be ~50%*40% of selling price of the AC to the end-consumer. For BSST, the TE part accounts for 12-15% of the selling price. Their other major costs are the fans and the electronics. The electronics are much simpler in the case of an AC so 40% seems a reasonable number.

Using these assumptions, we can calculate the lifetime cost of a mechanical unit: $400(purchasing cost)+$60[28] $\sum_{t=0}^{9} \frac{1}{(1+0.04)^t}$ (operation cost)≈$900.

Using an efficiency of 15% of the efficiency given by ZT, we can calculate the cost of operating a TE-based AC system, and then, with a target lifetime cost of $900, we can calculate the target selling price of such a system. 20% of that selling price can be assigned to the cost of the TE parts and installations[29].

---

[25] actual electricity cost according to DOE for Jan 06 http://www.eia.doe.gov/cncaf/electricity/epm/table5_6_a.html

[26] http://www.friedrich.com/

[27] For a car engine, efficiency is ~30%, with Carnot limit~67%, that is 45% of Carnot limit. Estimation of the COP of the mechanical refrigerant cycle is thus 0.45x42(Carnot limit)~19. Overall system efficiency for commercially available mechanical AC is 3.2, that is 17% of refrigerant cycle efficiency. This is obviously an educated engineering guess I could come up with. This means ZT>5 is required to compete with the compressor-based refrigerant cycle, which is higher that what is usually claimed (ZT~3).

[28] 5,500(BTU/hr)/EER*1200(hrs/yr)*0.1($/kWh)

[29] To find the target cost of a TE system which could replace the refrigerant cycle in an air-conditioner; it is necessary to find out what percentage of the selling price of the air conditioner the refrigerant cycle accounts for at present. A back-of-the envelope calculation gives: a 2kW cooling power room AC system is typically sold $500. ~50% of this is the transportation and distribution costs. The cost at the exit of the production line is thus ~$250. The refrigerant cycle being the most complex part of the system with the electronics control, its costs (purchasing & implementation) can account for maximum 40% of the production cost, namely $100. A TE cooler with the same cooling power and efficiency could thus be sold to the AC manufacturer up to $80 (implementation of a TE-module should be less costly than that of a compressor, a condenser and an evaporator, say $20).

The results are given in the following table:

	TE Air Conditioner						Standard "mechanical" AC conditioner
ZT	0.8	1	1.6	2	3	5	-
Theoretical COP	5.7	6.8	9.4	10.8	13.6	17.3	-
Achievable COP	0.9	1.0	1.4	1.6	2.0	2.6	3.2
lifetime operating cost of unit ($)	$1,917	$1,609	$1,154	$1,003	$799	$629	$550
Target selling price to consumer ($)	-	-	-	-	$101	$271	$400
Target cost of TE($)	-	-	-	-	$20	$54	-

Table 7:TE-based room AC, target cost of thermoelectric part

Note: The theoretical coefficient of performance is given by the material's ZT and the temperatures T_h and T_c. The target selling price to consumer is the lifetime cost of the system to the end-user of the currently compressor-based AC ($900) minus the cost of lifetime cost of operating the unit (=$799 for ZT=3). The target cost of TE is 20% of selling price. It sets an upper bound to the cost of the TE module in a room AC for the given performance.

Note: the operating costs are very close to those given by the DOE providing some validation to the model.

Comments:

1) To get more precise numbers, it would be necessary to have a better value for the percentage of the theoretical efficiency given by ZT that the overall system can achieve, and also a precise breakdown of the costs of the different parts of an AC. A sensitivity analysis would also have to be conducted.

2) If TE offer an alternative to compressor-based refrigerant cycles, because of the pollution generated by CFCs and other refrigerant compounds, environmentalist pressure might drive political decisions to raise the taxes on the use of CFCs, resulting in acceleration of the replacement of refrigerant cycles by thermoelectric technology.

Cost of compressor-based refrigerant cycles used in air-conditioning applications:

An internet search on compressors, evaporators and condensers for room air-conditioning applications gives us an estimate of ~$150 for a refrigerant cycle bought independently by an individual (compressor+evaporator+condenser). This sets an upper bond for the price AC manufacturers experience. It is likely that AC manufacturers get such parts for a total of

~$70. This is therefore the target cost for a thermoelectric module capable of delivering a cooling power of ~2000W with approximately the same efficiency as the current compressor-based refrigerant cycle.

Materials performance and number of couples

Another way to look at the impact of higher thermoelectric materials performance is in the number of thermocouples and its consequences in terms of costs. My estimate currently is that between 2000 and 5000 thermocouples would be needed to achieve a cooling power of 1500W.

ZT	0.8	1	1.6	2	3	5
Theoretical COP	η_0=5.7	6.8	9.4	10.8	13.6	17.30
η/η_0		1.2	1.7	1.9	2.4	3.0

Table 8: ZT and efficiency

This table shows how an improvement at the material level drives an improvement in efficiency. Therefore, all other things equal (module geometry, etc.) an improvement in ZT from 0.8 (current value for Bi_2Te_3 at room temperature) to 1.6 (MIT Lincoln Laboratory structure) would enable a 1.7 times reduction in couples, and therefore, all other things equal, divide the cost of TE-based cooling systems by 1.7.

b. Refrigerators

Family refrigerators and freezers require a cooling power roughly one order of magnitude lower than the cooling power required in an AC system. Furthermore, because the refrigerator is a more complex system with many "accessories" around the refrigerant cycle (box, doors, inside racks) which have to be esthetic, the cost of the refrigerant cycle accounts for a lower fraction of the total cost of manufacturing. From an economic point of view, because of these two reasons, a thermoelectric cooling system would be easier to incorporate in a refrigerator (even if it is more expensive on a $/Watt of cooling basis) than in a room AC system. For some low-power applications, such as portable cooling boxes or wine cellars, TE-based systems have been chosen over mechanical systems. Nevertheless, as for the case of room AC, little economic value can be drawn from thermoelectrics specificities, although a TE-based refrigerator should be slightly less noisy.

An analysis based on the lifetime cost of the system could be done for refrigerators, but would bring little information considering that too many parameters would have to be estimated.

Cost of compressor-based refrigerant cycles used in refrigeration applications:

An internet search (Ebay, AZpartsmaster) gives us the following prices for an individual looking for spare parts for a refrigerator:

- refrigerator compressor~$15
- evaporator fan motor and blades:~$20
- condenser fan motor:~$20
- refrigerant (4 to 8 ounces):~$2

The sum of the prices of all the spare parts for a refrigerant cycle for an individual would be around $70 or $80. This sets an upper bond for the price refrigerator manufacturers buy these pieces and they probably buy the set of pieces for ~$40. $40 is therefore the target cost for a thermoelectric module capable of delivering a cooling power of ~120W with approximately the same efficiency as the current compressor-based refrigerant cycle.

C Electronics cooling

Electronics systems often have specific cooling requirements. Researchers have identified the advantages of operating electronics at low temperatures. Among these advantages are:

- faster switching times for transistors
- increased speed due to lower electrical resistance of interconnecting materials
- a reduction in thermally induced failures of devices and components
- reduction of the thermal noise of electronic components and the leakage current of the electronic devices. For example, for a typical distributed feedback laser, the wavelength shifts with temperature by about 0.2-0.3 nm/°C. In high performance electronics, such as a wavelength division multiplexed (WDM) systems, cross-talk between different channels can be caused by only 1°C or 2°C temperature changes. [14]

a. Currently available thermal management solutions and advantages offered by thermoeletcrics

Thermal management solutions for electronics can be divided into two groups: passive heat spreading and active cooling (with temperature control).

In the former technique, one tries to lower the thermal resistance between the active region and the heat sink by increasing the spreading area and by using better thermal conductivity materials. The standard CPU cooling is usually handled by a copper heat sink. One flat surface ensures good thermal contact with the components to be cooled, and on the exterior side, an array of comb or fin like protrusions help expel the heat by increasing the surface contact with the air, and thus the rate of heat dissipation (semi-infinite blade model). A fan is usually used in conjunction with the heat sink to force convection on this side of the sink.

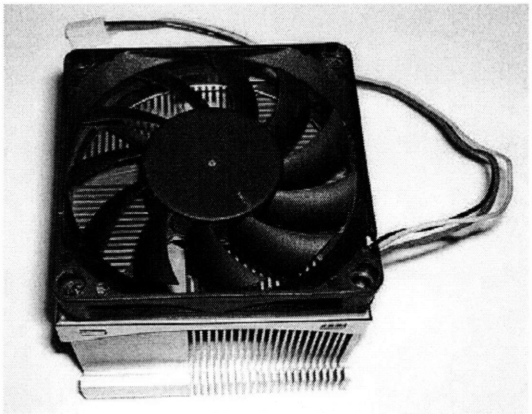


Fig 26: CPU heat sink with fan attached

Better copper or diamond-based heat sinks and thermal interface materials are being investigated. These techniques lower the junction temperature but they do not keep it at a constant value. Only active refrigeration can guarantee temperature stabilization of high performance optoelectronics. Thermoelectric coolers are very credible candidates for these applications, especially for the emerging thin-film (2 μm to 100 μm) microrefrigerators. Compressor-based refrigerators are limited for such applications since they do not scale well to low dimension, and there is a fundamental complexity and difficulty in manufacturing such micro-scale components. [14]

A few thoughts on passive cooling

We developed a 1D model of a two-legged TE cooler to establish how thermoelectric technology compares with passive cooling using copper. However, it must be noted that the level of performance predicted and achieved using single elements microrefrigerators

(Shakouri, *et al.*) is superior to the predicted performance of this model. The 1D model of a two-legged thermoelectric cooler is only interesting for bulk TE coolers.

The studied geometry is the following:

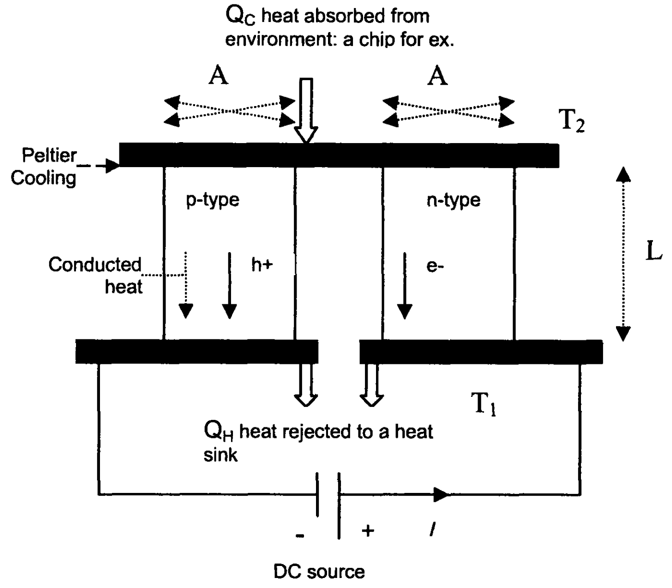


Fig 27: Peltier Cooling

In this case: $Q_c = (\alpha_p - \alpha_n)IT_2 - K\Delta T - \frac{1}{2}I^2R$. If the current is adjusted to give the maximum pumping rate: $Q_C^{\max} = (\lambda_p + \lambda_n)\frac{A}{L}\Delta T\left[\frac{ZT_2^2}{2\Delta T} - 1\right]$ with $\Delta T = T_1 - T_2 < 0$.

If we use the same module, but without running a current (just for the sake of understanding where the TE adds cooling power), the heat dissipated would be $\lambda(-\Delta T)\frac{A}{L}$ in each leg, which adds up to $(\lambda_p + \lambda_n)(-\Delta T)\frac{A}{L}$. The contribution of the Peltier effect is the factor: $\left[-\frac{ZT_2^2}{2\Delta T} + 1\right]$.

Now if we consider the case where the semiconductor legs are replaced by copper, which is known for its very high thermal conductivity (400W.m^{-1}.K^{-1}):

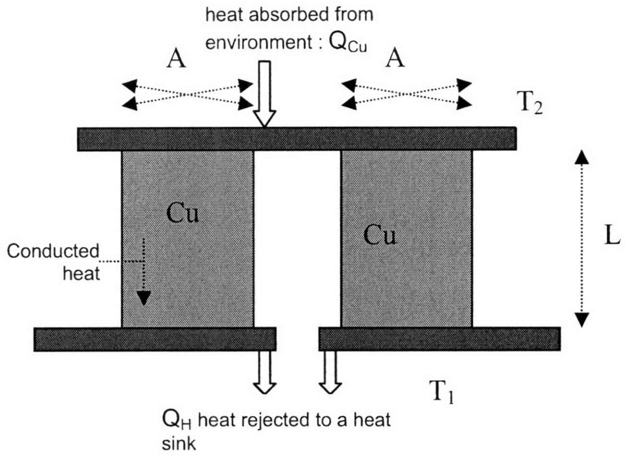


Fig 28: Heat dissipation through copper model

The heat dissipated would be $Q_{Cu} = \lambda_{Cu}\frac{-\Delta T}{L}(2A)$. Therefore, the ratio $\frac{Q_C^{\max}}{Q_{Cu}} = \frac{\lambda_p + \lambda_n}{2\lambda_{Cu}}\left[1 - \frac{ZT_2^2}{2\Delta T}\right]$ reflects the usefulness of thermoelectrics with respect to copper when comparing the two designs.

Using typical values for λ_p, λ_n, Z and the temperature, it is possible to compute the ratio, which gives an idea on how hard it is to beat copper for passive cooling. For typical values of T_1=30°C (slightly higher than ambient); T_2=100°C (chip), the ratio is:

λ_p	W/m-K	0.5	1	1.5	10	50
λ_n	W/m-K	0.5	1	1.5	10	50
ZT		0.8	0.8	0.8	0.8	0.8
Qc(max)/Qc(Cu)	W	0.004	0.008	0.013	0.084	0.419

λ_p	W/m-K	0.5	1	1.5	10	50
λ_n	W/m-K	0.5	1	1.5	10	50
ZT		1.6	1.6	1.6	1.6	1.6
Qc(max)/Qc(Cu)	W	0.007	0.014	0.021	0.143	0.713

Table 9: Comparison between heat spreading using copper and heat pumping using TE, T_1=303K, T_2=373K

Note: for the Lincoln Lab PbTe/PbTeSe alloy, the thermal conductivities are estimated in the range 5 $mW.cm^{-1}.K^{-1}$ to 15 $mW.cm^{-1}.K^{-1}$, with "ZT" up to 1.6 at these temperatures. λ_{Cu} is taken to be 400 $W.m^{-1}.K^{-1}$

It is obvious that passive cooling using copper will be very difficult to beat using thermoelectrics.

Note: It is not surprising that the higher the thermal conductivity of the SC-legs, the better the TE module performs *for a given Z*[30]. As a matter of fact, because the heat source side is at a higher temperature than the heat sink side; the higher λ_p and λ_n, the more heat is dissipated.

It is also important to note that, if copper were to be used, it would cover the entire contact surface with the hot spot (e.g. chip) (no need to have spacing between the legs, since there would be no legs), therefore leading to a (slightly) higher contact area and a larger amount of heat dissipated. Thus, we are conservative when we claim that copper is more efficient than a thermoelectric module.

Criticism of this simple model: Practically, we do not control the temperature, and therefore setting arbitrarily the temperatures on both sides is inexact and can only help us understand how the two technologies compare. Copper heat sinks are designed like an array of comb or fin like protrusions to maximize the contact with air and increase heat dissipation. Practically, what we know is the heat flux and the imposed temperature at t=0. The thermal conductivity of copper is also temperature dependent, but $400 W.m^{-1}.K^{-1}$ is still a good estimate. However, it is clear from these "back-of-the envelope" calculations that thermoelectrics are unlikely to compete with copper heat sinks at macro scale dimensions whenever only passive cooling is needed.

Nonetheless, as we already mentioned, this model fails at low dimensions (<1mm thickness). In addition, active cooling, with precise temperature response and fast response time is needed for some applications, for which copper is not suited at all. Furthermore, a tiny copper block may not be easy to integrate on a hot spot.

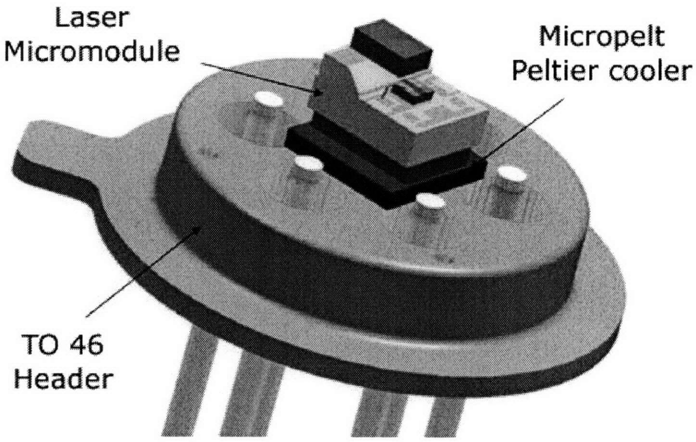
Laser cooling

Another application for thermoelectric cooling is laser diode cooling. Laser diodes dissipate a lot of heat, and their output wavelengths are very temperature-sensitive. For a typical distributed feedback laser, the wavelength shifts with temperature by about 0.2-0.3 nm/°C.

---

[30] This reinforces what we will see later, that for electronics cooling, the improvement in *Z* will not have the same effect whether it is due to a larger power factor or a lower thermal conductivity.

Active cooling with highly precise temperature control is thus needed for laser diode cooling.



from: http://www.micropelt.com/

Fig 29: Laser cooled by the use of a TE technology

Bulk thermoelectrics based on Bi_2Te_3 are already commonly used for laser diode cooling. For this application, response time is a key performance factor. In addition to being small enough to fit in a laser diode package, a microscale thermoelectric cooler also provides faster response times, less than 0.1 ms (see below). This is one of the most likely entry-applications for the new generation, thin-film high performance thermoelectric material.

Chip-cooling

Another distinguishing characteristic of IC chips is their uneven temperature distribution, which leads to "hot spots." The temperature inside a chip can vary by 30°C from one location to another [15]. Peak heat flux at hot spots could be five or six times the chip's average value of 10 to 50 W/cm^2. In the case of optoelectronic devices, temperature differences between the active region and the heat sink can be hundreds of degrees. On-chip solid-state TE coolers (TEC) can eliminate such "hot spots" on the order of hundreds of microns in size. The alternative approach to reduce hot spots in IC chips is through optimized cell placement. However, this technique presents a series of drawbacks, such as complex thermal design at a very early layout stage and increased die area, which can be very expensive. Therefore, it is believed that the development of on-chip thin-film TE with high cooling power density and compatible with the IC manufacturing could have a very strong impact on IC cooling.

b. Target performance of thin-film TE coolers for IC cooling

The main performances criteria are:

- Cooling power density (CPD), in W/cm^2. The average value for heat rejected by chips is 10-50 W/cm^2. Hot spots can experience heat flux up to 1000 W/cm^2
- Maximum cooling around room temperature, which is the difference of device temperature with and without the TE system (this is obviously related to the CPD)
- Cooling response time.

It is interesting to note that these criteria are different from those regarded for other types of cooling applications, such as food refrigerators or air-conditioners, for which the key performance features are efficiency and cost. Even though power consumption and cost have to be regarded, they are often small compared to the overall consumption of the electronic device or its cost. (Note that Shakouri *et al.* estimate the consumption of their microrefrigerator to be 10% of the 300mW that the chip consumes overall [16]).

The target performance for these on-site cooling TE is at least a 20°C temperature reduction along with at least 100 W/cm^2 cooling density, preferable 500 W/cm^2 and response time in the order of a millisecond [14 & 15].
Current bulk TE modules can achieve a maximum temperature difference with the cold side at room temperature. However, the cooling power density is low, on the order of 5-10 W/cm^2. A standard commercial TE refrigerator has a time response on the order of tenth of a second.

It is interesting to note that because of the thermal resistance they induce, TE modules have a negative impact on chip temperature above a certain heat load. [17]

c. Recent research breakthrough in IC cooling using TE

Ali Shakouri, Yan Zhang and co-workers, from the University of California Santa Cruz have investigated on-chip solid state cooling using a Si/Ge superlattice micro-refrigerator [14 & 16]. This microrefrigerator device is composed of a single element instead of an array of p-type and n-type legs arranged electrically in series and thermally in parallel. The cooling power density is only a function of the element leg length and it is independent of the number of elements. Although Silicon and Germanium are not the best TE materials at room temperature (Si/Ge are high temperature thermoelectrics), this research team chose to work with this material because it is relatively easy to integrate with most microprocessors (monolithic integration, which avoids electrical and thermal mismatch). Ramanathan and Chrysler have shown the critical role of electrical resistance [18]. High cooling densities are achieved by a combination of thermoelectric effect at the junctions between the thin-film of Si/Ge and the layers above (metal cap) and below (buffer substrate) along with a thermionic cooling[31].

They achieved a maximum cooling of 7°C [16] for a chip at 100°C, which is below the target of 20°C-30°C; but a maximum cooling power density of 600 W/cm^2. A typical performance of their 3 μm thick $Si_{0.75}Ge_{0.25}$ was a cooling density of 300 W/cm^2 along with a cooling of 1.2°C at room temperature. A theoretical analysis for an optimized refrigerator showed that a temperature reduction of 7.5°C could be achieved with a cooling power density of 300 W/cm^2. Their devices demonstrated fast response time on the order of 20 to 40 μs and were used successfully to minimize the impact of large hot spots heat flux of 300 W/cm^2 on chip temperature. [14]

Work was also done on an InP-based thin-film InGaAs/InAlAs superlattice (SL) microrefrigerator. The cooling power density (or equivalently the temperature decrement) was slightly lower than with the Si/Ge SL. However, two methods were presented to mount this TEC on top of an optoelectronic device (monolithic growth and fusion bonding) [19].

The major challenge once these thin-film TEC will have been demonstrated and optimized in the lab will be to find if such films can be deposited with such superior TEC properties at high deposition rates.

Rama Vankatasubramanian *et al* at the Research Triangle Institute have reported a 3–5 μm thick, 100 μm diameter Bi_2Te_3/Sb_2Te_3 superlattice coolers which exhibited a maximum cooling of 32°C and a maximum cooling power density of 700 W/cm^2 [4]. The reported response time was about 15 μs.

Böttner *et al.* at the Fraunhofer Institute in Germany have been working on monolithic integration of conventional BiTe and BiSbTe bulk material on silicon substrate. They have demonstrated maximum cooling of 12°C with an estimated maximum cooling power density 100 W/cm^2 [20].

---

[31] In the thermionic emission process, hot electrons from a cathode layer are selectively emitted over a barrier to the anode junction.

Optimum thickness

The optimum thickness results from a trade-off between thermoelectric cooling, heat spreading and electrical and thermal resistances[32]. Shakouri estimates the optimum thickness of their Si/Ge TEC to be 10-12μm[33]. A theoretical analysis of micro-scale TEC used for IC cooling and packaged in a chip by Ramanathan and Chrysler have demonstrated that the optimum thickness for TEC would be between 10 μm and 20 μm [18]. Their analysis suggest that the better the TE properties, the lower the optimal thickness. Although the two models are very different, since the Si/Ge micro-refrigerator developed by the group at UCSC is a single-segment TEC whereas the model of Ramanathan and Chrysler is based on several thermocouples, they give very similar results. To add to the credibility of this target thickness of 10 μm to 20 μm, it must be noted that the micro-refrigerators built by the group at UCSC have demonstrated results close to those simulated.

Simons and co-workers at IBM also studied the effect of geometry scaling in a particular module configuration. Even if it appears that the scaling of thermoelectric module downward should significantly improve the heat the micro-refrigerator can dissipate, they showed the COP=Cooling Power/Electrical Input will not improve in this scaling. However, they do not estimate an optimal length for TE legs.

Single crystal vs. polycrystalline materials:

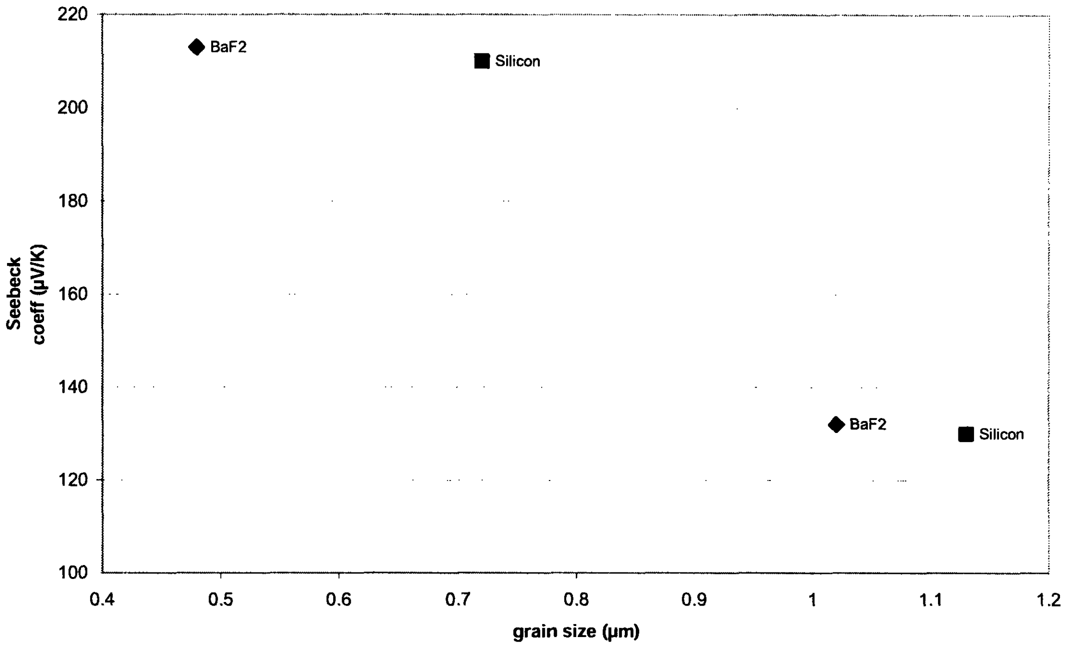
The group at UCSC works with single-crystal materials because they want to achieve the best results at the research level. However, Shakouri believes that the use of polycrystalline materials would reduce the performance of his device by a factor of 4[34]. Nonetheless, it is well known how to engineer properties of materials like silicon and germanium in a chosen crystallographic direction (especially electrical conductivity). Dr. Bulsara believes polycrystalline materials could be close to be as good as single crystal materials (at least non-randomly oriented crystal). Recent analysis of the Seebeck coefficient of QDSL PbTe/PbTeSe Lincoln Laboratory alloys indicates polycrystalline film may be suitable for TE applications. The optimal structure and properties still need to be determined.

---

[32] The reason for this improvement is that we have a cascade of two TE elements (Superlattice refrigerator between two other layers). Thicker SL increases the contribution of SL with respect to substrate and thus gives a better cooling. However, when the SL gets thicker, its electrical resistance also increases. Therefore, eventually, the increased Joule heating inside the SL will diminish the interface cooling. It is an explanation for the existence of an optimum thickness for a single element refrigerator.

[33] Phone interview, Pr. Ali Shakouri. 10μm is also the optimum length given in [16]

[34] Phone interview, Pr. Ali Shakouri.



from a poster by Dr. Mayank Bulsara

Fig 30: Influence of grain size on thermoelectric properties for PbTE/PbTeSe alloys

d. Potential effect of improvement of ZT

An infinite number of combinations of the three key materials properties α, ρ and λ, can give the same *ZT*. However, all combinations will not give similar performances in terms of cooling density. Simons and co-workers at IBM Research, and Shakouri *et al.* conducted analyses on this subject. Their results, although different in some ways, clearly show that the *ZT* of a material is not enough to judge its cooling performance.

The IBM group adopted an approach in several steps: (1) holding α and ρ constant to find the value of λ needed to achieve a given *Z*; (2) holding λ and ρ constant to find the value of α needed to achieve a given *Z*; (3) holding α and λ constant to find the value of ρ needed to achieve a given Z. They reported the theoretical cooling performance in the configuration they studied when varying these materials parameters to reach *ZT* values equal to 2, 3, and 4. Their results clearly demonstrate that materials with the same *ZT* will not necessarily give the same cooling performance. They suggest that it is preferable to increase α or decrease ρ rather than reduce λ.

The UCSC group ran simulations when: (1) increasing α by a factor of $\sqrt{5}$; (2) decreasing λ by a factor of 5; (3) decreasing ρ by a factor of 5, therefore leading an to increase in Z by a factor of 5. They also executed the simulations with the real values for their Si/Ge thin-film. According to their results, it is better to increase the Seebeck coefficient than decrease the thermal conductivity or the electrical resistivity.

The results are shown in the following charts:

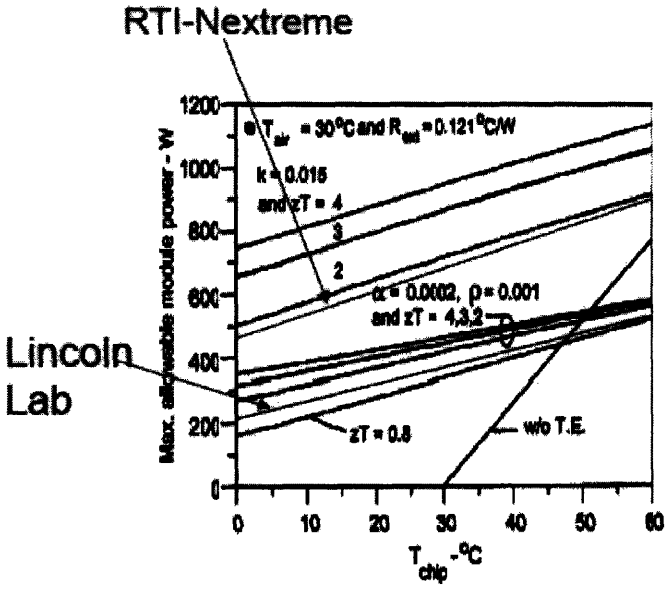


Fig 31: From an original chart by IBM Research. The line labeled ZT=0.8 is based upon values of α, ρ and λ for present BiTe material. The next group of line for ZT=2, 3, 4 is for α and ρ hold at present day values and using the value needed to get the respective values of ZT. The upper-most group of lines is for case (2) and (3), which give nearly identical results. Using the reported values for λ, ρ and α in papers on the RTI Bi_2Te_3/Sb_2Te_3 superlattice TE material and the PbTe/PbTeSe alloy of the MIT Lincoln Laboratory, I reported the expected maximum allowable load in the electronics module studied by the IBM research group. Even though the results brought by this paper must be taken with precaution (I could not redraw the charts from the numerical value they give-I assume these numerical values are incorrect), figure 31 clearly shows that the RTI/Nextreme material would give better cooling than the Lincoln Lab material. This is explained by a higher Seebeck coefficient and a significantly lower electrical resistivity for the Bi_2Te_3/Sb_2Te_3 superlattice TE.

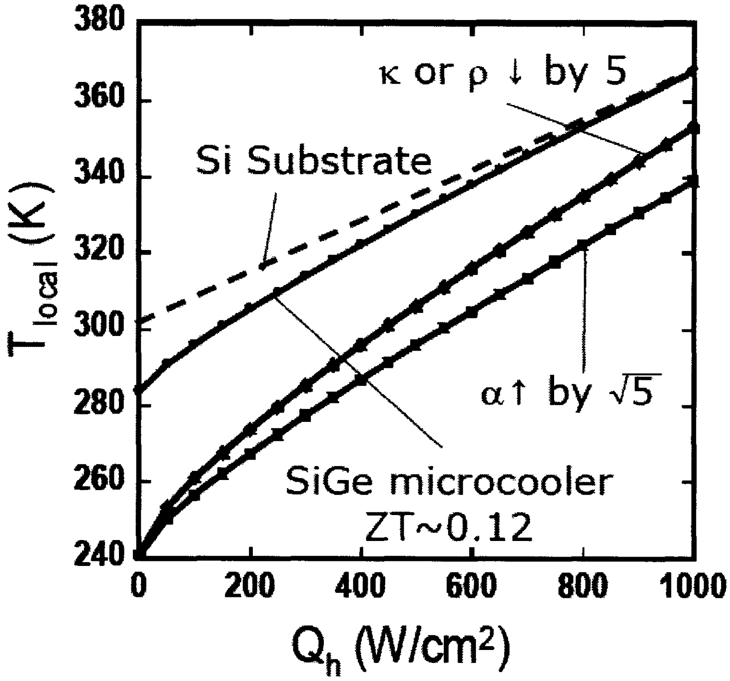


Fig 32: Temperature of the hot spot versus hot spot heat flux in Shakouri *et al.* model. The dashed line is without the TE cooler, the red line is the result with the currently available material, and the black and bleu lines are for a ZT increased by a factor of 5 controlling different parameters.

The material's figure of merit *ZT* is therefore not always the best way to assess performance. The different results regarding the importance of the electrical conductivity σ ($=1/\rho$) can be explained by the different configurations, models and materials used in both papers. However, looking at the cooling equation $Q_c = {}^1\!/_A(2\alpha I T_c - 2\lambda \Delta T\, A/L - (\rho L/A) I^2)$ makes it very clear that α, which refers to the pumping rate by the carriers, must be high, and that the better the electrical conductivity, the lower the Joule heating. However, the impact of λ is not as clear because in the case when the side to be cooled is at a higher temperature than the heat sink, ΔT is negative and the higher the thermal conductivity, the more heat is dissipated by conduction. This heat is thus not dissipated by the carriers. However, it is obvious from simulations and experimental results that high thermoelectric properties are more important than good thermal or electrical properties for a given *ZT*.

ZT is a good figure to assess the thermoelectric performance in terms of efficiency (heat-to-electricity conversion or electricity-to-cooling). It is not necessarily a good figure to assess performance, especially for cooling applications when the side to cool is at a higher temperature than the heat sink (for power generation applications or cooling when the side to cool is at a lower temperature than the other side, there is a need to maintain a high temperature gradient and thus for a low λ).

It is interesting to underline that because the recently developed materials are processed in the forms of thin-films, people often claim their entry application will be electronics cooling. However, despite the high *ZT* their thermoelectric properties may not be very good for cooling applications. Electronics cooling may not be a good initial application.

Review of the electronics cooling market, players in the thermoelectric coolers industry and competing technologies

Micropelt, which is a spin-off of Infineon, developed bismuth telluride based micro coolers. Using a sputtering process, n-type Bi_2Te_3 is deposited on a standard silicon/silicon dioxide wafer; and p-type posts are deposited on another substrate. Finally n- and p-wafers are structured by dry etching. Individual die from each wafer are then soldered face-to-face to form the thermoelectric element. The elements have an area of 0.01 cm^2 and a thickness of ~400µm. The Micropelt coolers demonstrated cooling densities up to 80 W/cm^2 and fast response times in the order of 50ms. Their technology is nonetheless a two-leg thermoelectric technology (not a single element) whose high performance comes from using a short leg length. Micropelt engineers expect to be able to process optimized coolers with a CPD of 250 W/cm^2.

NanoCooler, which was founded by a former IBM researcher, is developing thermoelectric cooling modules based on thin-film technology, but has not released many details so far. The company has strong VC backing, though. It had been splitting its efforts between TECs and a liquid metal cooling technology, but refocused solely on thermoelectric coolers in the course of 2005.

Nextreme Thermal, which was founded to commercialize the thin-film Bi_2Te_3 superlattice material of the Research Triangle Institute, is currently shipping its first prototypes (TEC packaged)[35].

Cool Chips plc, which is a European company based in Gibraltar, is also currently developing thermoionic-based coolers and processing prototypes in the lab.

---

[35] Phone interview, Jesko von Windheim, CEO, Nextreme Thermal.

Competing technologies include a wide array of technologies, viable for different applications.

Improvements in passive cooling include the development of better copper or diamond-based heat sink.

Pumped-liquid cooling systems, developed by start-ups such as *Cooligy* or *ICurie* are based on the circulation of water in microchannels. It is a mechanical technology which includes a micro-structure heat exchanger, a mechanical heat pump for delivering fluid with required flow rate and air pressure, and a liquid-air radiator heat exchanger. It is not as scalable as thermoelectric/thermoionic technology, though. Problems of particles control, water losses control and freeze protection are claimed to have been overwhelmed. Another technology, developed by *Thorrn Micro*, is based on tiny air pump to remove heat: electrical sparks between carbon nanotube electrodes ionize the surrounding air resulting in air flows.

NanoMarkets, a nanotechnology research firm, estimates that these new-generation cooling technologies may capture $417 million in sales by 2011. The research firm Business Communications Co. (BCC) forecasts that the world market for current electronics thermal-management products will grow from $3.3 billion in 2003 to $5.9 billion by 2008, with the largest market segment-computers-expanding from $1.3 billion to $2.3 billion.

Electronics thermal management sales forecasts for 2008, worldwide, in millions of $	
Computers	2,291
Telecom	1,131
Automotive	523
Consumer	397
Medial/office equipment	648
Industrial/Military	896
Total	5,886

Table 10: Electronics thermal management sales forecasts for 2008. Source: BCC, 2005

V.3 Applications as thermal sensors

A variety of applications of thermoelectrics as thermal sensors have been reported [11]. These applications are very specific and often of high added-value in a product or an industrial process. They constitute niche applications, some of which are likely to be entry points for new high performance TE materials.

V.4 Summary of key decision factors

The following table summarizes the key decision factor for some of the applications which are not using thermoelectric technology as the standard yet.

Application	Key Decision Factor	Efficiency key factor?	Explanation/Comments
Low-power generation from body heat	-Performance: amount of power generated; size -Cost: battery difficult to beat!	No	Heat is free
Power generation for remote locations applications	-Lifetime -Reliability -$/kWh generated	Yes	Heat is not free(fuel combustion)+higher efficiency allows longer lifetime
Industrial Waste Heat Recovery	-lifetime levelized cost of electricity generated -ease to implement	No	Heat is free
Heat recovery from car/ship exhaust	-$/quantity of fuel saved	No	Heat is free
Electronics Cooling	-Performance: Cooling Power(W/cm^2); ΔT enabled by TE; time response -Possibility to manufacture on-chip	No	E consumption by TE<<E consummed by overall of device
Room AC	-lifetime cost of operating a unit=$ purchase+$ operation or first cost as installed *or first cost as installed*	Yes	Electricity is not free!
Kitchen Refrigerator	-lifetime cost of operating a unit=$ purchase+$ operation *or first cost as installed*	Yes	Electricity is not free!
Car Seat Heating/Cooling	-Cost	No	E consumption by TE device<<E consummed by other car accessories, (eg. central HACV)
Motorcycle Helmet Cooling	-$/"additional comfort"	Yes	Battery provides energy,and the smaller the battery, the lighter the system (a cell phone battery is typically 3.6Whr; a laptop battery typically 80Whr)

Table 11: Key decision factors table

VI Commercialization of thermoelectric technology

VI.1 Walk-down the learning curve and niche markets

Established and soon-to-come thermoelectric technologies have efficiencies in energy conversion generally lower than their alternatives. As long as thermoelectrics are not competitive in terms of efficiency, they will remain non-competitive on a cost basis. However, the significant advantages they offer over other technologies have lead to early adoption in several niche applications. These applications should pave the way for technology developments and improvements. As the technology improves, the efficiency of thermoelectric devices will increase and the cost in term of $/W of electricity or $/W of cooling will go down; the technology will thus be more and more competitive which will open new markets and lead to higher production volumes, which, in turn, will lower the costs.

For initial developments of the technology, space and military applications, for which cost and environmental impact are rarely an issue, have contributed and continue to contribute to the development of materials and devices. As far as satellites generators are concerned, the reasons for the choice to go with thermoelectrics come from the more performing functionalities of TE over alternatives, such as the absence of mechanical vibrations or no-need for solar irradiance.

For initial commercialization of TE, one has to look at niche applications such as remote system power supply. Low volume applications in need of one or several of the advantages of thermoelectrics, with potential to pay a high ct/W price for the attributes of thermoelectric technology, are good entry points for the technology. Laboratory equipment is a good example of such products. As the technology improves, it will progressively move towards high volume-low margin applications for which the special features of technology are not as crucial.

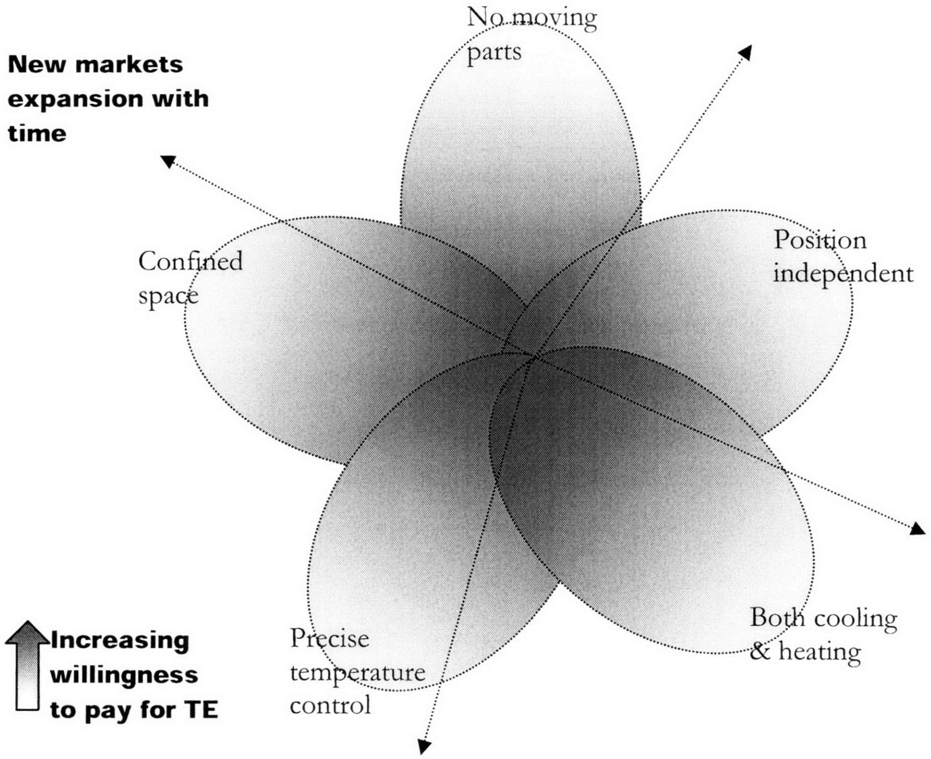
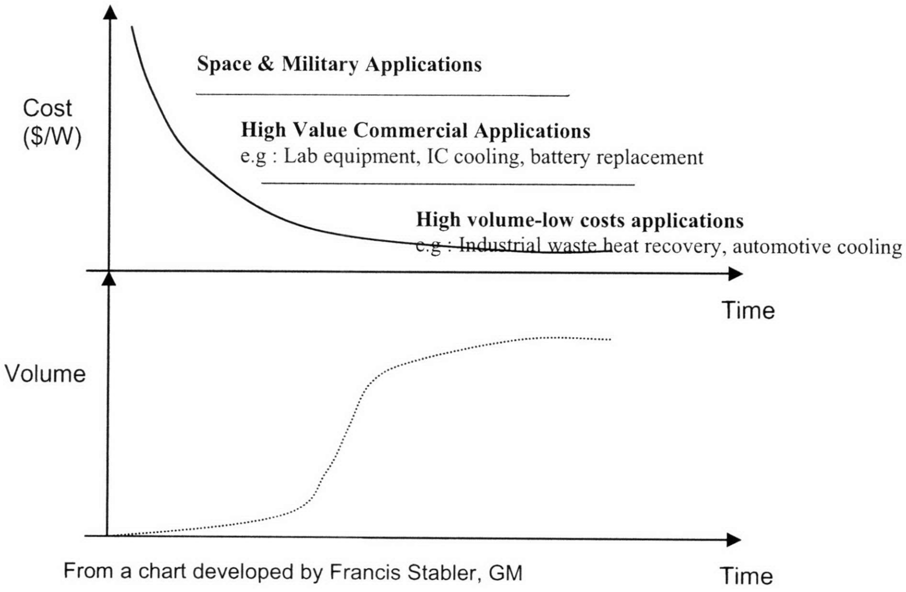


Fig 33: The willingness to pay a high price ($/W) generally increase when specific technical constraints make appear the technical and economic values of thermoelectric technology. It is thus at the crossroads of the competitive advantages of TE that the first niche applications have to be sought after. Then, with decreasing prices of the technology, larger market segments could be opened, for which the specific advantages of TE over other technologies are not as preponderant.

The following chart illustrates this walk down the learning curve.



From a chart developed by Francis Stabler, GM

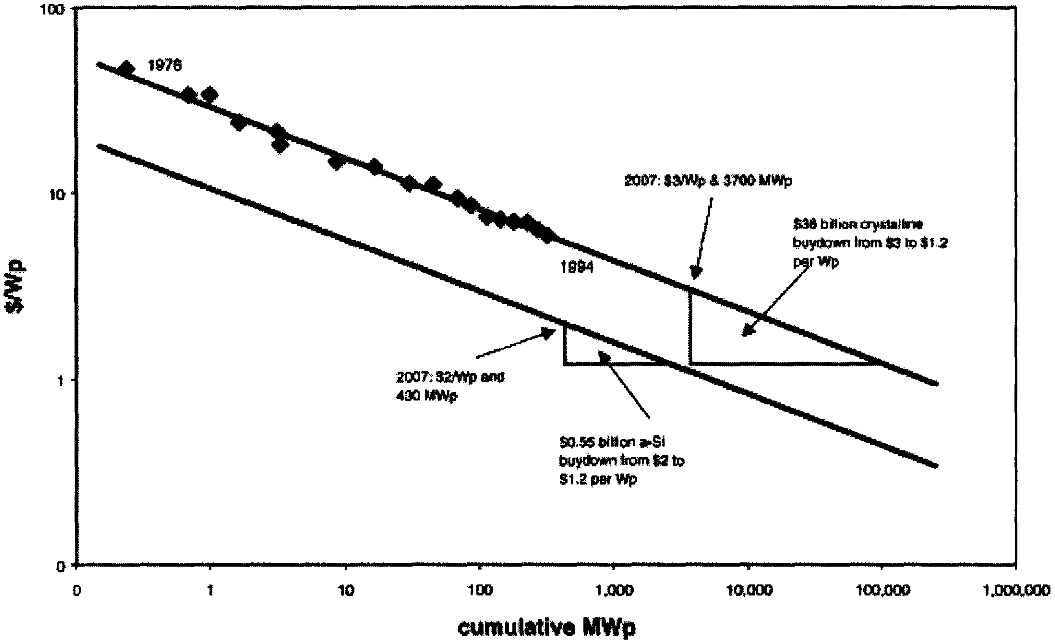
Fig 34: Commercialization of thermoelectric technology: evolution of volume and costs with time

Analogy with Photovoltaics

Thermoelectrics have common points with photovoltaics:

- Both can convert an energy source into electricity
- Both are based on the association of p-type and n-type semiconductor materials
- Both have low efficiency

However, the PV industry is more mature than the TE industry. It is therefore interesting to look back in time at the evolution of photovoltaic technology, as it gives an indication on what may happen to thermoelectrics. The following chart gives the evolution of the price of PV technology, in $/W, with time.



From: A Payne et al. Energy Policy 29 (2001), 787

Fig 35: Learning curve of the photovoltaic industry

The price of PV has been divided by close to 10 in the last 30 years. It is possible that a similar drop in the cost of thermoelectric technology will happen in the coming 20 years.

VI.2 Materials' place and role in the value and commercial chains

The value chain in the thermoelectric commercialization is the following: (Fig 36)

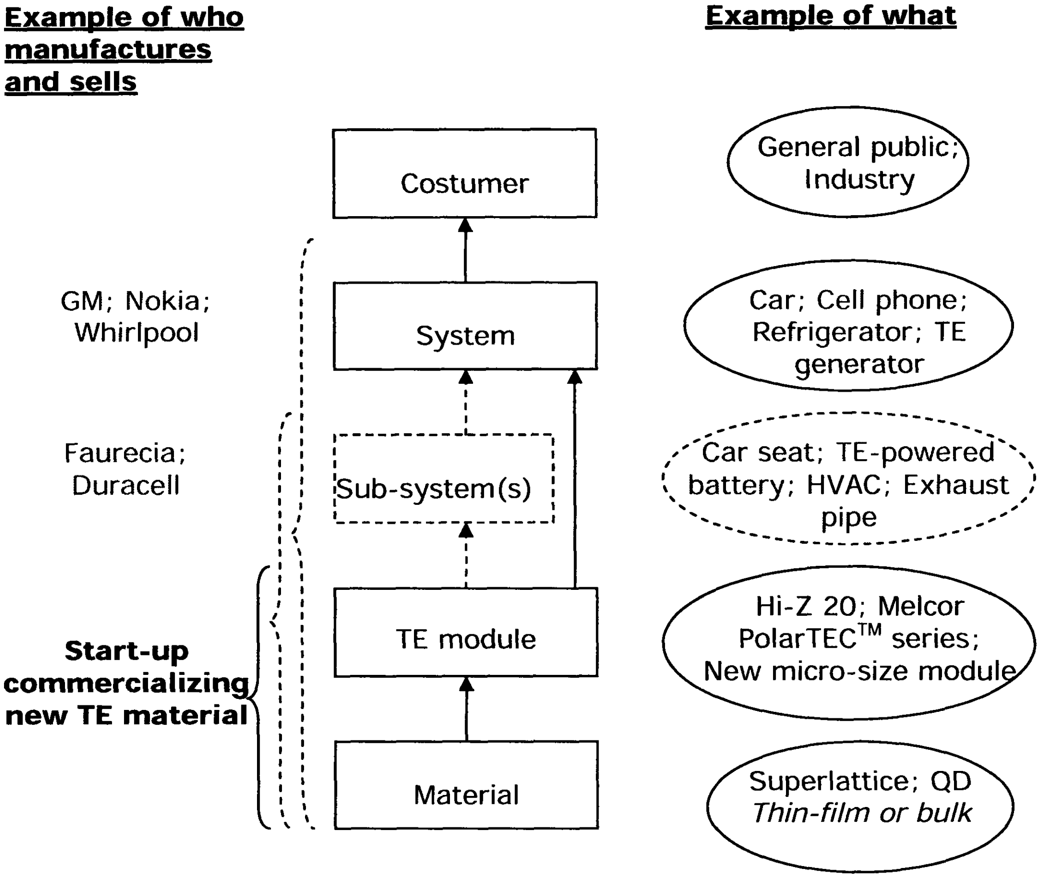


Fig 36: Commercialization chain of TE technology, macro scale applications

Macro scale applications

The material might well be the main value-adder in a device, as it is the case in photovoltaics or thermoelectrics, it is nevertheless the lowest level in the value chain, and therefore not generally the stage at which high margins are made. It is thus worth wondering how to get value from innovation at the material level in the thermoelectric business. The analogy with photovoltaics will be useful here, since the PV industry is more mature than the thermoelectric industry but, as already explained, shares points with the TE industry.

It is important to note that most PV manufacturers manufacture the whole array, not the PV cell or the PV module (assembly of 10 to 50 cells). This for several reasons:

- The PV array is higher in the value chain and a few stages only from the end-consumer
- It is relatively inexpensive to add the packaging of the the p-n junctions to the materials processing line with respect to the gain in selling price
- It is a relatively integrated technology and it is easier to package on-site than to move the cell to another factory to package it into PV arrays

In the PV industry, the materials cost is typically 30% to 40%.

The same reasoning applies to the thermoelectric industry. The phenomenon is actually accentuated in the case of TEs since the value chain often has one or more additional stages. For example, the cost of making the thermoelectric part for the cooling/heating car seats system is 12% to 15% of the system cost to Amerigon (system which is then sold to the seat manufacturer), because of expensive electronics control system and fan associated. The semi-conductor material cost must therefore be less than 10% of the thermoelectric system cost. A higher margin can obviously be made on the fan and the electronics, and the packaging of the whole. No player in the industry currently sells less than the module: for example Hi-Z sells modules; Melcor sells modules or the above-level systems, such as AC or chillers; Micropelt and Nextreme sells modules, Amerigon sells the CCS^{TM} systems; while its subsidiary BSST offers outsourced R&D.

If the chosen business model is to sell modules, bringing in the good people is absolutely crucial, as emphasized in the annual report of Amerigon, regarding its BSST subsidiary[36]. Good application engineers, capable of convincing that the company's technology is the best and to ensure the successful integration of the thermoelectrics in the clients' products are an absolute necessity and one of the key factors for success.

Micro scale applications

For use of thermoelectric technology in hot spot cooling, a high level of integration is necessary, it is therefore probably wiser to license a packaging process or a material technology to the chip packaging companies.

---

[36] 2005 annual report of Amerigon, p11

VI.3 Business model for industrial waste heat recovery

For this application for commercialization of TE technology, I would recommend the highest level of integration: consulting services in energy for industrial clients with a focus on thermoelectrics.

Company activity

Assess the potential of the client's industrial site for power generation using thermoelectric technology from industrial waste heat (Phase I):

- Measure the temperatures and heat flow on and close to potential spots for TE modules installation (furnaces, molds)
- Assess the constraints from the environment (corrosion, potential stresses, hot temperature potentially damaging electronic control of TE system, etc.)
- Assess the need for modules (number, capacity, shape); electronics (AC-DC converters). Design a TE system integrated to the industrial unit (furnace, mold, etc.) and estimate its installation costs, maintenance costs; electricity output and monetary value of this output (on-site use or net-metering)
- Propose to the client a design and a price for the installation of TE

Then, depending upon this preliminary survey and the client's decision, the company would take care of the execution of the suggested plan (Phase II):

- Provide and install the TE modules
- Connect the modules to the electricity grid or on-site network, install control commands

The company might also take care of the maintenance (Phase III).

Technology

I assume here that the company would own patents on an original and efficient TE material.

Requirements

Licenses for patents on heat transfer techniques might be needed

Getting started

The main problem will certainly be the production of the modules. The creation of a factory from scratch is probably unrealistic; since it would require a massive initial investment, the need for a minimum production volume to keep the plant operating. Furthermore, expertise in the packaging of the couples is necessary; and materials specialists are unlikely to gather all that expertise. It might be possible to partner with a company manufacturing TE modules, like Tellurec Corporation; or with a PV manufacturer (although they are currently facing such a high demand it might be difficult to get their attention), since they could provide some fab area, some equipment and expertise in packaging.

In such a case, most of the initial investment would be needed for the materials processing equipment.

The initial low production volume would not enable economies of scales on modules production, therefore leading to high costs in terms of $/W for these modules. However, this drawback is compensated by the fact that the client would pay for the overall service (system design and installation), which can serve as buffer for the cost of the modules.

An initial selling point may be to offer to install the system for free; but get a payment on the savings achieved by the client thanks to the system. This would create a (close to) risk free opportunity for the initial clients and thus be easier to get initial clients adopt a thermoelectric system. This association to the savings may also become the business model of the firm.

It would be necessary to have from the beginning very high caliber engineers and technicians for the feasibility assessment and system design, since successful results with the first clients would be crucial for credibility and greatly determine the success of the company.

Market

The potential market is gigantic, since 31% of the energy worldwide is used by the industrial sector, 30% of which is wasted (60% in the power generation sector[37]). With increasing energy prices and rising environmental concerns, it is likely that industrial waste heat recovery will gain attention in the forthcoming years. The decision factor for a plant manager to go for TE or not will be the lifetime levelized cost of electricity compared to the price utilities charge them. The firm will have to focus first on regions of the world where electricity prices are high.

---

[37] The Economist (US), 378 (8469): 76US, March 18, 2006

Competition

Any other waste heat recovery technique is a competitor a priori. Cogeneration is certainly the most simple and common way to recover energy wasted on industrial sites. Nevertheless, thermoelectrics can be fitted in a confined space and would thus enable an easy access to the installations, which cogeneration does not always enable.

VII Conclusion

Thermoelectric technology is a broad field with a wide range of materials but also a wide range of applications and markets.

All materials are not suitable for all applications because of temperature dependency of thermoelectric properties, and potential difficulties to package and integrate the thermoelectric material. Depending upon the application, some materials properties matter more than others.

Thermoelectrics are used at the macro scale and at the micro scale. Until recently, only macro scale applications could be considered. Because most of the recent breakthroughs come from nano-engineering of materials, micro modules with dimensions of a few hundreds of microns are being developed for electronics cooling, especially to cool CPU hotspots. At the micro scale (less than 1mm thick), two-leg couples are used. Single-element micro refrigerators are also developed, which combine thermoelectric and thermoionic cooling. The integration of micro thermoelectric coolers is an additional challenge. At the macro scale, mechanical strength of the elements is decisive.

Thermoelectric technology seems to have a wider reach for cooling applications than for electricity generation. It is indeed clear that, because of its integration complexity and low efficiency, the use for power generation is better suited for portable or transportation applications, for which its specific competitive advantages can overcome its drawbacks. Low-power electricity generation for portable applications is not a good entry-point for TE technology because of the competition from batteries. Large-power electricity generation could be drawn from waste heat recovery from industrial installations, but thermoelectric technology is not competitive at present. The transportation sector is a good candidate to witness the generalization of this technology for electricity generation, because the specific features of thermoelectrics can make them competitive, and also because the military is paving the way for technology improvements.

The main drawback of TE for cooling applications is their low performance levels and thus the need for a large number of couples, which makes the technology too expensive. There is also, most of the time, the need for a system to force convection, which prevents from exploiting one of the main advantages of TE, which is the absence of moving parts.

Improvements at the materials level will have to be followed by improvements in production processes and packaging techniques. As a matter of fact, the applications to electricity generation will require legs in the mm range, along with good mechanical strength (Bi_2Te_3 is a very brittle material) because it is necessary to wrap the heat source and stack as many couples as possible. The system will also need to be able to bear the electrical wires and to withstand mechanical vibrations from the environment. These manufacturing improvements will also have to drive a decrease in costs to open new markets.

In this paper, I described the recent materials breakthrough in the field of thermoelectrics; and tried to assess the potential applications and commercialization routes for TE technology.

Even though the materials are not ready yet to offer competitive mass-commercialization, niche applications should pave the way for high volume applications and market. TE can offer an environmentally friendly way to recover waste heat and transform it into electricity; enable the development of high performance computers and other electronics devices. They can provide new solutions for the thermal management of food and beverages; and new products for personal thermal management.

Thermoelectrics are likely to play a large role in every day life for future generations and to make a large contribution to the world.

VIII References

[1]: "Thermo-electrics: Basic Principles and New Materials Developments", G.S. Nolas, J. Sharp, H.J. Goldsmith
[2]: *Science*, vol 297, p2229-2232
[3]: *Journal of Electronic Materials,* vol 34, N°6, 2005
[4]: *Nature* 413, p597-602, Oct. 2001
[5]: *Science*, vol 303, 818-821, feb2004
[6]: "Thermoelectric Efficiency and Compatibility", G. Jeffrey Snyder and Tristan S. Ursell, *Physical Review Letters*, vol 91
[7]: "Commercialization of TE technology", F. Stabler, MRS Symposium, Dec 2005
[8]: *Energy Sources*, 23, 213-224, 2001
[9]: "Symbiotic" application of TE conversion for fluid preheating/power generation, *Energy Conversion and Management* 43 (2002) 221-228
[10]: Development of Thermoelectric generating modules and system, MRS Symp. Proc., Vol.886
[11]: "Thermoelectrics: a review of present and potential applications", *Applied Thermal Engineering* 23 (2003), 913-935
[12]: Handbook of Batteries-3rd edition Table 6.2b
[13]: "TE MEMS generators as a power supply for a body area Network", 13th Intern. Conf. on Solid-State Sensors, Actuators and Microsystems
[14]: "On-chip solid-state cooling for IC Using Thin-Film Microrefrigerators", *IEEE Transactions on Components and Packaging Technologies*, vol 28, N°1, March 2005
[15] "Building blocks for thermal management of electronics", G. M. Chrysler, *Proceedings of Next-Generation Thermal Management Materials and systems symposium*, Oct 2002, Dallas
[16] Solid-sate microrefrigerator on a chip, K. Fukutani, Y. Zhang, A. Shakouri, to be published in *Electronics Cooling magazine*, summer 2006
[17]: "An Assessment of Module Cooling Enhancement with thermoelectrics coolers", *Journal of Heat Transfer*, Jan 2005, vol 127, 76-84
[18] "Solid-State Refrigeration for Cooling Microprocessors", *IEEE Transactions on Components and Packaging Technologies*, vol 29, N°1, March 2006
[19] Superlattice Microrefrigerators Fusion Bonded with Optoelectronic Devices, *IEEE Transactions on Components and Packaging Technologies*, Vol. 28, N°24, Dec 2005]
[20]: *Proc IEEE 21st Int. Conf. Thermoelectrics (ICT'02)*, Piscataway, NJ, 2002, 511-518

IX Appendix: Economic model for industrial waste heat recovery

This model was made to estimate the value of the implementation of thermoelectric technology in industrial sites to recover waste heat. Contrary to the only study of this type which could be found in research papers [8] which focuses on macro-economic data, it is a bottom-up approach, which makes its originality.

The first method which could be employed woud have been to calculate the break-even year of an investment in TE to recover industrial waste heat, according to the way described in Fig 37. To get this break-even year, one calculates the time needed to make the net present value of the project equal to zero, at a given interest rate.

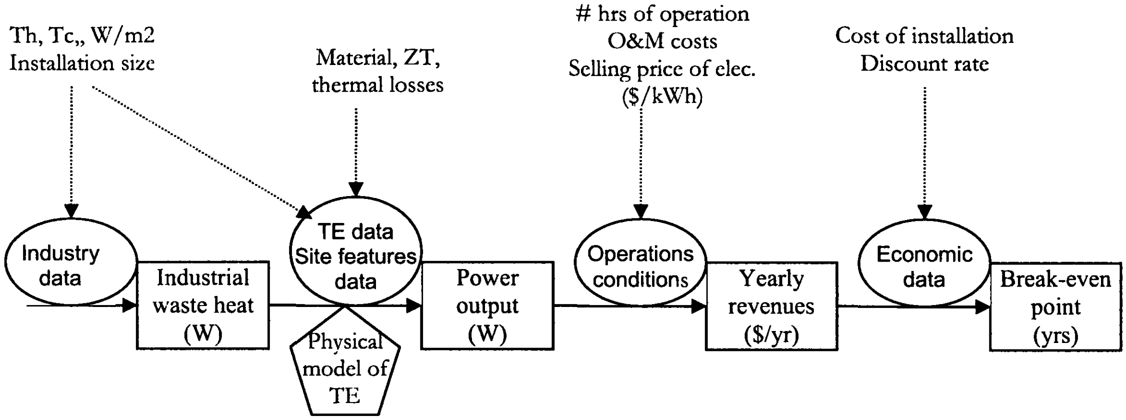


Fig 37: Economic model: break-even year

However, because in the US, most states have a legislation which enables net-metering, it was decided to calculate the price at which the electricity generated had to be sold to make the net present value of the investment equal to zero. The model then became:

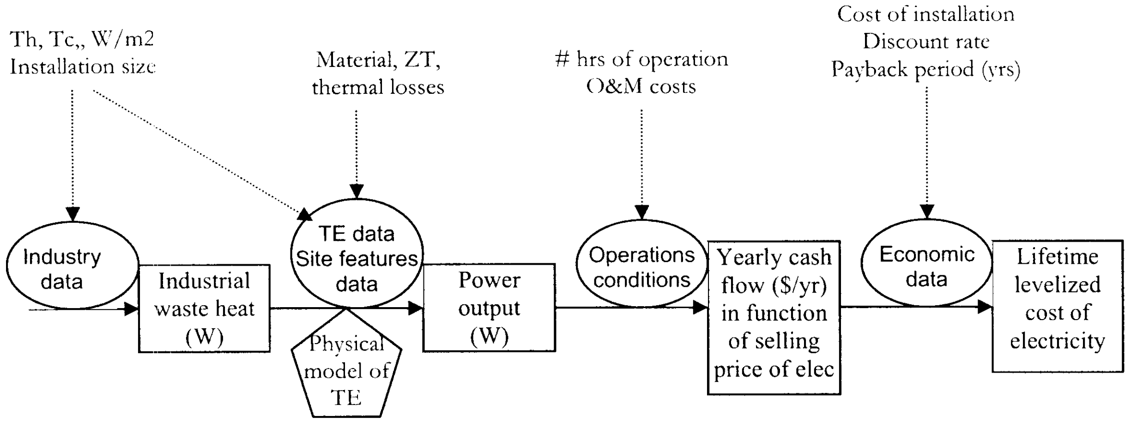


Fig 38: Economic model: cost of electricity

This cost of electricity can then be compared to the rate at which the industrial sector buys its electricity from the grid. If this cost of electricity is cheaper that what is charged by the grid, then it's worth investing in the project[38].

The parameters are the following

Site parameters:

- T_H the temperature of the hot side of the thermoelectric
- T_C the temperature of the cold side of the thermoelectric
- W_{in} the flux of waste heat from the industrial furnace, in W/m^2

Technology parameters:

- Material's ZT
- Fraction f of the ideal efficiency which is actually obtained
- Cost of installation I, in \$/m^2
- O&M costs, in \$/m^2/yr

Economic parameters:

- N: payback period. N=10years (reliability of thermoelectrics is ~100,000hrs and 10 years correspond to ~88,000 hrs)
- r the discount rate. It is the rate of investing in a similarly risky project. r=7% is a typical value for such an investment. (5% is the rate taken by Deutch and Lester for

---

[38] Nonetheless, a size factor has to be taken into consideration in addition.

their calculations of electricity from coal or wind, and the risk is lower for such technologies)

Calculations:

The power output from the system is given by $P = f \times \frac{T_H - T_C}{T_H} \times \frac{\sqrt{1+ZT_{av}}-1}{\sqrt{1+ZT_{av}}+\frac{T_C}{T_H}} \times W_{in}$ in kW/m^2 with W$_{\text{in}}$ in kW/m^2. The electricity production per year is $E = 8{,}766 \times f \times \frac{T_H - T_C}{T_H} \times \frac{\sqrt{1+ZT_{av}}-1}{\sqrt{1+ZT_{av}}+\frac{T_C}{T_H}} \times W_{in}$ in kWh/m^2. If we note p (in cts/kWh) the price at which this electricity is sold, then the yearly cash flow generated by the thermoelectric modules would be $CF_t = \frac{p}{100} \times 8{,}766 \times f \times \frac{T_H - T_C}{T_H} \times \frac{\sqrt{1+ZT_{av}}-1}{\sqrt{1+ZT_{av}}+\frac{T_C}{T_H}} \times W_{in} - (O\,\&\,M)$ in \$/m^2. The net-present-value of the project considered is then $NPV = -I + \sum_{1}^{N} \frac{CF_t}{(1+r)^t}$ and the cost of electricity (coe) is the value of p which makes the NPV equal to zero.

Value of the different parameters:

- W$_{\text{in}}$: Ota and coworkers from IHI in Japan worked on a waste heat recovery from one of the IHI cylindrical furnaces. From their paper, it can be estimated that the heat wasted out of this furnace is ~50kW//m^2 (They get a 3.195W out of a 3cmx3cm TE module with an efficiency of 6.59% working between 673K and 323K). According to M. Beauvais (Arcelor Research) a heat flux of 3MW/m^2 is lost from the copper mold of the continuous-casting process in steel making (mold wall temperature ~200°C). Because the industrial furnaces studied in the IHI are good candidates to receive thermoelectrics, (especially because they are closed systems with a cooling part and a heat source), the simulations will be run around this value of 50kW/m^2 and around these temperatures ranges.
- I: The cost of thermoelectric was estimated from the currently commercially available modules. The commercial price of some modules along with their dimensions is given in the table below:

Application	Company	model	Area (cm2)	Price	Price/area ($/m2)
Power generation	Hi-Z	HiZ-2	8.41	$30.00	35,672
Power generation	Hi-Z	HiZ-14	39.31	$100.00	25,437
Power generation	Hi-Z	HiZ-9	39.31	$85.00	21,621
Power generation	Hi-Z	HiZ-20	56.25	$130.00	23,111
Power generation	Tellurex Cop	G1-1.0-127-1.27-WTN1NN	10.54	$22.95	21,774
Power generation	Tellurex Cop	G1-1.4-127-1.65-WTN1NN	16.00	$24.95	15,594
Power generation	Tellurex Cop	G1-1.4-127-1.14-WTN1NN	17.60	$28.95	16,449
Power generation	Tellurex Cop	G1-1.4-219-1.14-WTN1NN	29.16	$43.95	15,072
Cooling	Melcor	CP 0.8-127-06L	6.25	$22.90	36,640
Cooling	Melcor	CP 1.0-127-08L	9.00	$14.75	16,389
Cooling	Melcor	CP 1.4-71-06L	9.00	$11.00	12,222
Cooling	Melcor	PT6-7-30	16.00	$16.10	10,063
Cooling	Melcor	PT6-12-40	16.00	$10.60	6,625
Cooling	Melcor	PT8-12-40	16.00	$16.10	10,063
Cooling	Kryothermusa	Drift 1,5	16.00	$24.75	15,469
Cooling	Kryothermusa	Drift 0,8	16.00	$25.75	16,094
Cooling	Kryothermusa	Chill	16.00	$14.20	8,875

Table 12: Estimate of the cost of thermoelectric modules per m^2

The purchasing price of modules therefore ranges from 5,000 \$/m^2 to 35,000 \$/m^2. To this has to be added the cost of installing the modules. A price in the upper range, around 20,000 \$/m^2 to 30,000 \$/m^2 is thus a good estimate of the cost of implementing the technology. Note that the Thailand's study used a range of 2,000 \$/kW to 3,000\$/kW in their simulation, which is what our model gives us for a price of installation of 20,000 \$/m^2 to 30,000 \$/m^2.

- O&M: Yodovard *et al.* take the maintenance costs (per yr) to be 0.5% of the installation price but do not explain why they take this figure. I took O&M=\$0, because of the high reliability of the technology and making the assumption that, because of the presence of qualified technicians and engineers in the plant, maintenance would not really add to the costs of running the plant. It is however an imperfection of the model.
- f, efficiency factor: We showed in section IV that ~77% of the ideal efficiency was achieved in power generation. This number should approach 85% in the forthcoming years. Nonetheless, because the power output is a low voltage DC current. Tensions must be added and an AC/DC converter must be used. These devices usually work at 90%-95% efficiency. We will take an efficiency factor f=75% in most of our simulations.