commentary

An inconvenient truth about thermoelectrics

Cronin B. Vining

Despite recent advances, thermoelectric energy conversion will never be as efficient as steam engines. That means thermoelectrics will remain limited to applications served poorly or not at all by existing technology. Bad news for thermoelectricians, but the climate crisis requires that we face bad news head on.

n the past, competition, peer review and free-market forces could be relied on to cull competing ideas to the general benefit of society. Even if someone shamelessly advocated a particular technology, the invisible hand of the marketplace would eventually sort out which solutions where best for society as a whole. But the climate crisis utterly disrupts this traditional business-as-usual calculus for R&D investment; unbridled advocacy need not lead to solutions that are optimal, or even acceptable. Indeed, by definition it is these business-as-usual methods that led to this crisis.

A better framework is needed such that scientists, engineers and technology advocates generally, first and foremost ask themselves: can this technology contribute to solving the climate crisis? Although the response will sometimes be 'no' or 'not greatly', an answer of 'no' can be as important as 'yes' because it allows resources to be more effectively redirected. By way of example, this commentary focuses on thermoelectric technology, a type of solidstate 'heat engine' capable of converting heat to electricity, or alternatively, converting electricity into cooling.

Thermoelectric technology has made significant scientific progress in recent years¹ and its potential to reduce the environmental impact of electrical power generation and air conditioning has been discussed²⁻⁵. Overall, the science, technology and business of thermoelectrics have never been stronger. Nevertheless, the opportunity for a substantial impact on the climate crisis seems limited. Only a very few applications (notably recovery of vehicle waste heat and automobile air conditioning), seem plausible in this respect, and even those applications face stiff barriers. The scale of the climate problem is such that even relatively minor contributions are welcome, but we must keep things in perspective and focus on the most promising solutions.



Figure 1 Integrating thermoelectrics into vehicles for improved fuel efficiency. Shown is a BMW 530i concept car with a thermoelectric generator (yellow; and inset) and radiator (red/blue).

Basics of thermoelectric technology

The basic thermoelectric energy conversion unit consists of two different (one n-type and one p-type) semiconducting materials connected together as a thermocouple. Thermoelectric devices are typically in the form of a module constructed from a number of these thermocouples. Heat applied to one side of the module will 'push' electrons (in the n-type material) and holes (in the p-type) from the hot side to the cold side. In effect, heat drives an electrical current, which can be used to perform work. In some sense, the electrons and holes are analogous to the process whereby a steam turbine is driven when heat causes steam to expand. A thermoelectric module can also be operated in reverse as a heat pump to produce cooling (refrigeration). Key advantages include high reliability, small size and no noise. By these measures of performance, thermoelectric technology is highly competitive. However, relatively low efficiency means that much R&D is devoted to seeking better n-type and

p-type thermoelectric materials. The key property in this regard is known as the 'thermoelectric figure of merit' often written as ZT — a unitless combination of three properties of a material: thermal conductivity (κ), electrical resistivity (ρ) and Seebeck coefficient (*S*), as well as the absolute temperature (*T*): *ZT* = *S*²*T*/ $\kappa\rho$.

The problem associtated with improving efficiency comes down to the materials science, physics and chemistry associated with producing high-ZT semiconductors. ZT values for 'best practice' thermoelectric materials (most of which have been in use for decades) have maximum ZT values near 1. Like all heat engines, a thermoelectric device operates between two temperatures: T_{hot} (the heat source temperature) and T_{cold} (the heat rejection temperature). Higher efficiency is achieved mainly by operating over a wider temperature range and using materials with the highest possible ZT — though efficiency improves only slowly with increasing ZT. Using materials available today, efficiency

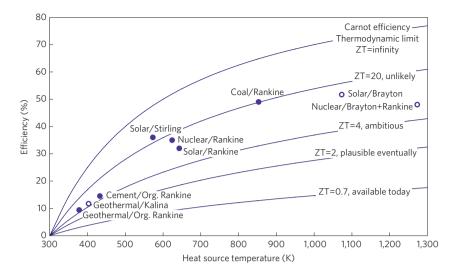


Figure 2 Assessing thermoelectrics. Efficiency of 'best practice' mechanical heat engines compared with an optimistic thermoelectric estimate (see main text for description).

is limited to perhaps 1/6 of the maximum possible Carnot efficiency.

Thermoelectric technology is used for a variety of applications. For example, radioisotope thermoelectric generators provide electrical power for deep-space missions. On Earth, the commercial market for thermoelectric power generation is limited mainly to remote power applications, amounting to perhaps US\$25–50 million per annum for full thermoelectric generator (TEG) systems. The world market for cooling modules (thermoelectric modules only, not final products or systems) is thought to be about US\$200-250 million per annum. In the early 1990s, new ideas and new funding spurred significant progress in thermoelectrics, some of which have been discussed in this journal. Yet only three efforts have produced ZT values in excess of 2: Harman's quantum-dot superlattice6 with a reported ZT ~3.5 at 575 K (ref. 7), Venkatasubramanian's superlattice with reported ZT ~2.4 at 300 K and ZT ~2.9 at 400 K (ref. 8), and Hsu's lead antimony silver telluride (LAST) bulk/'nanodot' material with a reported ZT ~2.2 at 800 K (ref. 9). Translation of these laboratory results to commercial quantities of materials and/or efficient devices, however, does not seem imminent.

Quite recently, ZT ~1.4 was reported for a 'fine grain' bulk bismuth-telluride material, made by grinding nanometresized powder and pressing the powder back into a bulk solid¹⁰. A start-up company, GMZ Energy, has announced intentions to produce commercial quantities of this substance, which would then become the highest-ZT material commercially available. A recent review⁵ stated that ZT = 3 is the ultimate goal of thermoelectrics and suggested that this "appears to be within reach in the next several years". Although scientifically plausible, no clear path for such a development has been identified, and engineering progress is therefore limited to existing, lower-ZT materials for the time being.

Possible thermoelectric power generation applications

The most promising thermoelectric power generation application with 'greentech' implications is vehicle waste heat recovery to improve fuel economy. In this concept, vehicle waste heat, usually from the exhaust, is redirected to a TEG to produce electricity (Fig. 1). More drive-train power is available to move the vehicle, and electricity is still available. Under the US Department of Energy's 'FreedomCar' programme, teams have been assembled to pursue this concept. The FreedomCar target is for both cars and trucks to improve overall fuel economy by 10%, and aims to reach production in the 2011-2014 timeframe. As none of the nano/high-ZT materials are yet available, development is proceeding with the best available materials. Most likely, some improvement of ZT will be required for commercialization, but even without this, the programme should provide better cost/benefit estimates. Significant barriers remain before deployment including costs, heat transfer to thermoelectric modules, dedicated radiators, system weight, acceptance of change and competition with alternate conversion technologies as well as with all other means of increasing fuel efficiency.

Even for vehicle waste heat, competition from mechanical engines can be expected to be fierce. Honda, for example, have tested a system using a Rankine steam engine to generate electricity from waste heat in a hybrid vehicle, increasing overall engine efficiency by 3.8% (ref. 11). BMW have for some years had a similar effort called Turbosteamer, but their added device is used to supplement the power train (rather than to generate electricity), improving fuel efficiency by 15%. Either of these projects seems to surpass the FreedomCar goal of 10% fuel savings.

In 2006, the US Department of Energy's Office of Basic Energy Sciences initiated support to develop improved thermoelectric materials as part of their solar energy project. The idea is simple enough^{2,3}: concentrate solar energy to create heat that a TEG turns into electricity. Engineering work has not yet started, though, because much higher ZT values are needed first.

Industrial waste heat (incinerators, cement, steel mills and so on) has also been discussed. NEDO (Japan) has invested in thermoelectric R&D for waste heat since at least 1997. Their most recent five-year, US\$25 million programme was completed satisfactorily in 2007, with reasonable progress made towards its goal of 15% system efficiency. Other potential applications have been occasionally mentioned: geothermal, home co-generation (fuel oil-fired furnaces or gas water-heaters plus TEGs) and woodstoves (efficient cooking for the developing world).

Possible thermoelectric cooling applications

The most common refrigerant used in home and automobile air conditioners is R-134a, which does not have the ozone-depleting properties of Freon that it replaced, but is nevertheless a terrible greenhouse gas and will be banned in new European cars by 2011. Soon enough it will have to be banned entirely, and that means we need alternative air-conditioning technologies. Thermoelectric cooling has been suggested as one such alternative, building on the successful use of thermoelectric cooler/ heaters in car seats⁴. The US Department of Energy recently announced a US\$13 million cost-shared programme to develop this technology.

Efficiency of power plants and the effect of size

Particularly for large-scale applications, efficiency will be paramount and future thermoelectric potential needs to be compared to currently available technologies. Figure 2 illustrates the efficiency (electrical power out/heat in) for several heat sources (geothermal, industrial waste, solar, nuclear and coal) in combination with several thermal-to-electric conversion technologies (organic Rankine, Kalina cycle, Stirling, Brayton and steam Rankine). The filled data points represent actual in-service power plants and the open data points correspond to design studies, but based on actual demonstrated technologies. Also plotted is the estimated efficiency of a thermoelectric converter. Note that the efficiency has been estimated from ZT using a simplified but optimistic method. The assumptions tend to overestimate efficiency (to give thermoelectrics a fighting chance), but not grossly so.

The systems shown in Fig. 2 represent an estimate of 'best practice', meaning these values are based on the actual performance of up-to-date systems. These are not 'best possible' values as each of these technologies can be expected to improve in the future. The smallest mechanical engine represented in Fig. 2 is the Solar/Stirling machine at 25 kWe. The others are at least nine-times larger and range up to 1,600 MWe for the Nuclear/Brayton+Rankine study. Figure 2 illustrates an important point: existing, practical mechanical systems are far more efficient than thermoelectrics, and are more efficient than thermoelectrics are likely to become in the foreseeable future. After fifteen years of R&D, the best reported thermoelectric material has a maximum (not average) value of ZT = 3.5, is n-type only (we need both) and is prohibitively expensive. But set that aside and assume one can achieve ZT = 4 averaged over the entire temperature range, for both nand p-type materials and with no losses. Assume all of that and you have the solid line labelled ZT = 4 in Fig. 2, which is still less efficient than existing, commercially available technology regardless of what temperature range is of interest. Unless some extraordinary system consideration firmly

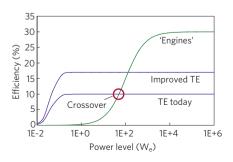


Figure 3 | Size can favour thermoelectrics. An illustrative plot of efficiency versus size for thermoelectrics (TE) and 'engines' (see main text for description).

Table 1 Chinate crisis impact of thermoelectric technology.				
Power scale (kW)	Framples	Required device 7T	ł	

Table 1. Climate evicie impact of the measure destric technology

Power scale (kW _e)	Examples	Required device ZT	Impact on climate crisis
>1,000s	Solar thermal 'engine' replacement	>8-20	Highly unlikely
>10s	Industrial waste heat, geothermal bottoming cycles	>4	Unlikely
0.5-several	Vehicle waste heat, car cooling/ heating, home co-generation	>1.5-2	To be determined
<0.5	Remote power, 'personal' micropower, all existing applications	>0.5-1	(almost) None

prohibits the use of mechanical engines, it seems unlikely that thermoelectric technology has anything to contribute for large-scale systems.

Size, however, can favour thermoelectric systems. Typical conversion systems become less efficient as they are scaled down in size. Figure 3 illustrates this principle in a purely schematic way (the numbers and shape of the curves are illustrative only). Thermoelectric converters have been built that deliver reasonable efficiency at the milliwatt and even microwatt power level. The efficiency of mechanical engines drops off at much higher power levels. This means there is a crossover point: below some power-level, thermoelectric technology will tend to be more efficient. Increasing ZT will move the crossover point to higher power levels, increasing the range of applications where thermoelectrics compete. Meanwhile, mechanical engine R&D focuses (among other goals) on pushing the size down — such is the nature of technology competition. No general value is possible as the precise crossover point will be different for each application: one value for waste heat in cars, another for geothermal systems. If thermoelectrics are to have some impact on the climate crisis, we should look at applications that involve relatively low power levels (where thermoelectric can compete), but occur in large numbers (in order that it has an overall impact). Of the applications considered until now, only a few meet these criteria, as summarized in Table 1. Of these, vehicle waste heat appears the most promising.

Concluding remarks

Thermoelectric technology has made admirable progress in recent years. Laboratory ZT values have increased several-fold, business has grown significantly, start-ups have emerged and next-generation thermoelectric technology and devices are now appearing in cars in significant numbers. Yet the last fifteen years of basic (ZT) R&D has hardly affected products and the nanoscale ZT > 2 materials reported in the literature are not yet commercially available. Moreover, even if future R&D achieves a fully fledged, device-level average of ZT = 4, it is still probably insufficient to displace mechanical engines for large-scale applications. Of course, ZT = 4 should greatly enhance the range and performance of niche applications that thermoelectric technology serves so well today. But the impact on the climate crisis, even with ZT = 4, seems limited to the smaller scale, decentralized applications, the most promising of which appears to be vehicle exhaust heat recovery. Even there, the benefit is potentially around 10% improved fuel economy assuming all the hurdles to market penetration are overcome. The opportunity for thermoelectric technology to help in the climate crisis seems limited.

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References

- Vining, C. B. in: European Conference on Thermoelectrics, ECT2007 (ed. Semenyuk, V.) (Odessa, Ukraine, 2007); http://ect2007.its.org/system/files/u1/pdf/02.pdf>.
- 2. Crabtree, G. W. & Lewis, N. S. Phys. Today 60, 37-42 (2007).
- Lewis, N. S. & Crabtree, G. W. Basic Research Needs for Solar Energy Utilization (US Department of Energy, 2005); http://www.sc.doe.gov/bes/reports/abstracts.html#SEU>
- 4. Bell, L. E. Science 321, 1457–1461 (2008).
- Tritt, T. M., Böttner, H. & Chen, L. Mater. Res. Soc. Bull. 33, 366–368 (2008).
- Harman, T. C., Taylor, P. J., Spears, D. L. & Walsh, M. P. J. Electron. Mater. 29, L1–L4 (2000).
- Harman, T. C., Walsh, M. P., Laforge, B. E. & Turner, G. W. J. Electron. Mater. 34, L19–L22 (2005).
- Venkatasubramanian, R., Silvola, E., Colpitts, T. & O'Quinn, B. Nature 413, 597–602 (2001).
- 9. Hsu, K. F. et al. Science 303, 818-821 (2004).
- 10. Poudel, B. et al. Science 320, 634-638 (2008)
- Kadota, M. & Yamamoto, K. in Advanced Hybrid Vehicle Powertrain 2008-01-310 (SAE International, 2008).

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Additional information

The author declares competing financial interests: details accompany the paper at www.nature.com/naturematerials