Thermoelectric power, previously limited to spacecraft, is seeing improvements in efficiency that could lead to applications in passenger cars by 2020.

Thermoelectric heat recovery could boost auto fuel economy

By **Philip Ball**
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The internal combustion engine (ICE), inefficient and polluting though it may be, is going to be with us for some time to come. Battery-driven electric vehicles remain a distant prospect for routine use, especially for long-haul heavy transport and construction machinery, and while hybrid vehicles can reduce the consumption of fossil fuels significantly, they too will remain a niche technology in the immediate future.

That doesn't sound like good news for reducing vehicle carbon dioxide emissions. Yet reductions are becoming legally obligatory: In 2020, for example, the average fuel consumption of all new passenger cars in Europe needs to be at least 25 km/l (70 miles per gallon). If such targets are to be met, gasoline-driven vehicles will have to work much more efficiently.

There's certainly plenty of scope for improvement. Only a third of each gallon of fuel burnt in a conventional ICE vehicle is converted to useful mechanical power; the rest is wasted, being converted into heat. Some of this thermal energy could be converted directly into electrical energy by thermoelectric (TE) generators, to be used for propulsion and to drive the vehicle's electrical components such as air conditioning, lights, windows, and—for transportation and construction vehicles—systems such as electric doors, platforms, and hydraulics. By reducing the load on the alternator (the electric-generating system that runs off the ICE), this sort of energy capture would ultimately improve fuel efficiency. TE conversion efficiencies of up to 15% have been recently demonstrated by the US National Aeronautics and Space Administration (NASA) for large temperature gradients—two to four times that of current commercial TE systems. If similar efficiencies could be achieved for the smaller temperature gradients typically in automobiles, then capturing 5–10% of a vehicle's waste heat this way could reduce fuel consumption by 3–6%, which is potentially significant for both cost and emissions savings.

The automotive industry is just one area in which TE conversion could provide a valuable boost for efforts to make energy generation cleaner and more efficient. Such systems could also recapture energy currently lost from the hot effluent of power-plant smokestacks, and could harvest the heat currently generated but not used by photovoltaic cells. TE generators are already used for energy generation in spacecraft. But because of the large scale of the automobile sector, the projections for future growth, and the current inefficiencies it suffers, the use of TEs in vehicles looks set to be particularly significant.

The possibility of converting differences in temperature to a flow of electricity, first identified by German physicist Thomas Seebeck in 1821, was used since the early 20th century for making electrical generators and heat pumps. Commercial systems since the 1950s have relied on semiconductors, especially bismuth telluride and lead telluride.

Seebeck's thermoelectric effect results from the diffusion of charge carriers—electrons and holes—away from the hot side of the junction and toward the cold. Provided that the material has a preponderance of just one type of charge carrier, this leads to a voltage difference across the junction. To extract current from this effect, a typical thermoelectric couple consists of a junction of two electrically conductive "legs" that bridge the hot and cold elements: one in which the carriers are electrons (*n*-type) and the other with hole carriers (*p*-type). (Bismuth telluride, naturally *p*-type, can be made *n*-type by doping with selenium.) Then the directional motions of the two types of charge carrier reinforce rather than cancel each other, with net flow of charge around the circuit.

This coupling of heat and electrical transport is generally weak: A lot of thermal energy is needed to generate a little electrical energy. The key technological challenge for exploiting TE power is to make the coupling stronger: to increase a performance measure denoted ZT (see Box). For many years ZT was limited to a value of less than 1, whereas for many practical applications, it needs to be closer to 2. The utility of TE power-generation systems was thus confined to rather exotic applications such as spacecraft.

One of the key attributes of a good TE material is low thermal conductivity. The problem is that good electrical conductivity tends to go hand in hand with *high* thermal conductivity because of heat transported by mobile charge carriers. Tweaking one without affecting the other is therefore a delicate affair.

"The trick is to keep the electrical conductivity small enough to limit heat transport by charge carriers," said Gregory Meisner of GM Global Research and Development in Warren, Mich.

A significant amount of heat is also conducted in a crystal through concerted atomic vibrations called phonons. These wave-like motions can be disrupted by imperfections in the material's ordered arrangement of atoms on the scale of phonon wavelengths,

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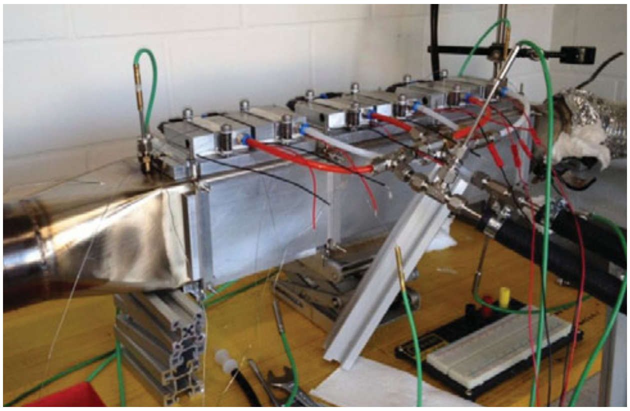
typically in the range of several to several hundreds of nanometers. Such defects may scatter and impede phonons while leaving electrons unaffected. “They act as a filter that stops phonons but admits charge carriers,” said chemist and materials scientist Mercouri Kanatzidis of Northwestern University in Evanston, Ill.

Thus, a general principle for engineering good TE materials is to separate electrical from thermal conductivity—in particular, to make them dependent on structures at different length scales, so as to achieve a “phonon glass” (poor thermal conductivity) but an “electron crystal” (good electrical conductivity). Metal oxides with so-called perovskite structures, such as lanthanum strontium titanium oxide and various manganese and cobalt oxides, offer this combination: Their thermoelectric behavior stems from the confinement of charge carriers to thin layers in the crystal, while interlayer regions scatter phonons. Another option is to use compounds with complex crystal structures and thus large unit cells, such as Ag_9TlTe_5 and Tl_9BiTe_6. Intermetallic alloys called half-Heusler phases, such as $Hf_{0.75}Zr_{0.25}NiSn$, which are considered by some researchers to be very promising candidates, can achieve a *ZT* of about 1. Alternatively, phonon-scattering defects can be produced in alloys laced with vacancies or rogue atoms (interstitials) in the crystal lattice. This has been explored in telluride alloys of semimetals such as bismuth and antimony. A class of compounds called filled skutterudites—in particular, cobalt antimonide $CoSb_3$ doped with transition metals and with crystal voids “filled” with guest atoms such as alkali, alkaline earth, and rare-earth metals—also offer options for creating defects in the crystal’s unit cell.

The realization that TE materials can be improved by careful attention to their nanoscale architectures created something of a renaissance in their study in the mid-1990s. One approach is to engineer phonon-scattering grain boundaries between nanoscale crystallites. Kanatzidis’s team recently reported *ZT* values of more than 2 in a nano- and mesostructured form of lead telluride doped with strontium and sodium.

It now seems likely that the high *ZT* values found in some complex alloys explored since the 1950s, such as $(AgSbTe_2)_{0.15}(GeTe)_{0.85}$ and $(AgSbTe_2)_x(PbTe)_{1-x}$, may be because of their complicated structures, such as the precipitation of nanoscale phases within the matrix. However, as these micro- and nanostructures become more complicated, they also get harder to reproduce reliably. Kanatzidis says that materials free from tellurium are attractive because of cost and concerns that this element might eventually run short. Mechanical engineer Li Shi of the University of Texas at Austin said, “Tellurium- and germanium-free materials such as selenides, silicides, and skutterudites are receiving increasing interest.”

What makes a good TE material?
The voltage developed in a thermoelectric material through the Seebeck effect is generally proportional to the temperature difference across it, with the coefficient of proportionality denoted by the Seebeck coefficient *S*. The performance or figure of merit of the material is measured by the dimensionless quantity *ZT*, where *T* is the operating temperature, and *Z* is proportional to S^2 and is inversely proportional to both the electrical resistivity (so that performance improves for lower resistance) and thermal conductivity (so that better heat conductors are poorer TE materials).



Thermoelectric converter tests on a methane/hydrogen motor of a customized hybrid vehicle—CCEM project cohyb—delivered 120 W electricity, which equals to 3% fuel saving. Credit: EMPA.

“After all the advances in the past four or five years, we now have materials good enough to go into products,” said Kanatzidis. “Now we can see that these systems really will save fuel.” In automobiles, where TE units would replace or augment the alternator, their best location is in the exhaust system, where they can exploit the heat of exhaust gases discharged at temperatures of 300–500°C. Prototype TE systems have already been demonstrated by General Motors, BMW, and Ford, while Volkswagen and Daimler-Benz are also working on designs.

Of course, materials issues are only half the problem: the automotive engineering also has to work. Daniel Jänsch, who heads TE research for IAV, a Berlin-based innovation company that provides engineering services to the automotive industry, admits that producing TE modules appropriate for passenger car applications is very challenging. “The current increase in fuel efficiency with the available TE materials and systems is small, and the costs are high,” he said. But environmental laws might tip the balance. “Legislation, especially in Europe, is a driving force, and manufacturers could decide to implement more expensive technologies instead of paying carbon-emissions penalties,” said Jänsch.

The materials with best *ZT* values are still based on lead telluride, but Meisner says that “these materials are very difficult to work with, especially because of their extremely poor mechanical strength—lead telluride will fall apart in a car.” He says that filled skutterudites, “with *ZT*s of more than 1.7 at exhaust-gas temperatures and superior mechanical properties, are widely considered the most promising new TE materials for near-term commercialization for waste-heat recovery.” Skutterudites and half-Heusler alloys both figure prominently in the research effort supported by the US Department of Energy’s Vehicle Technology Program.

Whatever their materials basis, TE systems in cars are likely to appear first in Europe, where the high price of gas makes the potential savings more worthwhile. “If TE materials research fulfills its promise,” said Jänsch, “we can expect systems in passenger cars to enter the market by 2020.” □