Semiconductors are cool

Cronin B. Vining

In the 1950s there were hopes that semiconductor thermocouples would replace mechanical refrigerators, just as semiconductor transistors supplanted vacuum tubes. New materials may bring that goal a bit closer.

Nothing so induces sleep as a lecture on thermodynamics. So we'll skip that part. But on page 597 of this issue[1] Venkatasubramanian *et al.* describe thin-film thermocouple devices made from new materials that could make all refrigerators and power generators in the world obsolete. Sounds too good to be true? Well, perhaps better picnic coolers at least.

Thermocouples based on metal wires are cheap, reliable and widely used for measuring temperature. A thermocouple is a simple electric circuit, formed by two dissimilar conductors joined at one end, that generates a voltage when the joint and the free ends are at different temperatures. But thermocouples can do more than just generate a voltage. They can operate as heat engines to convert heat into electrical energy (the Seebeck effect), or convert electrical energy into cooling (the Peltier effect; Fig. 1). Thermoelectric devices based on these effects could form a new generation of non-mechanical generators and refrigerators, if only they were more efficient.

Following the development of semiconductors in the 1950s, it was found that replacing the metal wires with semiconductors improved the efficiency of thermocouples by more than an order of magnitude. A big improvement, but normal thermoelectric technology would still cost too much and consume too much electricity to replace that compressor in your kitchen fridge. But semiconductor thermoelectrics are rugged, durable, solid-state energy-conversion devices, and have long been the technology of choice to provide power for deep-space missions, including the Voyager I and II probes to the outer planets and, more recently, the Cassini mission to Saturn. They are also well suited to certain remote, extreme environments (such as some oil pipelines) on Earth, and to small-scale cooling for defence and aerospace applications (such as cooling infrared detectors).

In the past decade or so, cost reductions have led to the introduction of thermoelectric (Peltier) coolers into consumer products, such as ice-less picnic baskets (putting cigarette lighters in cars to good use) and 'climate-controlled' (cooled or heated) car seats. Wristwatches powered exclusively by the heat from your wrist are also available, although they are expensive. But going beyond such niche markets requires much better performance. The problem isn't in the engineering; it is with the science — in particular, the science of thermoelectric materials.

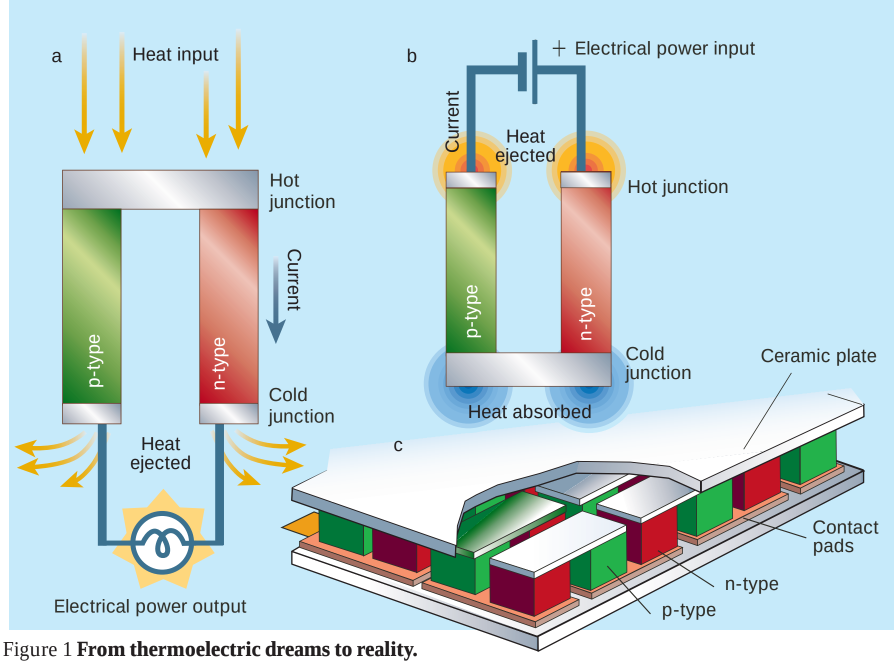

Figure 1 **From thermoelectric dreams to reality. Thermocouples are simple electric circuits used to measure temperatures owing to the voltage generated by temperature differences at the junctions formed by two dissimilar wires or semiconductors. They can also be used to generate:** a, **electrical power, or** b, **cooling. The efficiency of energy conversion is determined more by the properties of the thermoelectric materials (here the n-type and p-type semiconductors) than by the geometry.** c, **State-of-the-art thermoelectric devices can contain up to several thousand individual thermocouples. The electrical and thermal characteristics can be tailored to specific applications by adjusting the number of thermocouples in series and by varying geometric factors. The new thermoelectric materials developed by Venkatasubramanian *et al.*[1] are a major step towards more widespread use of thermoelectric technology beyond existing niche applications. (Graphics courtesy of S. Williams, www.thermoelectrics.com.)**

The problem is that the active materials themselves, the n-type and p-type semiconductor 'legs' indicated in Fig. 1, limit the efficiency. Electrons carry currents flowing in an n-type semiconductor, whereas the currents in a p-type semiconductor are carried by positively charged 'holes'. Both types have an electrical resistance, which must be overcome for the thermocouple to work. And each semiconductor leg conducts heat directly through the device, which limits the temperature difference a device can attain (for cooling) or maintain (for power generation). These losses detract from the ability of each leg to produce either a useful voltage or cooling, depending on the application.

How effective a material will be in a properly engineered thermocouple is measured by a combination of material properties known as the dimensionless thermoelectric figure of merit, usually written as ZT. Think of ZT as shorthand for 'efficiency'. ZT has the advantage that it can be measured on a single leg without building a full device. It can be zero, which means there is no energy conversion. As ZT increases towards infinity a thermoelectric device asymptotically approaches the usual Carnot efficiency limit, which applies to all heat engines (even solid-state ones).

Every material has a figure of merit, usually very small. The term 'thermoelectric material' probably should be reserved for materials with $ZT > 0.5$, which is rare enough to be interesting. For about 40 years, the best-known materials had ZT values between about 0.75 and 1.0. That's why the work by Venkatasubramanian and co-workers[1] is so interesting: they report a ZT of 2.4 in thin films of Bi_2Te_3/Sb_2Te_3 semiconductors. These materials appear to achieve such high ZTs thanks to their unusual structure — a superlattice formed by alternating layers of semiconductors. The previous record for ZT at room temperature was held by a bulk semiconductor alloy based on Bi_2Te_3 and Sb_2Te_3. The superlattice structure appears to enhance the transport of current-carrying electrons (and holes) while inhibiting transport of heat-carrying phonons (quantized vibrations of the crystal lattice). Both effects boost ZT.

When the modern era of thermoelectric science and technology began to emerge in the late 1950s, it seemed possible that thermoelectrics might approach the efficiency of mechanical refrigerators and power generators. By the 1970s, given the lack of progress, few thought it likely. There was even speculation that a ZT of 1 represented some sort of thermoelectric barrier. Certainly it was an empirical limit that nearly halted research and development. But in the early 1990s Rudolph Buser, then associated with the United States Army Night and Electro-Optics Directorate, called on scientists to re-examine thermoelectrics. A basic science programme to increase ZT was soon underway, with support principally from the US Navy's Office of Naval Research and DARPA (Defense Advanced Research Projects Agency). By the late 1990s there was some progress, but even then you had to be an optimist to believe the barrier had been broken[2].

With the results of Venkatasubramanian *et al.*[1], even sceptics and dispassionate observers can safely be encouraged. The material properties, as measured by the figure of merit ZT, are 2.5 times better than the current state of the art, have been verified by more than one method, and are useful at room temperature. It has been a long time in coming but any conjecture about a thermoelectric barrier of $ZT = 1$ seems to have been safely put to rest.

Is it time to replace your old-fashioned fridge? Not just yet. As promising as these new results are, the efficiency (estimated from ZT) remains significantly less than that of conventional refrigerators. And there is no telling when, or if, costs and various engineering issues can be resolved.

On the other hand, this result may be good enough to greatly expand the range of practical applications. After all, modern manufacturers are good at reducing costs and there is no reason to believe this is the last word in efficiency. And most physicists can remember when the upper limit for superconducting transition temperatures was rather firm at about 23 K (−250 °C), whereas the record now stands at 164 K (−109 °C) — still pretty cold, but few would now bet against it going higher. Experimentalists just love to prove theorists wrong. ■

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1. Venkatasubramanian, R., Siivola, E., Colpitts, T. & O'Quinn, B. *Nature* **413,** 597–602 (2001).
2. Dubois, L. H. *18th International Conference on Thermoelectrics* 1–4 (IEEE, Piscataway, New Jersey, 1999); http://www.zts.com/darpa/dubois99

Global change

Matter of time on the prairie

Lindsey Rustad

In some ecosystems at least, extrapolating from the short-term effects of global warming will give a misleading impression of the reaction over longer periods of time.

The Earth is warming. Given that CO_2 seems to be the main determinant of global temperature, predictions of climate conditions in the future depend in part on gauging the response of the carbon cycle to warming. This is a question that Luo *et al.* address on page 622 of this issue[1]. In their experiments on a terrestrial ecosystem in Oklahoma, they find that, in this case at least, acclimatization to increased temperature means that feedback of CO_2 into the atmosphere in the long term would be less than expected.

Over the past century, the Earth's mean surface temperature has increased by 0.6 °C. During the next 100 years, it is predicted to increase by a further 1.4 to 5.8 °C, and by even more at higher latitudes[2]. This predicted rate of change is unprecedented in at least the past 10,000 years, and is largely attributed to increases in the greenhouse gases, most notably CO_2, resulting from the burning of fossil fuels and changes in land use. Confidence in these predictions is increasing, but considerable uncertainties remain. We can't even be sure whether terrestrial ecosystems will take up atmospheric CO_2 (and so moderate further increases in temperature), or be a source of it (and so drive temperature even higher).

In predictions of these climate–ecosystem interactions it is often assumed that, if moisture and nutrients are not limiting factors, rates of both photosynthesis (which removes CO_2 from the atmosphere) and respiration (which releases CO_2 to the atmosphere) will increase with increasing temperature in a predictable way that will remain constant over time. Luo and colleagues[1] tested whether this assumption applies to soil respiration — the combined respiration of roots and micro- and macro-organisms in the soil. They used infrared heaters to warm plots of tall grass prairie by about 2 °C over a period of one year, and compared these plots with unheated control plots. Although soil respiration was expected to increase by 15–20%, there was no significant change. The authors attribute this to respiratory acclimatization to the warmer temperatures: as temperatures rise, they suggest, the sensitivity of respiration to increased temperature decreases, thereby weakening terrestrial feedback to global warming.

A similar conclusion was reached recently by Xu and Qi[3], who studied a forest in the Sierra Nevada. In their study, which took advantage of spatial and seasonal variations in soil respiration, the sensitivity of soil respiration to increased temperature was lowest in the summer, when temperatures were highest. But in this case it was difficult to distinguish between the effects of higher temperature and lower soil moisture.

These authors' emphasis on soil respiration is entirely appropriate because it constitutes the second largest pathway in the global carbon cycle, second only to gross primary productivity. Global estimates[4,5] of soil respiration are in the range 68–100 Pg C yr^{-1} (Pg being petagrams, 10^{15} g); to put this in perspective, the annual input of CO_2 to the atmosphere through human activities is about 7 Pg C yr^{-1}. Evidently, then, even a small increase in soil respiration could accelerate climate change in the twenty-first century; conversely, a small decrease could compensate for anthropogenic emissions, and so slow the expected rate of change.

It has long been known that there is a strong link between soil temperature and soil respiration — respiration increases with rising temperatures, and vice versa[5–7]. A standard way of defining this relationship is to calculate the Q_{10} value, which is the increase in respiration for each 10 °C rise in temperature. Reported Q_{10} values[5] for soil respiration are typically in the range 1.3–3.3, with a mean of about 2.4. But although the concept is a useful one, care is needed in using Q_{10} relationships to infer long-term trends: they are relatively simplistic, and are derived largely from laboratory experiments or short-term field studies of five years or less.

Unlike photosynthesis, soil respiration is not a single process. Rather, it is the summed activity of a complex and changing assemblage of below-ground organisms, including roots, microflora and micro- and macro-fauna. These organisms respond not only to