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A Silent Cool

Thermoelectrics may offer new ways to refrigerate and generate power

By CORINNA WU

At night, when all is quiet, a sound emerges from the kitchen: the faint, unmistakable hum of the refrigerator, working hard to keep the ice cream frozen and the milk cold. That sound comes from a compressor that repeatedly forces the evaporation and condensation of a fluid, often a chlorofluorocarbon. As the liquid boils, it absorbs heat from inside the refrigerator. Then, when the gas condenses, it dumps its heat outside, creating cool on the inside.

Someday, new materials may make clunky refrigerators more like old-fashioned iceboxes—quiet, reliable, and energy efficient. Many researchers hope that better thermoelectrics—materials that change temperature when an electric current passes through them and that also generate electric currents when heat is applied—could replace today's compressors with systems that have no moving parts and use no gases that deplete the ozone layer.

Thirty years ago, after a flurry of research failed to bring about the revolution that many had expected, some critics declared the field of thermoelectrics dead. Recent interest in more environmentally friendly refrigeration has reinvigorated the area. Moreover, advances in materials science during the last few decades signaled to many people that after 25 years, "there ought to be something they haven't tried," says Cronin B. Vining, a consultant based in Auburn, Ala., and president of the International Thermoelectric Society.

With thermoelectrics experiencing a rebirth, increasing numbers of researchers have set their sights on new classes of materials as well as new structures of the old ones. These new thermoelectrics could find their best applications in places where traditional vapor compression doesn't work, such as in cooling microelectronics or laser diodes. Thermoelectric materials are also being tapped as a way to convert the waste heat generated by car engines into usable power.

Still, scientists are proceeding cautiously, mindful of the previous disappointments. "It's not that we're going to save the world," says Hylan B. Lyon, vice president of research at Marlow Industries in Dallas, "but once [thermoelectrics] finds its niche, it will stay there a long time."

Even though the thermoelectric properties of certain materials were described as early as 1828, the big excitement didn't come until the 1950s. Thermoelectric studies rode on the coattails of the burgeoning semiconductor research, since thermoelectric materials and semiconductors share many of the same characteristics.

At the time, scientists had high expectations for these novel materials. Almost every major research institution worldwide had projects going, Vining says. He recounts that in 1958, one prominent scientist set a short-term goal of reaching 25 percent of the theoretically possible efficiency in a thermoelectric material's ability to heat or cool. Asked why he chose that number, the scientist replied, "because I want to be conservative." But today, Vining observes, efficiencies have risen no higher than about 10 percent.

The enthusiasm of those early days was fueled by successes with bismuth telluride, still the best thermoelectric material known. Vacationers, for example, now use it in the portable beverage coolers that plug into a car's cigarette lighter.

The way such thermoelectric refrigerators work is analogous to the strategy behind a conventional refrigerator. Instead of using a gas to absorb and release heat, however, a thermoelectric device expands and compresses electrons, Vining explains.

Each unit of a thermoelectric cooler consists of a pair of segments made up of two forms of the material—one with an excess of electrons and the other with a deficiency. The segments are connected at the ends, forming two junctions.

What happens at the junctions is the key: As current travels around the circuit, electrons undergo expansion and compression as they move between materials having different electron concentrations. The changes cause one junction to cool down while the other heats up.

Despite a few practical uses of bismuth telluride, there had been no significant advances in efficiency by the mid-1960s, so labs cut back on their research. Thermoelectricity, many say, collapsed under the weight of inflated hopes.

Without breakthroughs to cheer researchers along, basic research in thermoelectrics lay stagnant for nearly 30 years. By the 1990s, researchers "thought they'd done everything that could have been done," says Vining.

Part of the frustration of finding suitable materials arises from the combination of properties necessary for good thermoelectrics. The heart of a thermoelectric refrigerator would be a material that generates a significant temperature gradient in response to an applied voltage, explains Terry M. Tritt of Clemson (S.C.) University.

The greatest cooling efficiency comes from thermoelectrics that conduct electricity well but heat poorly. Unfortunately, "only a handful of materials fit in this category," Vining says. Often, optimizing one property sends the other one plummeting.

Scientists who work with thermoelectrics have devised what they call a figure of merit, or ZT, which combines a material's electric and thermal conductivities with a measure of its capacity to generate electricity from heat. Bismuth telluride, still state-of-the-art after 40 years, has a ZT of about 1. For a thermoelectric material to come close to replacing the compressors in standard refrigerators, Lyon says, it would need a figure of merit of 4 or 5.

In a car, two-thirds of the engine's power is lost as heat through the exhaust or cooling systems. Converting some of that heat into usable power could potentially improve fuel efficiency for a new generation of vehicles. Materials for thermoelectric systems in automobiles would need ZTs of at least 2, General Motors' Donald T. Morelli predicted at the San Francisco meeting of the Materials Research Society in April.

Researchers went so long without improving the figure of merit that they began to suspect that a ZT of 1 was a natural limit. Whether that's true is "the central intellectual question of the field," says Vining. Even though there doesn't seem to be any theoretical limit to ZT, perhaps "nature's trying to tell us something, and we don't know what it is."

Besides bismuth telluride, two other materials and their associated derivatives came to the forefront during those early research years: lead telluride and silicon-germanium alloys. The tried-and-true bismuth tellurides operate best between 0˚ and 47˚C and rapidly worsen as the temperature increases or decreases. Lead telluride operates well at temperatures around 427˚C, making it better for power generation.

There's also a need for materials that can achieve near–liquid nitrogen temperatures, below -70˚C, says Tritt. Hafnium telluride, zirconium telluride, and other pentatellurides are candidates for low-temperature operation, he says.

Silicon-germanium alloys, on the other hand, function best at very high temperatures, around 727˚C, restricting their applicability for cooling and power generation to a few specialized applications. For example, the Voyager spacecraft launched in 1977 use thermoelectrics heated by radioactive sources as a power supply.

"After a quarter of a billion device hours, not one of the 1,200 thermoelectric generators on each Voyager has failed," says Vining, who used to work at the Jet Propulsion Laboratory in Pasadena, Calif.

In 1993, a pair of studies by Mildred S. Dresselhaus, Lyndon Hicks, and Ted Harman of the Massachusetts Institute of Technology jump-started the field. They showed theoretically and experimentally that ZT increases above 1 for thin semiconductor films constituting so-called quantum wells, in which electrons can move only within a confined layer. Their results suggested that quantum wells could lead to thermoelectric devices competitive with conventional technology.

Subsequent modeling studies by Thomas L. Reinecke at the Naval Research Laboratory in Washington, D.C., and David A. Broido at Boston College in Chestnut Hill, Mass., suggest that putting several quantum wells together in a practical device may not yield a greatly improved figure of merit. One recent analysis appeared in the May 26 APPLIED PHYSICS LETTERS.

Meanwhile, scientists and engineers on the industrial side of thermoelectric research had also begun scheming to push ZT higher. In 1972, Raymond Marlow formed Marlow Industries as a spin-off of Texas Instruments, catering to niche markets and supplying thermoelectrics to the military.

In the early 1990s, customers began asking him why ZT was stuck at 1. His interest piqued, Marlow began prodding researchers to improve their theoretical understanding of the problem and to renew their search for materials that might break this barrier.

One set of materials newly discovered to have significant thermoelectric properties are the skutterudites, named after a mineral found in Skutterud, Norway. Skutterudites consist of metals such as iridium, cobalt, or rhodium combined with phosphorus, arsenic, or antimony. Their structure, first described in 1928, contains large, open voids, and "it's the ability to populate these voids [with other atoms] that makes them useful thermoelectrics," says Glen A. Slack of Rensselaer Polytechnic Institute in Troy, N.Y.

The ideal material would conduct electrons as well as a metal does and resist the passage of heat as well as a glass does, Slack says. Putting atoms of another element in the skutterudite voids makes the materials more glasslike. The caged atoms rattle around and disrupt vibrations of the crystal that carry heat energy. So far, rare earths such as lanthanum, neodymium, and gadolinium seem to work best; they are small enough to fit in the voids, yet heavy enough to absorb big vibrations.

Skutterudites "are truly interesting materials," says Vining, especially because there are hundreds of possibilities to test.

Another group that seems to fulfill all the necessary requirements for good thermoelectric materials is the quasicrystals (SN: 10/12/96, p. 232). Unlike true crystals, whose structures consist of small, repeating units, quasicrystals form orderly, complicated structures without a long-range pattern. Their electric conductivity can be tuned by changing their chemical composition, says Tritt, while their thermal conductivity remains inherently low.

This combination of properties spurred Tritt and his team to search for thermoelectric materials among quasicrystals. They are looking at compounds of aluminum-palladium-rhenium and aluminum-copper-iron. "This is one of the few applications for quasicrystals," he says. Last week, Tritt presented his group's recent work at a meeting of the International Thermoelectric Society in Dresden, Germany.

With a variety of materials in hand, engineers might design refrigerators that cool in stages, with different materials sandwiched together to take a computer chip, for instance, to extremely low temperatures.

Those who have spent a long time in the thermoelectrics field welcome its rejuvenation. "One of the milestones along the pathway is when new blood shows up," says Lyon. "That's happening. You're going to see a whole new bunch of faces. They don't have to accept the old ZT as a limit."

Still, researchers caution that a lot of work remains to be done to make thermoelectrics truly practical. "They're not looking for a small improvement," says Vining.

If history repeats itself, many researchers could be in for dashed dreams. On the other hand, if new approaches to an old problem produce significant advances, then perhaps kitchens will hear the sound of silence instead of the familiar, persistent rattle and hum. □