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Thermoelectric Technology of Today and Tomorrow

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Abstract

Today, more than ever before, means must be found to apply the full power of modern materials science to the important problem of efficient and environmentally friendly energy conversion devices. Applications ranging from high value–added aerospace power generation to consumer–oriented conveniences such as picnic baskets must be made smaller, more efficient, more economical, and perhaps most importantly, more compatible with the environment. Fortunately, the growth of materials science presents a variety of new experimental and theoretical techniques with the potential to crack the ZT barrier and usher in a new generation of high performance thermoelectric technology. From Kondo materials, thin–films and quantum wells to novel binary and ternary semiconductors, the number of recent suggestions is almost overwhelming. This presentation will outline the basic principles of thermoelectric devices, applications of thermoelectric technology (particularly NASA and JPL applications), and will survey several exciting possibilities for improving the performance of thermoelectric technology. Thermoelectric devices may one day achieve the age–old dream of efficiency levels comparable to today's best mechanical power generation and refrigeration devices.

What is Thermoelectric Technology

All thermoelectric technology is based on the same principles operating in one of the best known and simplest of all scientific instruments: the ordinary thermocouple. Thermocouples are widely used for temperature measurement and control applications because they are simple, inexpensive, and reliable. A load may be attached to a thermocouple, which completes the electrical circuit and generates electrical power in the load. Or alternatively, an electrical power source may be connected to a thermocouple to produce cooling at the junction between the two legs of the thermocouple.

Whether used for measurement purposes, electrical power generation or cooling, thermoelectricdevices retain the inherent advantages of solid–state devices: simplicity, relatively low cost and high reliability. With these advantages, thermoelectric devices have proven useful in a widevariety of applications, particularly for applications where reliability is an overriding concern.

NASA/JPL Interests and Applications

The National Aeronautics and Space Administration (NASA) and the Jet Propulsion Laboratory (JPL) have used thermoelectric devices since the earliest days of the Space Age. Power generation applications have been particularly prominent in the form of Radioisotope Thermoelectric Generators (RTGs). These generators use the heat generated by decay of a radioisotope such as ^{238}Pu or ^{90}Sr as the primary power source. Most of the high cost generally associated with RTGs is a result of extensive and prudent safety precautions due to the radioisotopes. Thermocouples are used to convert some of the heat into electricity.

Self-contained RTGs are particularly attractive for certain space missions because they eliminate reliance on solar energy and last a very long time. ^{238}Pu, for example, has a half-life of about 88 years. Perhaps the most spectacular success of RTGs in space would be the Voyager missions (I and II) which were launched in 1977 and are now well beyond Pluto. The thermoelectric devices onboard the Voyagers are still operating and have accumulated over 250 million device hours without a single failure! Consider that the thermocouple junctions have been glowing red-hot at 1000°C the entire time.

Other planetary fly-by missions such as Pioneers 10 and 11 to Jupiter and Saturn and most recently the Galileo mission now in transit to Jupiter have also used RTGs. For missions at such great distances from the sun, nuclear heat sources are practically the only alternative. NASA has also used RTGs on the Lunar and Martian surfaces. The Lunar surface is a particular challenge for solar and electrochemical power sources due to the long Lunar night (14 earth-days long). NASA, the US Air Force and Navy have used RTGs for navigational, meteorological and communications satellites, where orbital, attitude control or other considerations made alternative power sources less attractive.

The U.S. has been developing the next generation of RTGs utilizing a modular design for greater flexibility and a number of improvements to increase the specific power (W/kg). Improvements in the thermal insulation and the active thermoelectric materials have been incorporated into the new RTG design.

A number of future NASA missions may use RTGs. Planned missions to Saturn (Cassini) and Pluto (Pluto Fly-by) require such a power source and the MESUR (Mars Environmental Survey) Mission is evaluating the use of milliwatt level RTGs to power small probes on the surface of Mars. Ironically, a possible mission to study the Sun called Solar Probe would also require an RTG, in this case because the intense solar radiation would destroy ordinary solar cells.

In addition to the RTG power sources, the U.S. has launched an experimental nuclear-reactor powered spacecraft (the Snapshot, in 1965) and in recent years has been vigorously developing a nuclear reactor–based power source called SP–100. Both projects use thermoelectric devices to convert the reactor–produced heat into electrical power. The baseline design for this reactor would provide 100 kW of continuous electrical power and would be suitable to provide power for a Lunar or Martian outpost. Another use for the SP–100 reactor would be to power an electric propulsion system and reduced the transit time required to reach Mars. Astronauts are particularly interested in this due to concerns about prolonged exposure to cosmic rays during the long trip to Mars.

Other Applications

A number of other special power generation applications, such as underwater and remote monitoring applications and even heart pacemakers, have made use of RTGs and it seems very likely these special applications will continue. Thermoelectric coolers are utilized in similar range of special applications. Many types of sensors, such as infrared detectors, require cooling and multistage thermoelectric coolers are widely used in high added–value aerospace applications for this purpose. Perhaps the most interesting trend in commercial applications today is the lowly picnic box. A number of manufactures are now marketing these products for use in recreational vehicles, cars, trucks and boats. In this case, low manufacturing costs and marketing have resulted in a successful, thermoelectric product.

Even without major technological advances, applications for thermoelectric technology are likely to increase in the future. Two major trends will drive this effect: 1) increasing concern over the environment and 2) increasing energy costs. In the U.S., the first trend may be more important than the second due to relatively strong energy resources. In much of the world, however, the second trend may be more important. Both trends, however, are likely to increase in importance for a long time.

Thermoelectric cooling and refrigeration is environmentally benign and at least some environmentally conscious consumers will be willing to pay the slightly higher energy costs. This could be in many types of products, from picnic boxes and tabletop refrigerators to automobile air conditioners. Thermoelectric power generation, particularly in combination with other conversion systems, can in many cases improve the overall system efficiency by capturing heat that is difficult to utilize by other means. Bottoming cycles and waste heat recovery come to mind. Even at the low fuel costs dominant in the U.S., pilot studies indicate that thermoelectric generators capturing the waste heat from diesel engines can be a cost effective solution to the electric power requirements for commercial trucks.

Historical Perspective and Theoretical Limits

The real dream for the future, however, goes far beyond anything possible with today's thermoelectric technology. In principle, thermoelectric devices can be as efficient as any existing mechanical energy conversion device. Achieving such high efficiencies would be as revolutionary to energy sciences as the development of the transistor was to electronics. Indeed, in the 1940's and 1950's it seemed to some people that semiconductor technology would replace not only vacuum tubes, but turbines as well. Such was the enthusiasm of the time that it has been estimated that some 1000 organizations in the U.S. alone were involved in some type of thermoelectric work. In 1959 no less an authority than Zener considered 25% efficiency a "conservative goal" for a thermoelectric generator.

The underlying quantum mechanics of semiconductors was still relatively new and semiconductors were only recently available in the required quantities and purities. Progress in thermoelectricity was very rapid from the mid-1950's through the mid-1960's. By this time, many of the simplest and most easily studied systems had been examined. All the common thermoelectric materials in use today were developed in this period and performance levels achieved in 1960 proved difficult to improve further. As a result, the support for research in thermoelectrics has been severely reduced for most of the past several decades.

Today, we know a great deal more about materials than we did in 1960. We know why SiGe has the thermoelectric performance it has. We know why Bi_2Te_3 has the performance it has. We also know about entire families of materials and variations of materials which were entirely unknown in 1960. But one thing has not changed: there still is no fundamental reason why *all* thermoelectric materials have such poor performance. Isn't it least a little surprising that, given the wide range of materials properties possible, *no material at all with really high thermoelectric properties is known?*

New Approaches

The potential impact of discovering new thermoelectric materials is so great that, so long as no theoretical limits are known, attempts should be made to find new materials. With all the advances made in other branches of materials science, this is a good time to reexamine thermoelectricity. It is clear at the start that most attempts will fail. But after enough failures perhaps, just perhaps, understanding will improve and eventually progress will be made. The best way to avoid the failures is to do nothing at all. But the best way to succeed is to move forward with the best ideas available. In this final section, several general types of ideas for new approaches will be briefly discussed.

Bulk Materials

Several groups have been examining various novel semiconductors for their thermoelectric properties. In the 1980's JPL, Thermotrex (then called Thermo Electron), General Atomics and General Electric performed studies on resulting in thermoelectric properties comparable to (although not yet superior to) state of the art SiGe alloys. This work lay a foundation for examining even more novel semiconductors. The list of possible thermoelectric materials examined experimentally in recent years at JPL is now rather long and includes: B_4C, $La_{3-x}S_4$, $La_{3-x}Te_4$, Ru_2Si_3, Ir_3Si_5, $IrSi_3$, Ru_2Ge_3, Re_3Ge_7, $Mo_{13}Ge_{23}$, $Cr_{11}Ge_{19}$, $CoGe_2$, $RuSb_2$, Ru_2Ge_3, $IrSb_2$, $IrSb_3$, and $CoSb_3$.

Slack at General Electric has recently surveyed basically all the known binary compounds and has tabulated about 28 known binary compounds which meet certain criteria thought to be required for a good thermoelectric material. The thermoelectric properties of most of these materials are essentially unknown. Among those he identifies as most promising are: $IrSb_3$, Re_6Te_{15}, and Mo_6Te_8.

Considerable work, by Birkholz's group in Germany and by Matsubara and several other groups in Japan, has been directed at various forms of $FeSi_2$. Other silicide-based systems such as $MnSi_{1.75}$ and $Mg_2(Si, Ge, Sn)$ have also received attention.

True compounds described are all binary compounds, or solid solutions between binary compounds. And even though several binary compounds with considerable promise for thermoelectric applications remain to be studied, more complex materials may prove even more promising.

The ternary compounds, in which each of three elements occupies distinct crystallographic sites, have hardly been examined for thermoelectric properties even though there are vastly more ternary compounds compared to the number of binary compounds. A few systems have begun to be studied, however.

For example, rules for the occurrence of semiconducting behavior have been described by Dashevsky for ternary compounds with the composition ABC with A=Ti, Zr, Hf, V, Nb, and B=Fe, Ru, Os, Co, Rh, Ir, Ni, Pd or Pt, and C=Sn or Sb. Several of these compounds have already been shown to exhibit attractive thermal conductivity and power factor values.

Also, Slack has suggested that $U_3Pt_3Sb_4$ may be of interest. This, and a number of isostructural compounds, represents an entirely new class of semiconductor known as a "heavy fermion semiconductor." The name "heavy fermion" reflects the unusual electronic properties of these materials, which behave as if the carriers have effective masses many times greater than typical of ordinary semiconductors. While much remains unknown about these materials, heavy fermion materials typically have enhanced Seebeck coefficients, which is sufficient reason for further study.

Thermoelectricity in Heterostructures

The advent of modern semiconductor fabrication techniques enables the manufacture of materials and structures with properties never previously possible. Today, theoretical and experimental attempts to apply these techniques to engineering the thermal and thermoelectric properties of materials is still in its infancy.

Particularly noteworthy, however, are calculations by Hick and Dresselhaus on the thermoelectric figure of merit in one and two dimensional quantum well structures. They estimate that two dimensional quantum well structures of Bi_2Te_3–based materials may have thermoelectric figure of merit values up to 13 times greater than found in analogous bulk materials. Another factor of 2 improvement may be possible in a one dimensional structure.

The enhancements suggested by Hick and Dresselhaus are based on modifying the electronic density of states. Other beneficial effects are also possible with heterostructures, such as mobility enhancements and increased phonon scattering.

Summary

The potentially enormous impact of really high efficiency thermoelectric devices on the environment and economy, combined with the large number of possible new thermoelectric materials suggests an exciting future for thermoelectric research and development. The greatest challenge, in fact, may be how to rapidly and accurately evaluate the options available. New preparation and measurement techniques are needed so that many materials and structures can be studied. Also, new analytical techniques are needed to ensure that promising options are not eliminated prematurely and to ensure that too much effort is not wasted. The risks are high, but for those willing to accept the challenge, the potential rewards are very great.