Agentschap NL
Ministerie van Economische Zaken, Landbouw en Innovatie

PRESENTATION TRANSCRIPT

THERMOELECTRIC MATERIALS, SÉBASTIEN MOITZHEIM, IA-TOKYO

PRINCIPLE

THE SEEBECK EFFECT

The Seebeck effect gives materials the ability to create electrical energy through a temperature difference. By heating up one side of the material, the concentration of the charge carriers increases. The diffusion of these carriers to the colder side leads to the formation of an electrical potential across the material, similar to a battery.

DEVICE CONFIGURATION

A typical device consists of n-type (electron) and p-type (hole) semiconductors connected in series. A device can easily be scaled by adding more p- and n- type elements. Furthermore it is possible to create micro-structures of these materials which can be used for micro- energy harvesters. In developing thermo-electric materials, it has to be noted that not all materials have p- and n-type counterparts. Therefore, in these cases another material has to be chosen for the carrier counterpart.

CHALLENGE

There are three parameters that influence the efficiency of thermo-electric materials: The electrical conductivity, the thermal conductivity and the Seebeck coefficient. The figure of merit (related to the efficiency of the material), is given by ZT.

The carrier concentration is dependent on the temperature. When the temperature increases, the thermal and electrical conductivity increase, while the Seebeck coefficient decreases. This results in a maximum for ZT at a certain carrier concentration (i.e. temperature). The carrier concentration can furthermore be controlled to a certain extent by doping.

Also it is important to note, that the efficiency of the material is not necessarily the same for a complete device compared to the value for the material alone. That is due to the fact that the device efficiency can also have (heat) losses which can be attributed to sub-optimal design.

It is generally accepted that in order for thermo-electrics to become widespread, a ZT > 2 is necessary.

A viable route for increasing the thermoelectric efficiency is by creating nanostructured materials. In this way, the thermal and electrical conductivity can be decoupled.

MATERIALS

OVERVIEW

Each material has its own optimal working temperature. It is therefore important to chose the right material for the right application. Important factors are cost, efficiency and stability of the material. For example, bismuth telluride, a material which is widely being produced by KELK (Komatsu) has one of the highest thermo-electric efficiencies at lower temperatures, but is brittle and not resistant to higher temperatures. Also, environmentally friendly and abundant materials are an important criterion for the research of thermoelectric materials in Japan.

Dr. T. Kajikawa, the chairman of the Thermoelectric society of Japan (TSJ), has made an overview of the different thermoelectric materials being developed and specified the ones that are being developed in Japan (denoted by the red star). This illustrated the diversity and magnitude of the research into thermoelectric materials that is being done in Japan.

EXAMPLES

As mentioned before, there are many different materials under investigation in Japan which are furthermore funded by government agencies. Two of those are: Bulk nano-silicon and oxide nanocubes.

BULK NANO-SILICON

By decreasing the size of silicon nanoparticles, in the order of ten nanometers, one is able to decrease the thermal conductivity while maintaining the same electrical conductivity. A simplified explanation is, that the heat carriers (phonons) have a larger wavelength and are more effectively scattered by these nanparticles, while the electrons (with a smaller wavelength) are relatively unhindered.

A way to create these nanostructures in bulk is as follows: Use a ball-milling technique to create silicon nanoparticles in the order of 100 nm. Then oxidize these nanoparticles by heat treatment, and subsequently etch away the SiO_2 with an acid such as hydrogen fluoride (HF). Then, by using spark plasma sintering (SPS), make a solid bulk mass of the 10 nm sized silicon nanoparticles.

Until now, Professor Ken Kurosaki from Osaka University has already made samples of bulk nano-silicon. The next step is to use doped silicon to add thermoelectric properties. According to Kurosaki, if the goal of this project is reached (i.e. ZT>1 between RT and 300°C) the range of applications will become countless.

SPARK PLASMA SINTERING

The Spark Plasma Sintering (SPS) technique used is becoming more and more widespread. With this technique, the highest (bulk) ZT value of 2.4 was obtained by a research group from the USA. However this uses Lead Telluride which is a toxic material.

The method enables the use of a large variety of different materials, such as polymers, ceramics, metals and composite materials. Compared to normal sintering it is faster, and it is better suited to keep the original structure of the particles intact.

The Spark Plasma Sintering technique uses plasma that is generated between the particles. This plasma is generated by applying an electric field on the material. This electric field locally generates plasma in between individual (nano)particles, and due to vaporization of the material, a sudden spark fuses the particles together. Mostly the surface of the particle will be fused together, so that the structure is reasonably intact.

OXIDE NANOCUBES

Another strategy that is being adopted at the Nagoya University, by professor Kunihito Koumoto and assistant professor Feng Deng, is the use of strontium titanate nanocubes. A Japanese researcher was the first one to find out that oxides posses thermoelectric properties. After that this property was also found in other materials.

Such an oxide is strontium titanate ($SrTiO_3$ or STO). When strontium titanate is doped with a niobium, it suddenly shows thermo-electric properties. Furthermore, when a thin layer of STO is created, the thermo-electric efficiency is further enhanced. This can be attributed to the formation of a 2-dimensional electric gas. Due to quantum confinement effects, electrons are moved to a region where they have less resistance. This can be seen as a sort of electron highway. The heat carriers however (the phonons) cannot use this “ electron highway” and cannot penetrate the material so easily. This is in simple terms why the efficiency suddenly becomes higher.

In order to make use of this effect, but on a larger scale, Dang is trying to create a material which consists of nanocubes of STO, with a thin niobium shell. By growing these STO nanocubes, and doping them with a thin layer of niobium, he can use these blocks to create a three-dimensional STO nanocube complex. This is done by dispersing the nanocubes in a solvent, and by subsequently evaporating the solvent, the nanocubes form, through selfassembly, a three dimensional organized complex. In this way, the electrons have a high mobility at the surface of the individual nanocubes, but the phonons are easily scattered by the many interfaces.

GOVERNMENT SUPPORT

There are many different projects that are being funded by governmental agencies, which can found in the table. This shows the extent of the potential that the Japanese government and researcher see in thermoelectric materials.

APPLICATIONS

There are currently different applications for which thermoelectric modules are being tested and developed. The application range can grossly be divided into three categories: Waste heat recovery, renewable energy sources and micro-thermoelectric generators.

STEEL FURNACE, DESALINATION PLANT, BIOMASS

STEEL FURNACE

One of the potential applications for thermoelectric power generators, is in the recovery of waste heat in industrial processes. In order to investigate the feasibility, JFE Steel is slowly scaling up a test where thermo-electric modules are installed in the production line of a steel furnace. The warmth of the produces steel is converted into electricity. The goal is to build a 10kW system in this production line, which could deliver energy for example lighting.

DESALINATION PLANT

Another exciting application is the use of renewable energy sources such as solar energy. A project to build a desalination plant in the Middle-East was started by TDS, JAXA and the Chinese government. In this project a facility was built which concentrates solar power to heat up a molten salt. This molten salt is lead to heat-exchange system to boil water, and at the same time harvest electrical energy through thermoelectric generators with an efficieny of 7%. The steam is also used for reverse osmosis, which also gives pure water. The power generated by the thermoelectric generators is used for multiple-effect distillation. The capacity of the plant is 10.000 tons of water per day, and the expected life-time is 20 years. The benefit of this kind of desalination plant is the cost; since a steam generator is not necessary to produce electricity, the total cost can be decreased. Also, at the time of building this facility it was cheaper than to use solar panels (although it is doubtful if this is still valid since the price of solar panels is gradually decreasing. Professor Takenobu Kajikawa was an advisor for this project.

BIOMASS

A third use for thermoelectric generators has already been developed by the company TES energy. The company produces cooking pots with integrated thermoelectric generators. This way, not only can it make your coffee, but also power your mobile phone. According to the company, the idea came after the energy crisis last year due to the great eastern earthquake. With this system, it is possible to stay connected even if the power grid is not working. Additionally for the more power hungry devices, they offer the Firepower 40, which has to be water cooled and can be put on a gas stove or (wood) fire. This generates enough electricity to for example power a laptop, a filtering system or lights.

ROADMAP

Professor Takenobu Kajikawa, the chairman of the Thermoelectric Society of Japan (TSJ), has given a roadmap on the applications for thermo-electric generators. In order for thermoelectric generators to become commonplace, the cost, stability and most importantly efficiency have to be improved. The roadmap gives the different applications possible related to the efficiency. If all goes according to plan, by 2025, an efficiency of 17% will enable the construction of thermoelectric power plants driven by geothermal energyand concentrated solar energy.

CONCLUSION

- Japan highly involved with top research on thermoelectric materials
    - Especially the use of cheap, safe and abundant materials
    - Nanostructuring for better efficiency, but challenge remains making bulk while retaining nanostructure
- Thermoelectric generators might become an additional source of (renewable) energy in the near future

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