Lecture 8

Thermoelectric Devices

Focused on Generators for this class but coolers are designed nearly identically

https://eyvor.org/exhaust-thermoelectric-generator-for-military-vehicle-application/


2/3 of Fuel in an internal combustion engine is wasted as heat!
Heat Flow in a Slab

Since energy flows from high energy to lower energy, heat will flow from a hot surface to cold surface.

Heat conduction (inside the material) can be mediated in several ways:
- Phonons
- Mobile carriers
  - Metal: electrons and holes in a metal
  - Doped Semiconductor: Either electrons or holes
- Ionic Conductor: Ions
Thermoelectric Effect or Thermoelectricity: Differs from thermophotovoltaics in that thermophotovoltaics is merely small bandgap solar cells that can absorb and convert infrared heat energy.

Critical work was performed by Jean Charles Athanase Peltier (French), and Thomas Johann Seebeck (German).

Seebeck Effect is the generation of a voltage across a material as a result of a temperature difference. – Power generation!

Peltier Effect is the opposite – generating a temperature difference as a result of an applied voltage/current. This is used for refrigerant free cooling.
In a n-type material, hot electrons diffuse to the cold side and cold electrons diffuse to the hot side eventually resulting in a constant temperature structure. Note also that a high thermal conductivity (heat flow dominated by phonon transport) material will also result in a near constant temperature profile (equilibrium).
If something changes the imbalance of hot/cold electron diffusion, a net charge can result on one side relative to the other. For example, if hot electrons are scattered more than cold electrons, the flux of electrons from hot to cold is less than from cold to hot creating a charge imbalance and thus a “thermovoltage”. Note that just as when a semiconductor p-n junction forms, an opposing electric field creates a “drift current” balancing diffusion current.

Thermopower (do not be confused with the measurement called thermopower which is not power at all) can result from the voltage and current created.
The same effect in a p-type material produces the opposite sign thermovoltage.

If you combine them in electrical series, the voltages add.

Note: Both the Seebeck effect and the Peltier effect require two dissimilar materials to be observed. While the voltage exists across one material, as soon as you connect a “wire” or other junction to the hot side to collect power, you essentially have two thermal connections. Thus, complementary sets of materials – one n-type and one p-type – are required to either cool or generate power.
Heat Flow from a Source to Sink

Many such junctions can be added in electrical series but thermal parallel.
Heat Flow from a Source to Sink

Many such junctions can be added in electrical series but thermal parallel.
What makes a good thermal electric material?

• Thermal Considerations –
  • Low Thermal Conductivity (unit W/m-K) required to maintain substantial heat differential
  • Thermal transfer needs to be electronically NOT phononically dominated.
  • Efficiency scales as the difference in temperatures of source and sink but total system efficiency begins to reduce when heat transfer mechanisms other than conduction begin to kick in.
    • Convection scales $\approx T$ but radiation scales as $\approx T^4$

• Electrical Considerations –
  • Highly conductive (unit 1/ohm-cm) materials preferred (want heavily doped semiconductors)
  • Significant heat dependent mobility is preferred
    • Impurity/dopant scattering, polar scattering, random alloy scattering
    • Thermal impedance designed - phononic quantum well reflectors, and nano-clustered phonon scattering centers.

• Geometry considerations –
  • Generally large (mm) devices are required to provide adequate thermal separation
  • Some thin films using exotic materials and phonon engineered structures exist
Thermoelectric Generator Figures of Merit

Seebeck coefficient “S”: Also called thermopower (although it is not power) and thermoelectric power. A measure of a material’s ability to generate a voltage for a given change in temperature. Symbol S. Unit: $\mu$V/Degree Kelvin

$$V = \int_{T_1}^{T_2} S(T) \, dT \quad \text{or} \quad V = S(T_1 - T_2) \quad \text{if S is temperature independent}$$

Alternative representations of Seebeck coefficient or thermopower

$$S = \frac{\Delta V}{\Delta T} = \frac{E}{\nabla T} = \int \frac{\mu}{T} \, dT \quad \text{where} \quad \mu = T \frac{dS}{dT} \quad \text{is the Thompson coefficient}$$
Thermoelectric Generator Figures of Merit

Z number:

\[ Z = \frac{\sigma S^2}{\kappa} \]

where \( \sigma \) is electrical conductivity and \( \kappa \) is the thermal conductivity.

Z has units of 1/T so often a normalized version is used \( ZT \) where \( T \) is the average temperature between source and sink.

\( ZT \approx 1 \) is good but \( ZT > 3 \) generally needed for even modest thermoelectric devices.

When a “couple” (two materials needed to form the device, often n-type and p-type) are used, an average \( ZT \) value must be used.

\[ \bar{ZT} = \frac{\left(S_{p\text{-type}} - S_{n\text{-type}}\right)^2 \bar{T}}{\left(\sqrt{\rho_{n\text{-type}}\kappa_{n\text{-type}}} + \sqrt{\rho_{p\text{-type}}\kappa_{p\text{-type}}}\right)^2} \]

where \( \rho \) is electrical resistivity.
Thermoelectric Generator Efficiency

Thermoelectrics are not yet efficient power sources due to many factors including the inherent coupling of phonon and electrical properties (good electrical conductors generally conduct heat reasonably well and good thermal insulators generally are bad electrical conductors).

\[
\eta = \frac{\text{Energy Supplied}}{\text{Heat Energy Absorbed at the Hot Junction}}
\]

\[
\eta_{\text{max limit}} = \frac{\sqrt{1+Z_T} - 1}{\sqrt{1+Z_T} + \left(\frac{T_{\text{Cold}}}{T_{\text{Hot}}}\right)} \left(\frac{T_{\text{Hot}} - T_{\text{Cold}}}{T_{\text{Hot}}}\right)
\]

For example: Using a ZT-bar of 3 and a 125°C hot and 25°C cold junction

\[
\eta_{\text{max limit}} = \frac{2 - 1}{2 + \left(\frac{1}{5}\right)} \left(\frac{4}{5}\right) = 0.37
\]

Efforts at heat recovery (automobiles for example) are presently being tried but inefficiencies limit practical use to a small fraction of the electrical needs and come at very high expense.

A promising new approach:
https://www.cell.com/joule/fulltext/S2542-4351(21)00135-5
Thermoelectric Generator Future

Efforts are continuously being sought to improve the efficiency of TEG’s. Some include:

• Engineered “nano”-composites where nanoscopic precipitates attempt to disrupt phonon transfer creating artificially poor thermal conductors

• Engineered quantum phonon reflectors that are essentially acoustic impedance mismatches that act to reflect phonons but allow electrical conduction.

• Exploration of new exotic materials including materials capable of higher temperature operation to give a bigger $\Delta T$.

• Present leading materials include Bismuth telluride, lead telluride and thallium doped lead telluride. As you can see, serious toxicity issues could ensue if widespread use of these materials results and would likely need to be handled through recycling efforts (similar to some solar cells).