Thermoelectrics 101

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Outline

1) Fundamentals
2) Applications
3) Final Remarks
Definition and Usage

thermoelectric

/ˌθɜrˌmiːˈelektrɪk/

adjective
adjective: thermoelectric
producing electricity by a difference of temperatures.

Translate thermoelectric to: Choose language

Use over time for: thermoelectric

- Peltier effect, 1834
- discovery, 1821 (Seebeck)
- first commercial TE generator (TEG), 1925
- semiconductor TEs, ZnSb and Bi₂Te₃ (1950s)
- space and remote power applications, US-USSR cold war
Seebeck vs. Peltier

• Seebeck effect (1821):
  – Loop of Cu and Bi wires (thermocouple)
  – Heating one end deflected magnetic needle, initial confused with thermomagnetism
  – Ørsted (1823) correctly explained that electric flow occurred due to temperature gradient

\[ \Delta V \equiv (S_B - S_A) \Delta T \]

– \( S_{A,B} \) = Seebeck coefficient = thermopower specific to material A or B (units of \( \mu \text{V/K} \))
– Ex: \( \Delta S \sim 300 \, \mu \text{V/K} \) and \( \Delta T = 100 \, \text{K} \), we generate 30 mV
– Q: how do we generate 1.5 V like AA battery?
Seebeck vs. Peltier

• Peltier effect (1834):
  – Opposite of Seebeck effect
  – Electric current flow through a junction of materials A and B can be used to heat or cool

\[ Q \equiv \Pi_{AB} I = (S_B - S_A)TI \]

  – \( \Pi_{AB} = S_{AB} T \) = Peltier coefficient of junction
  – Heating and cooling are reversible, depending on the direction (± sign) of the current \( I \)
  – Ex: \( I = 1 \) mA, \( \Delta S \sim 300 \) µV/K and \( T = 300 \) K gives us cooling power of 90 µW
  – \( Q \): how do we generate greater cooling (or heating) power?

Jean Peltier
Answer (Look Ahead)

- Commercial TE modules are typically arranged in a series of alternating “n” and “p”-doped semiconductor legs.

- TE legs are “electrically in series” and “thermally in parallel.”
Seebeck vs. Peltier vs. Thomson Effect

• Thomson effect (1851):
  – Continuous version of Seebeck effect, no junction needed
  – Gradual change in $S (\nabla S)$ due to temperature variation ($\nabla T$) inside a material creates local electric field ($\nabla V$) and local heating or cooling ($Q$)

  \[
  \nabla V = T \nabla S \\
  Q = TJ \cdot \nabla S
  \]
  
  – Thomson effect directly measurable in one material
  – Peltier and Seebeck more easily measurable for pairs of materials
  – Seebeck, Peltier, Thomson effects are reversible
  – Joule heating ($I^2R$) is not reversible
Combining TE, Joule & Heat Flow

• Electric field:

\[
E = -\nabla V = \frac{J}{\sigma} + S\nabla T
\]

Ohm Seebeck

• Heat flux:

\[
Q'' = -k\nabla T + STJ
\]

• Local current density:

\[
J = \sigma(-\nabla V - S\nabla T)
\]

• Heat diffusion equation with Seebeck effects and Joule heating

\[
-Q''' = \nabla \cdot (k\nabla T) + J \cdot E - TJ \cdot \nabla S
\]
# Common Seebeck Coefficients

<table>
<thead>
<tr>
<th>Material</th>
<th>Seebeck coefficient S relative to platinum (μV/K)</th>
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<tbody>
<tr>
<td>Selenium</td>
<td>900</td>
</tr>
<tr>
<td>Tellurium</td>
<td>500</td>
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<tr>
<td>Silicon</td>
<td>440</td>
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<tr>
<td>Germanium</td>
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<td>Nichrome</td>
<td>25</td>
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<tr>
<td>Molybdenum</td>
<td>10</td>
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<tr>
<td>Cadmium, tungsten</td>
<td>7.5</td>
</tr>
<tr>
<td>Gold, silver, copper</td>
<td>6.5</td>
</tr>
<tr>
<td>Rhodium</td>
<td>6.0</td>
</tr>
<tr>
<td>Tantalum</td>
<td>4.5</td>
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<tr>
<td>Lead</td>
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<tr>
<td>Aluminium</td>
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<tr>
<td>Carbon</td>
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<tr>
<td>Mercury</td>
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<tr>
<td>Platinum</td>
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<tr>
<td>Sodium</td>
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<tr>
<td>Potassium</td>
<td>-9.0</td>
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<tr>
<td>Nickel</td>
<td>-15</td>
</tr>
<tr>
<td>Constantan</td>
<td>-35</td>
</tr>
<tr>
<td>Bismuth</td>
<td>-72</td>
</tr>
</tbody>
</table>

### Notes
- Semiconductors tend to have high $|S|$, but magnitude and sign depend on doping ($S_p > 0$ and $S_n < 0$).
- Metals tend to have low $S$.

What Is the Microscopic Origin of TE?

• Seebeck = electrons (or holes*) **diffuse** in a temperature gradient, leading to $\Delta V$
  - Diffusion from hot to cold $\rightarrow$ like hot air molecules (O$_2$, N$_2$) diffusing from space heater to farthest corners of the room
  - Kinetic energy $\rightarrow$ $(3/2)k_BT \approx (1/2)mv^2 \rightarrow v = (3k_BT/m)^{1/2}$
  - Hotter electrons (or holes) are faster, but they also carry charge, which sets up the voltage gradient

• Peltier = electrons (or holes*) **carry kinetic energy** (in addition to charge) as they move with current flow
  - Explains why we prefer materials with higher $\sigma$ (electrical conductivity), i.e. metals or highly doped semiconductors

*hole = missing electron in a material = broken bond
Seebeck Coefficient (Classical & Metals)

- Seebeck coefficient can be thought of as the heat per carrier per degree K (specific heat per carrier), \( S \approx C/q \)

- In **classical electron gas** (recall \( k_B/q = 86 \, \mu V/K \)):
  \[
  S_{\text{classic}} \approx \frac{3}{2} \frac{k_B}{q} \approx 130 \, \mu V/K
  \]

- In **normal metals** only small fraction around \( E_F \) contribute, so the thermopower is very small:
  \[
  S_{\text{metal}} \approx \frac{k_B T}{E_F} \frac{k_B}{q} \approx 1 \, \mu V/K
  \]

- In **semiconductors**, energy carriers can be “far” from \( E_F \), so the thermopower can be large:
  \[
  S_{\text{semi}} \approx \frac{E - E_F}{qT} \approx 1 \, mV/K
  \]
Seebeck Coefficient (In General)

- Keeping track of particle motion (Boltzmann transport equation)

\[ \mathbf{v} \cdot \nabla_r f + \frac{qF}{\hbar} \cdot \nabla_k f = -\frac{f(r,k) - f_{eq}(r,k)}{\tau(k)} \]

- Where

\[ f_{eq} = \frac{1}{1 + \exp \left( \frac{E - E_F}{k_B T} \right)} \]

- The electrical conductivity and Seebeck coefficient are:

\[ \sigma = \int \sigma(E) dE \]

\[ S = \frac{1}{qT} \frac{\int (E - E_F) \sigma(E) dE}{\int \sigma(E) dE} \]

- Where the differential conductivity

\[ \sigma(E) = q^2 \tau(E) v^2(E) D(E) \left( -\frac{\partial f_{eq}}{\partial E} \right) \]

\[ \text{density of states (DOS)} \]
Picturing the Transport “Window”

• In metals, density of states (DOS) does not vary sharply around $E_F$

• In doped semiconductors, $E_F$ is at band edge where DOS varies sharply (ex: in $n$-type semiconductor, more states available for transport above than below $E_F$) → for high $S$, need asymmetric DOS near $E_F$

Thermoelectric Figure of Merit (ZT)

• How efficient are TEs?

Obtain highest

\[ Q = STI - I^2 \left( \frac{L}{\sigma A} \right) - \frac{kA\Delta T}{L} \]

When maximizing

\[ ZT = \frac{S^2 \sigma T}{k} \]

\( k = k_e + k_L \)
Thermoelectric Figure of Merit (ZT)

• How efficient are TEs?
• Figure of merit:

\[ ZT = \frac{S^2 \sigma T}{k} \]

• Thus, one must simultaneously maximize S and \( \sigma \) (electrical conductivity) while minimizing k (thermal conductivity)

• These quantities are inter-related, such that increasing S typically leads to decreasing \( \sigma \)

• Also, \( k = k_e + k_L \), thermal conductivity is sum of electron and lattice (phonon) contributions, so increasing \( \sigma \) leads to increasing \( k_e \) \( \leftrightarrow \) Wiedemann-Franz-Lorenz (WFL) law
Trade-Offs in Maximizing ZT

a.k.a. “power factor”

Interesting: if $k_L = 0$ (hypothetically) then $(ZT)_{\text{max}} = \frac{S^2}{L_0}$

Ex: if $S = 300 \ \mu\text{V/K}$ then $(ZT)_{\text{max}} = 3.7$

$k_e = L_0 T \sigma$ \hspace{1cm} (WFL)

$L_0$ must be minimized

Lorenz constant $L_0 = 2.45 \times 10^{-8} \ \text{W} \Omega/\text{K}^2$
ZT for Commercial Materials

- $0.6 < ZT < 1$ for commercially available materials over 300-1200 K temperature range
- Note different materials are best at different temperatures
Evolution of ZT over Time

Over ~5 decades ZT has been limited to ≤ 1 (at room temperature)

Improvements have often come from artificially lowering thermal $k_L$

How Can We Lower Thermal K?

- Introduce features that scatter phonons, not electrons
- “Phonon glass, electron crystal” (G. Slack, 1960s)
Reducing Thermal Conductivity

- Reduce thermal $k_L$ using nanoscale scattering features

$$k_L = \frac{1}{3} C v \lambda$$

reduce mean free path by increasing number of interfaces
Reducing Thermal Conductivity

• Using edge roughness of Si nanowires
Effects of Nanostructuring on TEs

- Hicks and Dresselhaus (1993)* pioneered the concept of quantum confinement effects for TEs.
- Sharp features in the 1D and 2D density of states (DOS) lead to asymmetric $\sigma(E)$ and should increase $S$.
- Challenge: sharp DOS features become “blurred” if there is size non-uniformity in the system.
- Most recent breakthroughs benefitted from reduction in $k_L$.

*http://dx.doi.org/10.1103/PhysRevB.47.12727
How High ZT?

- **TE efficiency**
  \[ \eta = \frac{\Delta T}{T_h} \cdot \frac{\sqrt{1 + ZT} - 1}{\sqrt{1 + ZT} + T_c/T_h} \]

- **Cooling** comparison: modern (mechanical) refrigerator efficiency equivalent to ZT ~ 3

- **Power generation** comparison: steam power plants are ~40% efficient
Alternative: Thermionic (TI) Energy Conversion

- Design tunnel barrier that blocks (filters out) the cold electron distribution, to obtain maximum energy transmission
- Nanoscale vacuum gap is best electron (tunneling) conductor and worst thermal (phonon) conductor
- Challenges in controlling uniform tunnel gaps and efficiency only at higher temperatures

source: Shakouri (2010)
Alternative: Thermophotovoltaics (TPV)

- Filter peak emission of thermal radiation from hot source
- Transmitted photons converted to electron-hole pairs in pn junction
  - TPV avoids some losses of conventional PV and heat backflow problem of TE
  - However, must avoid non-radiative recombination in pn junction
Questions?
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Thermoelectric Applications

Electric Cooling

Power Generation
Thermocouples

• Junction of two dissimilar materials, used to measure temperature (based on Seebeck’s original experiment)

inside water heater

inside meat thermometer

connected to multimeter
Recap: Thermoelectric Modules

- Use electrons and holes to carry heat and cool a body (e.g. cup holder)
  - Must have good electron and hole conductivity (high $\sigma$, $S$)
  - Must block heat “backflow” through (low $k$)
- Use temperature gradient (e.g. hot engine to ambient) to generate power
- No moving parts (=quiet and reliable), no freon (=clean)
More Historical Perspective

• During and after world wars TE research grew, for both cooling and power generation for military and civilian uses

• Some advances could not be shared or were slow (US vs. USSR)

• 1950s: cooling from ambient to 0 °C demonstrated (with Bi₂Te₃)

• Energy harvesting from oil lamp or camp fire to power radios
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Today: the BioLite camp stove phone charger ($130 at REI.com)
Radioisotope Thermoelectric Generators (RTGs)

• For remote applications (e.g. lighthouses) and space exploration, electrical power provided by RTG
• RTG converts heat from decaying Pu-238 into electricity
  – Half-life of 90 years and 1 g sufficient for ~0.5 W power
• NASA used RTGs to power Apollo, Voyager, Viking, Curiosity…
Current-Voltage-Power Curve of a TEG

- In practice, the internal resistance of TEG and the external load resistance both matter.
- Open circuit → max voltage, but no power produced.
- High current → voltage is lost on the internal TEG resistance.
Energy Harvesting from Waste Heat

- Almost everything we do wastes heat
  - Power generation
  - Transportation (engine + friction)
  - Computing

- 15 TW (60%) wasted as heat in the world*

- Most is “low-grade” $T \leq 200$ °C

- Recovering even a few percent would be HUGE, equivalent of several power plants (GW)

thermoelectrics could be a solution

*Dept. of Energy (2012). By comparison, ALL data center power consumption world-wide is ~30 GW!
Recap: TEs for Refrigeration

- Use junction \((\Delta S)\) and current to electrically heat or cool
  - Peltier effect: \(Q_{\text{heat,cool}} = \pm I \Delta ST\)
- Used in small refrigerators, cooled car seats, cup holders
- No moving parts (=quiet and reliable), no freon (=clean)
Recap: TEs for Power Generation

- Use temperature gradient ($\Delta T$) to generate power
  - Seebeck effect: $\Delta V \equiv S \Delta T$
- Used in car engines & exhaust, Mars rover (~100 W)
- No moving parts (=quiet and reliable), no freon (=clean)
Ex: Automobile Waste Heat Recovery

- About 75% of energy from combustion lost as heat in exhaust or coolant
- Catalytic converters reach 300-500 °C and TEGs can be used to harvest 100s of W
- Small fraction power recovery (consider 1 HP ≈ 750 W) but sufficient to power radio or AC and lessen alternator load
An Important Perspective

• “Thermoelectric energy conversion will never be as efficient as steam engines. That means thermoelectrics will remain limited to applications served poorly or not at all by existing technology” (Vining, 2009*)

• However:
  – TEs could play a big role in waste heat recovery
  – Cooling in small size applications (e.g. lasers, seats, cup holders)
  – What matters is not just efficiency (ZT), but cost per Watt
    • Many groups are looking at polymer TEs even though efficiency is lower than traditional semiconductors, paralleling work in solar cell community
  – Power generation in communities without power plants and electric grid
    • TE modules in cooking stoves and solar thermal systems

*Vining, “An Inconvenient Truth About TEs” (2009)
New Materials for Thermal Energy Harvesting

- Traditional thermoelectrics: Bi, Te, Pb → rare, expensive, toxic, brittle

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<td>Bi$_2$Te$_3$ (bulk)</td>
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<tr>
<td>Bi$<em>{0.52}$Sb$</em>{1.48}$Te$_3$</td>
<td>125</td>
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<tr>
<td>PEDOT:PSS (polymer)</td>
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G. Snyder, *Nature Mat.* (2008); S. Yee et al. (2013)
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*Start with low-cost polymers* that already have low $k$, high $\sigma$
- Use nanostructuring (nanotubes, nanowires) to increase $S$

Bonus:
- mechanically flexible
- solution processable

Abundance of Materials

source: http://pubs.usgs.gov/fs/2002/fs087-02
Energy Harvesting From the Human Body

Power Consumption

desktop PC ~ 100 W
notebook PC ~ 10 W
low-power sensor, μchip ~ μW – mW
human body output at rest ~ 100 W

Usable Power From The Body:

Arm Motion: 0.3 W

Footfalls: ~4 W

Body heat: 0.5 - 5 W

1998 Seiko Thermic

2012 Orange Wellies (Thermoelectric)

What’s The Upper Limit (Carnot)?

\[ \eta_{carnot} = \frac{T_{body} - T_{ambient}}{T_{body}} = \frac{310 - 293}{310} K \approx 5\% \]

\[ \eta_{carnot} \times \eta_{TE} \approx 0.5\% \]

must maximize \( ZT = \frac{S^2 \sigma T}{k_{th}} \)

Optimizing Human Energy Harvesting

- Body heat powered watches, boots already demonstrated
- Maximum power harvested is \(~180 \ \mu \text{W/cm}^2\) between skin (34 \(^\circ\)C) and air (22 \(^\circ\)C)
- However, full \(\Delta T = 12 \ ^\circ\text{C}\) is not dropped across TEG
- Key is maximizing internal TEG thermal resistance \(R_{\text{TEG}}\) and minimizing TEG-air thermal resistance \(R_{\text{air}}\)
- Most also minimize TEG contact resistance (flex-TEG)

source: V. Leonov (2009)
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What Motivates Our Research Group

(IBM Watson, Jeopardy! champion)

20 Watts

200 kiloWatts

10,000x

(conventional Moore’s Law size scaling can get us ~10x)
Our Work: Two Sides of the Same Coin

Lower power at its source
(devices, sensors, circuits)

Harvest and manage heat
(energy, thermoelectrics)

fundamental understanding
practical applications
Pop Lab: Energy and Electronics

http://poplab.stanford.edu

new course: EE 323 “Energy in Electronics” in Autumn 2014

Electronics, limited by power & heat since 2005!

Computing on flexible 2D fabrics (graphene, MoS_2)

Energy harvesting: up to ~1 W from body heat using flexible thermoelectrics (TE)

Energy-efficient data storage:
100x lower power in phase-change memory (PCM)

Xiong et al, Science (2011)
Thermoelectric Effects at Nanoscale Contacts


- **AFM-based thermometry (SJEM)**
- **Contact temperature due to:**
  - Current crowding (CC)
  - **Thermoelectric effect (TE)**
- **Some 2D materials have large thermopower $S$**
  - Engineer cooling at device contacts?
  - Design built-in TE coolers?
Looking Ahead: Unusual 2D Materials

- **Large in-plane** thermal conductivity of graphene (>1000 W/m/K)
- **Ultra-low cross-plane** thermal conductivity of layered WSe$_2$ (<0.1 W/m/K)
  - Lower than plastics and *comparable to air*
- Huge thermal anisotropy in all layered 2D materials (>10-100x)
- **Large thermopower** in some 2D materials (~0.5 mV/K)
- Favorable properties for thermoelectrics

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*C. Chiritescu et al., Science (2007)*


Looking Ahead: Future Opportunities

Could we:

– Exploit **anisotropy** for low-power electronics? (e.g. phase-change memory)
– Separate thermal and electrical flow? (thermal transistor)
– Design **electronics with built-in thermoelectric cooling**?
– Achieve transparent heat spreaders and flexible thermoelectrics?

Substrate (silicon, plastics, fabrics; often poor thermal properties)
What Is 10,000x Electrical Power Reduction?

- **10 GW**
  - (all data centers in US)

- **1 MW**
  - (2 Ferrari F430)
  - (solar power from 1 parking lot)

- **50 mW**
  - (average)

- **5 μW**
  - (powered by body heat)
Low Power Devices + Energy Harvesting

up to ~1 W body heat (thermoelectrics)

up to ~4 W walking (piezoelectricity)

flexible thermoelectrics

50 mW (average)

meet in the middle?

± 10,000

5 μW (powered by body heat)
Summary

• Moore’s Law $\sim 10^x$ → slowing down
• Energy scaling & harvesting $\sim 10^4x$ → exciting

• Opportunity for convergence of:
  – Low power electronics
  – Energy harvesting
  – Novel nanomaterials

• Towards fundamental limits of energy use
  (up to $10,000^x$ improvements may be possible)

MUCH room for optimization of energy dissipation, use, and harvesting from the “atomic” level
Key References

• [http://www.thermoelectrics.caltech.edu](http://www.thermoelectrics.caltech.edu) (web tutorial)
• [http://dx.doi.org/10.1002/adma.201000839](http://dx.doi.org/10.1002/adma.201000839) (nanostructured TEs)
• [http://dx.doi.org/10.1146/annurev-matsci-062910-100445](http://dx.doi.org/10.1146/annurev-matsci-062910-100445) (recent developments)
• [http://dx.doi.org/10.1038/nmat2361](http://dx.doi.org/10.1038/nmat2361) (inconvenient truth)
• [http://dx.doi.org/10.1039/C3EE41504J](http://dx.doi.org/10.1039/C3EE41504J) ($/W metrics)
• [http://dx.doi.org/10.1063/1.4803172](http://dx.doi.org/10.1063/1.4803172) (nanoscale Peltier in data storage)
• [http://dx.doi.org/10.1007/s11664-008-0638-6](http://dx.doi.org/10.1007/s11664-008-0638-6) (wearable TEGs)