Develop Thermoelectric Technology for Automotive Waste Heat Recovery

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Energy Efficiency Renewable Energy (EERE)
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Outline
- Background
  - Objective, partnering, ...
  - Motivation: fuel economy

- Technology Development
  - Subsystem modeling
  - Cost
  - Cost-effective materials

- Summary

Jihui Yang
GM Research & Development Center
Demonstrate a 10% fuel economy improvement using thermoelectric waste heat recovery technology, without increased emissions and at a cost-effective way.
Partnering

- **GM**
  - Materials Research
  - Subsystem design, integration, modeling, and validation

- **GE**
  - TE module design and construction
  - Subsystem design and construction

- **Oak Ridge National Lab**
  - High temperature materials properties measurement

- **RTI**
  - Superlattice-base materials and modules

- **University of South Florida**
  - bulk materials development: clathrates, nano-grain PbTe, …

- **University of Michigan**
  - Bulk materials development, skutterudites, nano-composites,…
Energy Distribution –
Typical Mid-Size Vehicle on Federal Test Procedure (FTP)
- Urban (Highway) % energy use

- Standby/Idle: 17.2 (3.6)%
- Engine Losses: 62.4 (69.2)%
- Engine: 100% (25.6%)
- Driveline Losses: 5.6 (5.4)%
- D/L: 12.6% (20.2%)
- Aero: 2.6 (10.9)%
- Rolling: 4.2 (7.1)%
- Kinetic: Braking 5.8 (2.2)%

PNGV source
Alternate: make the radiator into an energy recovery device. (smaller $\Delta T$)
Exhaust as Potential TE Heat Source

Exhaust Heat

Test Time (s)

kW

0 500 1000 1500 2000 2500

0 10 20 30 40 50 60 70 80
Thermoelectric Energy Conversion

Heat Flow $Q_{\text{mh}}$

Heat Leakage $Q_{\text{L}}$

Electrical Power $P_{\text{m}}$

Efficiency: 
$$\varepsilon = \frac{T_H - T_C}{T_H} \frac{1 + ZT}{\sqrt{1 + ZT}} - 1$$

![Graph showing ZT vs. temperature for various materials](image-url)
Generic Concept for a Thermoelectric Energy Recovery Augmented Electrical System

Electric Power Controls

Vehicle Electrical System

Catalytic Converter

Cooling Thermoelectric Device

Heat Collector

Exhaust

Electrical Storage

Alternator

IC Engine

Transmission

Powertrain Control Electronics
Subsystem Modeling

![Diagram of Subsystem Modeling](image-url)
Joule heating from all electrical contacts are accounted for.
Preliminary Temperature Profile

Position in TE device (node)

Temperature (K)

60 kW exhaust flow

20%
15%
5%
Validation of GE’s subsystem Model with GEN I TE Generator

<table>
<thead>
<tr>
<th></th>
<th>Experiment</th>
<th>Model</th>
</tr>
</thead>
<tbody>
<tr>
<td>Output Power</td>
<td>109W</td>
<td>121W</td>
</tr>
<tr>
<td>$V_{\text{load}}$</td>
<td>16.5V</td>
<td>17.4V</td>
</tr>
<tr>
<td>Current, I</td>
<td>6.6A</td>
<td>7.0A</td>
</tr>
<tr>
<td>Hot side temperature</td>
<td>183°C</td>
<td>189°C</td>
</tr>
<tr>
<td>Cold side temperature</td>
<td>35°C</td>
<td>35°C</td>
</tr>
</tbody>
</table>
Cost of fuel economy - $/\Delta \text{mpg}

- This kind of calculation can be used to balance technology options

$/\Delta \text{mpg} \leq \text{Savings}/\Delta \text{mpg}$ is necessary to provide consumer value

Consumer Fuel Savings/$\Delta \text{mpg} \approx$ $300-400/\Delta \text{mpg}$ (15000 mile/yr., 3yrs., 18-20 mpg)
Skutterudites Nano-101

- CoAs$_3$-based minerals found in region of Skutterud, Norway
- Compounds with the same crystal structure are known as “skutterudites”
- Filled skutterudites are electron-crystal-phonon-glass materials

$$Z = \frac{S^2}{\kappa T \rho} = \frac{S^2}{(\kappa_L + \kappa_e) \rho}$$

$\square_2\text{Co}_4\text{Sb}_{12}$

Co Sb Filler atoms
Filled skutterudites as Candidate Materials for Exhaust Heat Recovery

- High ZT values near the exhaust temperature
- Both high performance n- and p-type exist – suitable for TE module
**Mischmetal**

- Mischmetal: from German - “mixed metals”; a naturally occurring alloy of rare earth elements
- Composition (wt%):
  - Ce: 50-55
  - La: 30-35
  - Nd: 5-10
  - Pr: 5-10
- Cost Comparison*:
  - Mischmetal (99.0%): $0.19/g
  - Cerium rod (99.9%): $8.37/g
  - Lanthanum rod (99.9%): $6.40/g

* source: Alfa Aesar
**Mischmetal Starting Material**

<table>
<thead>
<tr>
<th>Element</th>
<th>Wt.%</th>
</tr>
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<tbody>
<tr>
<td>Ce</td>
<td>52.4</td>
</tr>
<tr>
<td>La</td>
<td>23.5</td>
</tr>
<tr>
<td>Nd</td>
<td>17.1</td>
</tr>
<tr>
<td>Pr</td>
<td>5.9</td>
</tr>
<tr>
<td>Si</td>
<td>0.6</td>
</tr>
<tr>
<td>Fe</td>
<td>0.3</td>
</tr>
<tr>
<td>Al</td>
<td>0.1</td>
</tr>
<tr>
<td><strong>Sum</strong></td>
<td><strong>99.9</strong></td>
</tr>
</tbody>
</table>

- **electron probe microanalysis**

- **wet chemistry**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ce</th>
<th>La</th>
<th>Nd</th>
<th>Pr</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>53</td>
<td>23</td>
<td>18</td>
<td>5</td>
</tr>
</tbody>
</table>
Electron Probe Microanalysis of Mischmetal-filled Skutterudites

<table>
<thead>
<tr>
<th>Nominal composition</th>
<th>Actual composition</th>
<th>Room temperature lattice parameter (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mm$<em>{0.71}$Fe$</em>{2.5}$Co$<em>{1.4}$Sb$</em>{12}$</td>
<td>Mm$<em>{0.55}$Fe$</em>{2.44}$Co$<em>{1.56}$Sb$</em>{11.96}$</td>
<td>9.109(1)</td>
</tr>
<tr>
<td>Mm$_{0.82}$Fe$<em>2$CoSb$</em>{12}$</td>
<td>Mm$<em>{0.65}$Fe$</em>{2.92}$Co$<em>{1.08}$Sb$</em>{11.98}$</td>
<td>9.117(1)</td>
</tr>
<tr>
<td>Mm$<em>{0.93}$Fe$</em>{3.5}$Co$<em>{0.5}$Sb$</em>{12}$</td>
<td>Mm$<em>{0.72}$Fe$</em>{3.45}$Co$<em>{0.57}$Sb$</em>{11.97}$</td>
<td>9.126(1)</td>
</tr>
<tr>
<td>MmFe$<em>4$Sb$</em>{12}$</td>
<td>Mm$<em>{0.82}$Fe$</em>{2.92}$Sb$_{11.96}$</td>
<td>9.146(1)</td>
</tr>
<tr>
<td>Mm$<em>{0.93}$Fe$</em>{3.5}$Co$<em>{0.5}$Sb$</em>{12}$</td>
<td>Mm$<em>{0.82}$Fe$</em>{3.55}$Co$<em>{0.49}$Sb$</em>{11.99}$</td>
<td>9.1294(2)</td>
</tr>
<tr>
<td>MmFe$<em>4$Sb$</em>{12}$</td>
<td>Mm$<em>{0.88}$Fe$</em>{4}$Sb$_{12.06}$</td>
<td>9.1433(2)</td>
</tr>
</tbody>
</table>

- nominal comp. chosen according to the optimal filled skutterudites Ce$_{y}$Fe$_{4-x}$Co$_x$Sb$_{12}$ ~ PRL 80, 3551 (1998)
- Mm actual concentration < nominal due to high Mm vapor pressure
- all samples are nearly phase pure
- typical secondary phase: MnSb$_2$ or CoSb$_2$ < 1 vol. %
Isotropic Atomic Displacement Parameter – Evidence of Rattling

- Low T intercepts of $U_{iso}$ represent a combination of zero-point vibration and static disorder at the corresponding crystallographic sites.
- Zero-point vibration $\propto 1/M$, expected contribution $\sim$ Mn < Sb < Fe $\rightarrow$ static disorder at the Sb sites, more so at the Mn sites (Mn vs. ☐).
- $\theta_E \sim 71.5$ K (La: 80 K, Ce: 78 K, Eu: 83 K, and Yb: 65 K)
Room Temperature Properties Comparison

- $\frac{S^2}{\rho}$ (μW/cm K$^2$)
- Lattice thermal resistivity (m K/W)

- $Ce_{y}Fe_{4-x}Co_{x}Sb_{12}$
- $Mm_{y}Fe_{4-x}Co_{x}Sb_{12}$
- $La_{0.9}Fe_{3}CoSb_{12}$
- $Ce_{0.9}Fe_{3}CoSb_{12}$

$p (10^{18} \text{ cm}^{-3})$

$y$
Summary of Challenges for Automotive TE Waste Heat Recovery

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- Background
  - Objective, partnering, …
  - Motivation: fuel economy
- Technology Development
  - Subsystem modeling
  - Cost
  - Cost-effective materials
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Need better materials, heat exchanger, contact joining, thermal & mechanical stability, …

Consumer focus: consider $/\Delta\text{mpg}
(also valuable for balancing tech. options)

Low cost materials is a must

Thank you! Questions?