Progress Status of Skutterudite-Based Segmented Thermoelectric Technology Development

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Jet Propulsion Laboratory/California Institute of Technology

Acknowledgements:
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NASA (Project Prometheus), ONR & DARPA
Power Technology

- Flight times are long
  - Need power systems with >15 years life
- Mass is at an absolute premium
  - Power systems with high specific power and scalability desired

- 3 orders of magnitude reduction in solar irradiance from Earth to Pluto
- Nuclear power sources preferable
Advanced Radioisotope Power Systems (APRS) for NASA missions

- Overall objective
  Develop low mass, high efficiency, low-cost Advanced Radioisotope Power System with double the Specific Power and Efficiency over state-of-the-art radioisotope thermoelectric generators R(TGs)
Segmented Thermoelectric Technology (STE)

- **New high ZT materials**
  - Development initiated in 1991 and supported by ONR and DARPA (Skutterudites and Zn₄Sb₃)
  - Substantial increase in efficiency over state-of-the-art

- **Segmented unicouples**
  - Large ΔT, high ZT -> high efficiency
  - Using a combination of state-of-the-art TE materials (Bi₂Te₃-based materials) and new, high ZT materials developed at JPL
    - Skutterudites: CeFe₄Sb₁₂ and CoSb₃
    - Zn₄Sb₃
  - Current new materials operation limited to ~ 975K
  - Higher average ZT values
  - Higher material conversion efficiency
    - Up to 15 % for a 300-975K temperature gradient

Efficiency  \[ \eta = \frac{T_H - T_C}{T_H} \frac{\sqrt{1 + ZT} - 1}{\sqrt{1 + ZT} + \frac{T_C}{T_H}} \]
JPL Segmented Thermoelectrics (STE) Task overview

Overall objectives
- Develop Segmented Thermoelectric technology to from TRL 3 to TRL4 by end of FY06
- Transfer technology to industry/DOE for integration into a radioisotope power system that can provide ~7-8 W/kg specific power and ~10% system efficiency

FY04-06 Major Goals
- Optimize unicouple fabrication technique
- Develop a unicouple thermo-mechanical model
- Perform life testing of STE materials, coupons, components and unicouples
- Further develop sublimation control techniques/materials
- Develop lifetime model

Schedule

<table>
<thead>
<tr>
<th>Top-level Tasks</th>
<th>FY04</th>
<th>FY05</th>
<th>FY06</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unicouple development</td>
<td></td>
<td></td>
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<tr>
<td>Baseline TE materials/coupons life testing and modeling</td>
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<tr>
<td>Unicouple/components life testing</td>
<td></td>
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<tr>
<td>Unicouple/TE materials optimization</td>
<td></td>
<td></td>
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<tr>
<td>Manage and report</td>
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</table>
Key Technology Challenges

Key technology challenges

- TE materials processing and segmented leg fabrication
- Low electrical contact resistance between segments and between segments and cold- and hot-shoes
- Unicouple mechanical integrity
- Lifetime
  - Sublimation control
  - Stable thermoelectric properties
  - Life time prediction model
- Demonstrate unicouple performance
  - Testing and modeling
Converter efficiency: state-of-the-art vs. segmented thermoelectric technology

A 2x increase in efficiency over SOA thermoelectrics has been demonstrated for the STE technology.
The three Radioisotope Thermoelectric Generators (RTGs) provide electrical power for Cassini's instruments and computers. They are being provided by the U.S. Department of Energy.

**GPHS-RTG Performance Data**

<table>
<thead>
<tr>
<th>Specification</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power output-We</td>
<td>290 beginning of life, 250 end of life</td>
</tr>
<tr>
<td>Operational life - hrs</td>
<td>40,000 after launch</td>
</tr>
<tr>
<td>Weight-kg</td>
<td>55.5</td>
</tr>
<tr>
<td>Output voltage</td>
<td>28</td>
</tr>
<tr>
<td>Dimensions</td>
<td>42.2 diameter, 114 long</td>
</tr>
<tr>
<td>Hot junction temperature-K</td>
<td>1270</td>
</tr>
<tr>
<td>Cold junction temperature-K</td>
<td>566</td>
</tr>
<tr>
<td>Fuel</td>
<td>PuO₂</td>
</tr>
<tr>
<td>Thermoelectric material</td>
<td>SiGe</td>
</tr>
<tr>
<td>Numbers of unicouples</td>
<td>572</td>
</tr>
<tr>
<td>Mass of Pu-238-g</td>
<td>7,561</td>
</tr>
</tbody>
</table>
**STE-ARPS**

- Would use advanced materials segmented legs
- 700 to 100°C operation
- Current GPHS-RTG unicouple design would be mostly conserved
- Modifications required to radiator fins to accommodate for lower rejection temperature
- Shorter housing
- New segmented unicouples could “replace” unicouples almost “one for one”

**Advantages of thermoelectrics**

- Flight proven, long life demonstrated
- Solid state energy conversion -> reliability, no vibration, no moving parts
- Scalable
- No single point failure
- Significant system heritage
Projected STE 100W class ARPS specifications vs. SOA

<table>
<thead>
<tr>
<th>Item/Converter</th>
<th>SiGe-RTG</th>
<th>PbTe/TAGS MMRTG</th>
<th>Low T STE (LSTE)</th>
<th>High Temperature TE (HSTE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hot side temperature (K)</td>
<td>1273</td>
<td>823</td>
<td>975</td>
<td>1200</td>
</tr>
<tr>
<td>Cold side temperature (K)</td>
<td>573</td>
<td>453</td>
<td>375</td>
<td>375</td>
</tr>
<tr>
<td>Converter efficiency (%)</td>
<td>7.2</td>
<td>7.6</td>
<td>12.5</td>
<td>14.7</td>
</tr>
<tr>
<td>System efficiency (%)</td>
<td>6.5</td>
<td>6.4</td>
<td>11.18</td>
<td>13.3</td>
</tr>
<tr>
<td>Thermal power (BOM) (W&lt;sub&gt;in&lt;/sub&gt;)</td>
<td>2000</td>
<td>2000</td>
<td>1250</td>
<td>1000</td>
</tr>
<tr>
<td>Thermal efficiency (%)</td>
<td>85</td>
<td>85</td>
<td>85</td>
<td>85</td>
</tr>
<tr>
<td>Electrical power (BOM) (W&lt;sub&gt;e&lt;/sub&gt;)</td>
<td>107</td>
<td>110</td>
<td>118.8</td>
<td>113.0</td>
</tr>
<tr>
<td>Number of modules</td>
<td>8</td>
<td>8</td>
<td>5</td>
<td>4</td>
</tr>
<tr>
<td>Total PuO&lt;sub&gt;2&lt;/sub&gt; mass (kg)</td>
<td>5.02</td>
<td>5.02</td>
<td>3.138</td>
<td>2.51</td>
</tr>
<tr>
<td>Total system mass estimate (kg)</td>
<td>23.24</td>
<td>38.1</td>
<td>16.3</td>
<td>13.1</td>
</tr>
<tr>
<td>- GPHs mass (kg)</td>
<td>11.54</td>
<td>12.83</td>
<td>7.215</td>
<td>5.77</td>
</tr>
<tr>
<td>- Housing (Kg)</td>
<td>3.1</td>
<td>4.2</td>
<td>1.90</td>
<td>1.55</td>
</tr>
<tr>
<td>- Radiator fins (kg)</td>
<td>0.45</td>
<td>3.32</td>
<td>1.7</td>
<td>1.36</td>
</tr>
<tr>
<td>- Converter (kg)</td>
<td>5.65</td>
<td>10</td>
<td>3.9</td>
<td>3.12</td>
</tr>
<tr>
<td>- Other structure (kg)</td>
<td>2.5</td>
<td>5.5</td>
<td>1.6</td>
<td>1.28</td>
</tr>
<tr>
<td>Specific power estimate (W&lt;sub&gt;e&lt;/sub&gt;/kg)</td>
<td>4.6</td>
<td>2.88</td>
<td>7.28</td>
<td>8.64</td>
</tr>
</tbody>
</table>

Unicouples

* 90% of converter efficiency
Segmented legs fabrication and characterization
Unicouples legs

- Developed uniaxial hot-pressing technique for legs fabrication
  - Powdered materials stacked on the top of each other
  - Temperature optimized → density close to theoretical value
  - In graphite dies and under argon atmosphere
  - With metallic diffusion barriers between the TE materials
  - Metallic contacts at hot- and cold-side
  - Low electrical resistance bonds (<5µΩcm²) achieved → negligible impact on overall unicouple performance
Unicouple legs - In-gradient testing

- N- and p-type in gradient (975K-350K) testing of n- and p-skutterudite legs confirm model performance prediction and show little voltage decrease after ~ 100 hours of testing

**n and p leg opencircuit voltage vs. time (NP35)**

![Graph showing opencircuit voltage vs. time for n and p legs](image)
1-D Analytical Model of Segmented Thermoelectric Unicouples

- One-dimensional analytical model of STEs, with up to 5 segments per leg, is coupled to a genetic algorithm for maximizing either electrical power or efficiency

- Input:
  - TE materials properties
  - Total length and composition of n- and p-legs
  - Cross sectional area of the p-leg (or the n-leg)
  - Hot and cold shoe temperatures
  - Total contact resistance per leg

- Output
  - Number of needed segments in n- and p-legs
  - Interface temperatures between various segments
  - Lengths of various segments in n- and p-legs
  - Cross sectional area of n-leg and p-legs
  - Electrical power and conversion efficiency curves
  - Operation I-V characteristics

![Diagram of a segmented thermoelectric unicycle]
Unicouple thermal and electrical testing
Thermal and electrical Testing:
Skutterudite only unicouple

- **Unicouple performance**
  - Low electrical contact resistance
  - Thermal to electrical efficiency: calculated $\approx$ experimental ($\sim 10\%$)
  - Open circuit voltage = 170 mV
  - Maximum power output $\sim 1.3W$
Achieved 12.5% efficiency for 975K-300K $\Delta T$

- With p-segmented leg and n-skutterudite leg
- Consistent with model prediction
Achieved ~14% efficiency for 975K-300K $\Delta T$
- For fully segmented unicouple

Translate into 12.5% efficiency for 975K-375K $\Delta T$

- Fully validate projected efficiency performance
FY01-03 efficiency demonstration

- Latest results fully validate projected performance
Preliminary lifetime & Sublimation studies
### Lifetime performance testing and modeling development

#### THERMOELECTRIC PROPERTIES (FY04)
- **Examples:**
  - SiGe: dopant precipitation
  - Fine grained SiGe: grain growth
  - TAGS: compositional change
- **Testing:**
  - Coupons
- **Impact:**
  - Change in efficiency, P output
- **Solution:**
  - Composition, doping control

#### MATERIALS SUBLIMATION (FY04)
- **Examples:**
  - SiGe: Si & Ge
  - TAGS, PbTe: Te, Se, Ag, Sb
  - Skutterudites: Sb
- **Testing:**
  - Coupons
- **Impact:**
  - A/1, porosity, contact resistance, mechanical failure
- **Solution:**
  - Encapsulation, coatings
  - More refractory materials

#### THERMAL INSULATION (FY05-06)
- **Examples:**
  - Si in MFI
- **Testing:**
  - Unicouple
- **Impact:**
  - Shorting
  - Contamination
- **Solution:**
  - Processing and engineering control

#### THERMO-MECHANICAL INTEGRITY (FY05-06)
- **Testing:**
  - Unicouple
- **Impact:**
  - Contact resistance
  - Mechanical failure
- **Solution:**
  - Device engineering/modeling

**LIFETIME MODEL**

**FUEL DECAY**
Sublimation control experiments

- Isothermal anneal studies
  - Confirmed that n- and p-type skutterudites are phase stable at 700°C
- Uncoated samples
  - Weight loss and temperature stability showed Sb sublimation in dynamic vacuum for T from ~875 to 975K for N- and p-type skutterudites
  - Decomposition into lower antimonide compounds
  - Appears to be diffusion limited

- Initial Sb sublimation control studies
  - Use of cover gas significantly suppresses Sb sublimation
  - Thin metallic film applied during hot-pressing to the sample also significantly suppresses sublimation
  - Thermal/mechanical modeling performed to evaluate impact on unicouple performance
Coated n-type tested in-gradient for 20 days

- No apparent degradation after 20 days
- Metal junction still intact
- Significant improvement over uncoated
Mass loss experiments results

- Ti coating results in a significant mass loss reduction over uncoated
975K-375K Segmented TE Unicouple performance modeling (UNM)

Coating Material: Ti (length 5 mm and thickness = 0-25 μm)
Aerogel encapsulated skutterudite sublimation test

Skutterudite leg coated with graphite-opacified, silica aerogel. At 10⁻⁶ torr for 6 days. The absence of condensate on the inner-wall of the bell jar indicates that sublimation is completely suppressed.

Vacuum test station used to test sublimation coatings.

Condensation pattern of previous non-encapsulated sample sublimation test provides evidence of antimony sublimation.
Aerogel encapsulated samples weight loss experiments

% mass loss vs. time for CoSb₃ disks
(700°C 10⁻⁶ torr)

- aerogel coated disk
- uncoated disk

Aerogel coated CoSb₃:
despite some cracks in aerogel, no depletion layer after 48h at 700°C

Cracks most likely result from aerogel shrinkage around disk: need to improve thermal stability and/or strength of aerogel

before heating    after 48h at 700°C
Summary

- Demonstrated ~ 14% efficiency for STE unicouples for 975K-300K ΔT
- Initiated life time studies

FY04-06 Major Focus Areas

- Optimize unicouple fabrication technique; develop unicouple thermo-mechanical model
- Perform life testing of STE materials, coupons, components and unicouples
- Further develop sublimation control techniques/materials
- Develop lifetime model
High Temperature Materials

- Chevrel chalcogenides (Mo$_6$Se$_8$-based)
  - Synthesized several additional Cu and Fe filled Mo$_6$Se$_8$ compositions using a powder metallurgy technique
  - Measured Seebeck coefficient, electrical resistivity, and thermal conductivity from 300K to 1275K
  - Achieved $ZT \approx 0.6$ at 1275K for Cu$_4$Mo$_6$Se$_8$ composition, comparable to SiGe
  - Tested Cu$_4$Mo$_6$Se$_8$ sample under electrical load (potential Cu electromigration)
    * Sample shows no indication of electromigration after 6 days at 900°C under 5A load current

CuMo$_6$Se$_8$ sample tested for 6 days at 900°C under 5A load
Impact of electrical contact resistance on unicouple efficiency

- Electrical contact resistance needs to be $< 5 \mu \Omega \text{cm}^2$ to prevent impact on converter efficiency
Electrical contact resistance measurements

- Achieved electrical contact resistance < 5 $\mu\Omega\text{cm}^2$ at the segmented legs interfaces
Segmented legs electrical contact resistance measurements

- Bond quality
  - Electrical contact resistance measurement
  - Microprobe analysis
    - Diffusion
    - Chemical reaction and interface layer analysis

Electrical contact resistance measurements set-up
Unicouple fabrication process developed

- Developed a process to fabricate unicouple by hot-pressing
  - P- and n-leg alternatively hot-pressed onto a Ti hot-shoe
  - No measurable electrical contact resistance between TE legs and Ti hot-shoe
  - Requires further optimization but very promising

- Process compatible with batch manufacturing