III. SOLID STATE ENERGY CONVERSION

III.1 Developing Thermoelectric Technology for Automotive Waste Heat Recovery

Jihui Yang (Primary Contact), T. Anderson, G. S. Nolas, C. Uher, D. T. Morelli, A. Wereszczak, and H. Wang
GM Research and Development Center
30500 Mound Road, MC 480-106-224
Warren, MI 48090

DOE Technology Development Manager: John W. Fairbanks

NETL Project Manager: Carl Maronde

Subcontractors:
- General Electric (GE), Niskayuna, NY
- University of South Florida, Tampa, FL
- University of Michigan, Ann Arbor, MI
- Michigan State University, East Lansing, MI
- Oak Ridge National Laboratory, Oak Ridge, TN

Objectives

- Provide a manufacturability and feasibility assessment of thermoelectric (TE) devices based on bulk and thin film materials, and provide a recommendation going forward.
- Optimization of the cost-effective bulk materials.
- Finalize material selections for exhaust and/or radiator heat recovery.
- Finalize design for exhaust and/or radiator waste heat recovery devices, with estimated performance.
- Identify volume capable and cost-effective manufacturing processes for TE modules.

Accomplishments

- We found that existing bulk TE materials in an exhaust generator can meet the minimum 350 W requirement; the exhaust TE waste heat recovery has higher, but not significantly higher, cost than the existing fuel economy improving technologies
- We found that low quality heat at the radiator makes recovering significant heat cost prohibitive using existing materials, and requires both TE figure of merit (ZT) enhancement and cost reduction.
- Finalized our material selections for exhaust TE waste heat recovery subsystem.
- Established thermal conductivity reduction mechanisms in multiple-filled skutterudites, and achieved record high ZT in double-filled skutterudites in the temperature range relevant to automotive TE exhaust waste heat recovery.

Future Directions

- Finalize TE waste heat recovery subsystem design.
- Provide initial production-ready TE modules for application-based testing.
- Start TE exhaust waste heat recovery subsystem prototype construction.
- Develop cost-effective TE materials and modules.

✧ ✧ ✧ ✧ ✧

Introduction

In the past year, the project has been focused on several areas: feasibility of automotive TE waste heat recovery subsystem based on exhaust and radiator heat; design and performance estimates of the exhaust and radiator heat recovery subsystems; materials down-select; and the search for high performance and cost-effective TE materials and modules.

The discovery part of this project has demonstrated cost-effective skutterudite materials as potential material candidates. We have also achieved record ZT values in filled skutterudites in the temperature range relevant to automotive exhaust TE waste heat recovery. We have identified a method of enhancing ZT in clathrate compounds. We have also determined the correlation between lattice thermal conductivity and structural properties of antifluorite materials. High temperature mechanical property characterizations have been carried out for many materials chosen for module construction.

Approach

The overall approach we use to achieve the project goal is to combine science and engineering. Existing and newly developed materials are carefully selected by the materials research partners of the project and supplied to the system engineers at GE. Most of the material properties are also validated at Oak Ridge National Laboratory to avoid potential pitfalls. System engineers work closely with vehicle engineers at GM to ensure that accurate vehicle level information is used for developing subsystem models and designs. Subsystem output is then analyzed by GM for potential fuel economy gains.

Our project incorporates material, module, subsystem, and integration costs into the material selection criteria. Dollars/W has been chosen as the metric for balancing various materials, module and subsystem design, and vehicle integration options.

Results

Dual-Frequency Resonant Phonon Scattering in Multiple-Element-Filled Skutterudites

We have realized such behavior in a series of polycrystalline $Ba_xR_yCo_4Sb_{12}$ (R = La, Ce, and Sr) samples. Fe-doping on the Co site was intentionally avoided to isolate the influence of rattlers. The reduction of lattice thermal conductivity could lead to ZT enhancement, if x and y are optimized so as not to substantially degrade the electronic properties. Samples used for this study were fabricated by solid-state reaction and spark plasma sintering (SPS); the detailed procedures were described previously [1]. The nominal and actual compositions are listed in Table 1, along with some room temperature transport property data.

Figure 1 shows the temperature (T) dependence of total thermal conductivity (κ) for all samples and lattice thermal conductivity (κ_L) for selected samples, between 2 K and 310 K. The total thermal conductivity of all samples (Figure 1 (a)) is consistent with a large body of literature developed for filled skutterudites [2], with room temperature values between 2 W/m-K and 6 W/m-K and the peak values significantly lower than that of $CoSb_3$. For almost the entire temperature range studied, $Ba_{0.07}La_{0.04}Co_4Sb_{12.08}$ and $Ba_{0.12}Ce_{0.06}Co_4Sb_{12.08}$ have the lowest κ values, while samples with both Ba and Sr filling have lower κ values than those of Ba-only samples.

Our calculations show that the filler elements for filled skutterudites can be approximately categorized into three groups according to their resonant phonon frequencies: rare-earths, alkaline-earths, and alkalines (Table 2) [3]. The phonon resonant frequencies are comparable for filler elements with similar chemical nature; however, they are significantly different amongst various groups. This further suggests that multiple-filling using elements from different groups can be an effective method for additional κ_L reduction in filled skutterudites. Data shown in Figure 1 (b) clearly demonstrate that dual-filling of $CoSb_3$ with Ba and Ce, or Ba and La is much more effective than Ba and Sr in lowering κ_L. Our recent study using misch-metal (a rare earth alloy having the naturally occurring La, Ce, Pr, and Nd composition)

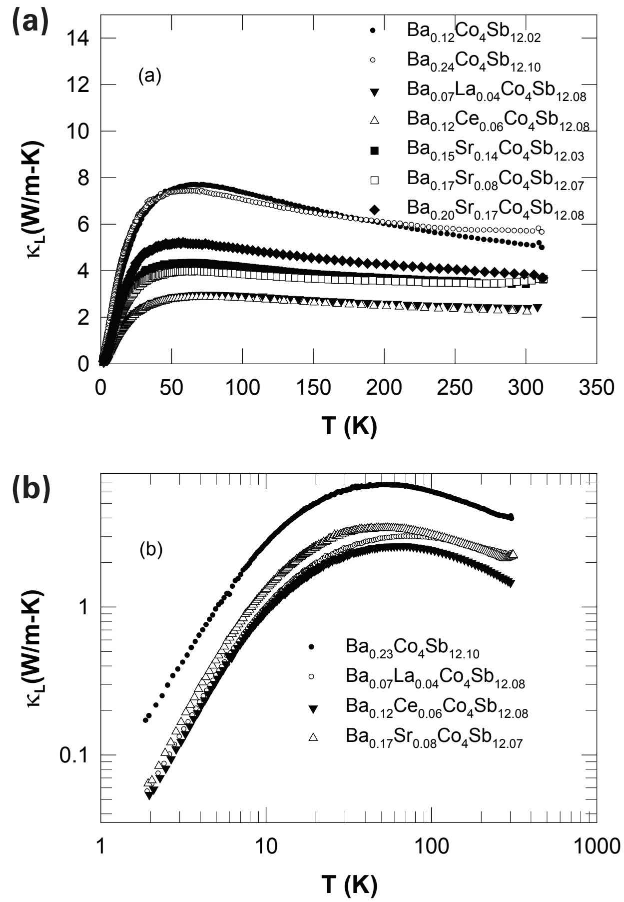

FIGURE 1. (a) Total thermal conductivity vs. temperature between 2 K and 310 K for $Ba_xR_yCo_4Sb_{12}$ (R = La, Ce, and Sr) samples, (b) Lattice thermal conductivity vs. temperature between 2 K and 310 K for selected samples.

TABLE 1. Nominal composition, actual composition (determined by electron probe micro-analyzer), and room temperature total thermal conductivity κ, lattice thermal conductivity κ_L, thermopower S, electrical resistivity ρ, power factor S^2/ρ, carrier concentration n, and thermoelectric figure of merit ZT.

Nominal composition	Actual composition	κ (W/m K)	κ_L (W/m K)	S (μV/K)	ρ (mΩ cm)	S^2/ρ (μW/cm K^2)	n (10^{20} cm^{-3})	ZT
$Ba_{0.15}Co_4Sb_{12}$	$Ba_{0.12}Co_4Sb_{12.02}$	5.04	4.32	−120.46	1.03	14.09	2.19	0.08
$Ba_{0.25}Co_4Sb_{12}$	$Ba_{0.23}Co_4Sb_{12.10}$	5.63	3.92	−106.63	0.43	26.44	3.29	0.14
$Ba_{0.1}La_{0.05}Co_4Sb_{12}$	$Ba_{0.07}La_{0.04}Co_4Sb_{12.08}$	2.40	2.21	−119.47	4.10	3.48	2.12	0.04
$Ba_{0.15}Ce_{0.1}Co_4Sb_{12}$	$Ba_{0.12}Ce_{0.06}Co_4Sb_{12.08}$	2.24	1.46	−104.64	0.95	11.53	10.70	0.16
$Ba_{0.17}Sr_{0.15}Co_4Sb_{12}$	$Ba_{0.15}Sr_{0.14}Co_4Sb_{12.03}$	3.44	2.33	−79.51	0.85	7.43	11.50	0.06
$Ba_{0.20}Sr_{0.1}Co_4Sb_{12}$	$Ba_{0.17}Sr_{0.08}Co_4Sb_{12.07}$	3.54	2.18	−79.03	0.54	11.57	3.81	0.10
$Ba_{0.22}Sr_{0.2}Co_4Sb_{12}$	$Ba_{0.20}Sr_{0.17}Co_4Sb_{12.08}$	3.85	2.39	−72.38	0.50	10.48	14.40	0.08

as filler in $CoSb_3$-based skutterudites shows that κ_L of misch-metal-filled skutterudites is comparable to those single-rare-earth-filled skutterudites [4], further substantiating our conclusions.

Based on these result, the project has achieved record ZT values for skutterudite compounds in the range of automotive exhaust temperatures. We expect that the concept of reducing lattice thermal conductivity by dual-frequency resonant phonon scattering is also effective for other cage-structure compounds, such as clathrates.

Spark Plasma Sintering Process

TE materials can be produced by conventional ceramic processing techniques or from single crystal growth techniques. However, single crystals are limited by the size of the crystals, poor mechanical properties, and chemical heterogeneity. In the polycrystalline approach, dopants are incorporated into the alloy by melting the precursors and casting an ingot. The ingot is then crushed followed by consolidation by cold pressing, sintering, and low temperature anneal.

Our team has set in place a manufacturing process for processing various TE materials following the above general powder processing approach. GM and GE have in-house sintering capabilities of inert atmosphere sintering, hot pressing, hot isostatic pressing and SPS. Currently, our project is pursuing the SPS approach for sintering of its TE materials.

SPS has been used to successfully sinter many materials to greater than 99% theoretical density in a short time (<15 minutes) using the SPS unit (Figure 2). Fully dense n- and p-type disks with outer diameter of 15 mm were processed using the SPS with thickness ranging from 3 to 6 mm.

Diffusion barrier layers (thickness ~250 to 300 μm) were also successfully bonded by a one-step SPS process from particulate sources.

TABLE 2. Spring constant k and resonance frequency ω in the [111] and [100] directions of $R_{0.125}Co_4Sb_{12}$, where R = la, Ce, Eu, Yb, Ba, Sr, Na, and K.

		[111]		[100]	
R	Mass (10^{-26} kg)	*k* (N/m)	ω_0 (cm^{-1})	*k* (N/m)	ω_0 (cm^{-1})
La	23.07	36.10	66	37.42	68
Ce	23.27	23.72	54	25.18	55
Eu	25.34	30.16	58	31.37	59
Yb	28.74	18.04	42	18.88	43
Ba	22.81	69.60	93	70.85	94
Sr	14.55	41.62	90	42.56	91
Na	3.819	16.87	112	17.18	113
K	6.495	46.04	141	46.70	142

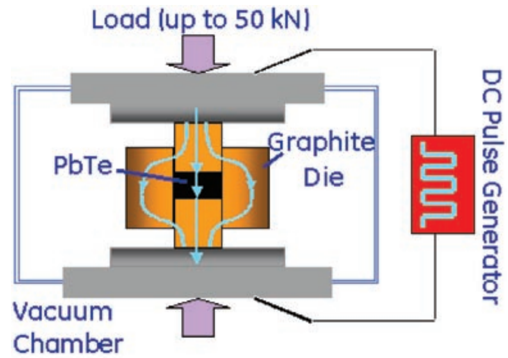

FIGURE 2. Schematic of the SPS Process and SPS Unit

Anticipated Output of TE Exhaust Waste Heat Subsystem over the FTP City Driving Cycle

Based on our TE module, heat exchanger, and subsystem design, we expect that the average electrical power output over the FTP city cycle of an exhaust waste recovery system would be higher than the 350 W minimum requirement. Figure 3 shows the output as a function of the exhaust mass flow and temperature using a specific candidate material.

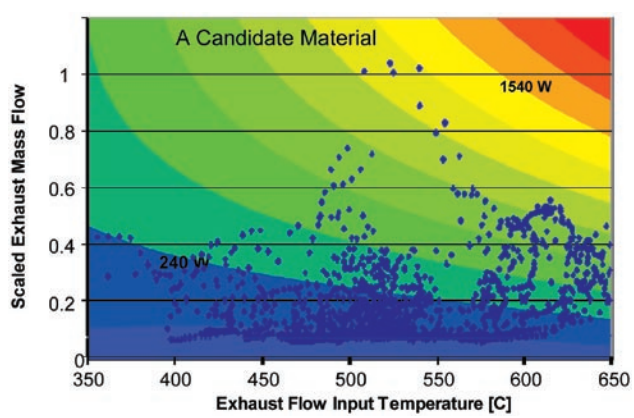

FIGURE 3. Anticipated Electrical Output of a TE Exhaust Waste Heat Recovery Subsystem over the FTP City Cycle

Conclusions

The project has made significant progress in the areas of feasibility of automotive TE waste heat recovery subsystems based on both exhaust and radiator heat; design and performance estimates of the exhaust and radiator heat recovery subsystems; materials down-select; and the search for high performance and cost-effective TE materials and modules. The next phase of our project will be focused on module and subsystem construction and testing.

References

1. L. D. Chen, X. F. Tang, T. Kawahara, J. S. Dyck, W. Chen, C. Uher, T. Goto, and T. Hirai, Proceedings of the 20th International Conference on Thermoelectrics (IEEE, Piscataway, NJ, 2001), p. 57.

2. C. Uher, in Recent Trends in Thermoelectric Materials Research I, Semiconductors and Semimetals, Vol. 69, edited by T. M. Tritt (Academic, San Diego, 2000), p. 139, and references therein.

3. J. Yang, G. P. Meisner, and L. Chen, Appl. Phys. Lett. **90**, 192111 (2007).

4. J. Yang, G. P. Meisner, C. J. Rawn, H. Wang, B. C. Chakoumakos, J. Martin, G. S. Nolas, B. L. Pedersen, and J. K. Stalick, J. Appl. Phys. **102**, 083702 (2007).

FY 2007 Publications/Presentations

1. J. Yang, W. Zhang, S. Q. Bai, Z. Mei, and L. D. Chen, "Dual-frequency resonant phonon scattering in $Ba_xR_yCo_4Sb_{12}$ (R=La, Ce, and Sr)", Appl. Phys. Lett. **90**, 192111, 2007.

2. J. Yang, G. P. Meisner, C. J. Rawn, H. Wang, B. C. Chakoumakos, J. Martin, G. S. Nolas, B. L. Pedersen, and J. K. Stalick, "Low temperature transport and structural properties of misch-metal-filled skutterudites", Journal of Applied Physics **102**, 083702 (2007).

3. J. Yang, invited, Department of Mechanical Engineering, University of Colorado at Boulder, Boulder, CO, March 2007: "Materials for High-efficiency Automobiles".

4. J. Yang, invited, United States Council for Automotive Research, Southfield, MI, May 2007: "Thermoelectric Technology for Automotive Waste Heat Recovery".

5. J. Yang, invited, GM Global Electrical Council Meeting, Warren, MI, June 2007: "Cost of Automotive Electric Power and Thermoelectric Waste Heat Recovery Program".

6. J. Yang, 26th International Conference on Thermoelectrics, Jeju, Korea, June, 2007: "Dual-frequency resonant phonon scattering in $Ba_xR_yCo_4Sb_{12}$ (R=La, Ce, and Sr)".

7. J. Yang, invited, Electronic Structure and Functionality of Thermoelectric Materials Workshop, Reykjavik, Iceland, July 2007: "Thermoelectric Waste Heat Recovery Based Efficient Automobiles".

8. J. Yang, invited, Electronic Structure and Functionality of Thermoelectric Materials Workshop, Reykjavik, Iceland, July 2007: "Properties of Novel Skutterudites".

9. J. Yang, 2007 Diesel Engine-Efficiency and Emissions Research (DEER) Conference, Detroit, MI, August 2007: "Developing Thermoelectric Technology for Automotive Waste Heat Recovery".

10. J. Yang, invited, Ceramics Division, National Institute of Standards and Technology, Gaithersburg, MD, October 2007: "Novel Materials for Thermoelectric Waste Heat Recovery Based Efficient Automobiles".

11. G. P. Meisner "Developing Thermoelectric Technology for Automotive Waste Heat Recovery", Direct Energy Conversion Review and Workshop, Vail, CO, August 20–23, 2007.

12. De Bock, P. and Novak, V., "An Efficiency Entitlement Study for Thermoelectric Generators," Proceedings of 2nd Energy Nanotechnology International Conference, ENIC2007-45040, Santa Clara, CA, September 5–7, 2007.

13. Anderson, T.A., De Bock, P., Jiang, J. and Nagarkar, K., "Development of a Thermoelectric Automotive Waste Heat Recovery Generator," Direct Energy Conversion Review and Workshop, Vail, CO, August 20–23, 2007.

14. Shi X., Zhou Z., Zhang W., Chen L. D., Yang J., and Uher C., "Solid Solubility of Ir and Rh at the Co Site of Skutterudites", *J. Appl., Phys.*, 101, 123525 (2007).

15. Shi X., Zhang W., Chen L. D., Yang J., and Uher C., "Theoretical Study of the Filling Fraction Limits for Impurities in $CoSb_3$", *Phys. Rev. B,* 75, 235208 (2007).

16. Shi X., Chen L. D., Bai S. Q., Huang X. Y., Zhao X. Y., Yao Q., and Uher C., "Influence of Fullerene Dispersion on High Temperature Thermoelectric Properties of $Ba_yCo_4Sb_{12}$-based Composites", *J. Appl. Phys.* (in press)

17. Shi X., Zhang W., Chen L. D., Yang J., and Uher C., "Ab Initio Study on the Filling Fraction Limits for Impurities in $CoSb_3$: II. Thermodynamic Analysis" (submitted to *Acta Mater.*).

18. Shi X., Kong H., Yang J., Salvador J. R., Wang H., and Uher C., "Low Thermal Conductivity and High Thermoelectric Figure of Merit in *n*-type $Ba_xYb_yCo_4Sb_{12}$ Double-Filled Skutterudites" (to be submitted to *Appl. Phys. Lett.*).

19. Uher C., Shi X., and Kong H., "Filled $Ir_xCo_{1-x}Sb_3$-based Skutterudite Solid Solutions", *Proceedings of the 26th International Conference on Thermoelectrics* (2007) (in press).

20. J H. Wang, W.D. Porter, Jihui Yang and G. Meisner, "High Temperature Thermoelectric Properties of Misch-metal-filled Skutterudites", submitted to Applied Physics Letter, September 2007.

21. H. Wang, "Thermal Conductivity and Figure of Merit of Bulk Thermoelectric Materials", Invited Talk at MS&T06: MS & T 2006 Cincinnati OH, Oct. 16–19, 2006.

22. H. Wang, J. Yang, W.D. Porter, and G.P. Meisner, “Thermoelectric Properties of Misch-metal-filled Skutterudites from 300K to 800K”, International Conference of Thermoelectrics (ICT2007) Jeju Island, South Korea, June 4–7 2007.

23. H. Wang, “Thermoelectrics Power Generation: A Review of DOE Waste Heat Recovery Program at ORNL”, invited talk at Material Science and Engineering Department, Seoul National University, Seoul, South Korea, June 11 2007.

24. H. Wang, J. Yang and G.S. Nolas, “Low Thermal Conductivity Bulk Thermoelectrics”, Thermal Conductivity 29, June 25–27, Birmingham, AL, 2007.

25. Timothy P. Hogan, H. Wang, Chun-I Wu, Joseph Sootsman, Duck-Young Chung, Mercouri G. Kanatzidis, Edward Timm, Harold Schock, “Transport Properties of Bulk Nanostructured Thermoelectric Materials”, invited talk, Thermal Conductivity 29, June 25–27, Birmingham, AL, 2007.

26. Jane Y. Howe, H. Wang, and Jihui Yang, “ Structure of the Polycrystalline Thermoelectric Bulk Material $AgPb_mSbTe_{2+m}$”, Microscopy and Microanalysis 2007 in Ft. Lauderdale, Florida, USA, August 5-9, pp. 852-853, 2007.

27. G.S. Nolas, D. Wang and M. Beekman, ‘Transport properties of polycrystalline $Mg_2Si_{1-y}Sb_y$’, Phys. Rev. B (in press).

28. J. Martin, G.S. Nolas, H. Wang and J. Yang, ‘Thermoelectric properties of silicon-germanium type I clathrates’, J. Appl. Phys. (in press).

29. G.S. Nolas, D. Wang and X. Lin, ‘Synthesis and low temperature transport properties of $Mg_2Ge_{1-y}Sb_y$’, Physica Status Solidi (Rapid Research Letter) 1, 223 (2007).

30. J. Martin, G.S. Nolas, W. Zhang and L. Chen ‘PbTe nanocomposites synthesized from PbTe nanocrystals’, Appl. Phys. Lett. 90, 222112 (2007).

31. D. Wang and G.S. Nolas, “Thermoelectric Properties of mix-crystals of Mg_2E (E=Si, Ge)-Mg_3Sb_2”, Proc. Adv. Elec. Ceramics 28(8), 185 (2007).

32. J. Martin, D. Wang and G.S. Nolas, “Synthesis and characterization of nanocrystalline chalcogenides” Proc. Adv. Elec. Ceramics 28(8), 221 (2007).

33. G.S. Nolas, given an Invited presentation to The International Conference on New Quantum Phenomena in Skutterudite and Related Systems (Skutterudite2007), Kobe, Japan, Sept 26 – 30, 2007 (due to scheduling conflicts, I was not able to attend this conference).

34. G.S. Nolas, ‘Fundamental study of inorganic clathrates’, Invited, Max Planck Institute for Chemical Physics of Solids, Dresden, Germany, August 7, 2007.

35. G.S. Nolas, ‘Novel Materials for Energy Technology”, Invited, University of Kentucky Physics Seminar, Lexington, KY, March 21, 2007.

36. G.S. Nolas, ‘Overview and new directions in bulk materials research for thermoelectric power generation applications’, Invited, Presented at the 31^{st} International Cocoa Beach Conference & Exposition on Advanced Ceramics and Composites, Daytona, FL, January 21, 2007.

37. J. Martin, W. Zhang, L. Chen and G.S. Nolas, “Synthesis and Characterization of Nanocomposite Chalcogenides”, presented at the American Physical Society, Denver, CO, March 7, 2007.

Special Recognitions & Awards/Patents Issued

1. J. Yang - The John M. Campbell Award (outstanding contributions to pure or applied science), GM R&D Center.

III.2 High-Efficiency Thermoelectric Waste Energy Recovery System for Passenger Vehicle Applications

J. LaGrandeur (Primary Contact), D. Crane
BSST LLC
5462 Irwindale Avenue
Irwindale, CA 91706

DOE Technology Development Manager:
John Fairbanks

NETL Project Manager: Aaron Yocum

Subcontractors:
- BMW, Palo Alto, CA
- Visteon, Van Buren Township, MI
- Marlow Inc., Dallas, TX

Objectives

The primary objective of 2007 is to operate the key subsystems of the waste heat recovery system (WHRS) in a bench test environment using a hot gas torch to simulate engine exhaust. Gas flow and temperature will be varied to simulate a variety of driving conditions. The key subsystems include the primary heat exchanger (PHX), thermoelectric (TE) generator module (TGM) and power conversion system (PCS). The test results will be finalized and used to update the computer simulation model. Predicted performance using the model will be compared to the test results and fuel efficiency gains will be predicted for the system operating in a variety of driving conditions. An architectural simplification will be evaluated to determine how commercialization may be accelerated without degrading fuel efficiency or other performance factors.

Key objectives for 2007 include:

1. Build and test of a low-temperature TGM incorporating BiTe TE material:
   - An initial 100 watt BiTe TGM
   - A full-scale (>500 watt) BiTe TGM
   - Operation and test of the TGM with Phase 2 PCS electronics
2. Build and test of a high-temperature TGM incorporating PbTe/TAGs/BiTe TE material:
   - An initial 100 watt Pb/TAGS/BiTe TGM
   - Operation and test of the 100 watt Pb/TAGS/BiTe TGM with Phase 2 PCS electronics
3. Evolution of the system model to predict transient performance conditions that are critical during engine start-up and city driving conditions where wide variations in exhaust gas mass flow are encountered.
4. Evaluation of a simplified system architecture to accelerate the commercialization and economic viability of the system.

Accomplishments

1. A fractional BiTe TGM has been built and tested that produced 130 watts of electric power.
2. A full-scale BiTe TGM was built and tested that produced over 500 watts of electric power.
3. A fractional high temperature TGM has been built using PbTe/TAGS that produced 20 watts electric power.
4. A fractional high temperature TGM has been built using PbTe/TAGS/BiTe that demonstrated 10% conversion efficiency.
5. The system model has been updated to predict transient performance and is being used to evaluate system performance over a variety of driving conditions including engine start-up.
6. A simplified architecture has been modeled and preliminary results are being evaluated.

Future Directions

Phase 3 activities are scheduled to conclude at the end of February 2008. In 2008 BSST will complete the build of a full-scale high temperature TGM and perform a bench test including the PHX and PCS subsystems.

Phase 4 activities include engine integration and test and are planned to begin early Q2 2008.

✧ ✧ ✧ ✧ ✧

Introduction

BSST began work to develop a high efficiency TE waste energy recovery system for passenger vehicle applications in November 2004.

In Phase 1, the team created an initial system architecture shown in Figure 1, developed a system model to predict performance, and established system and subsystem design requirements. Phase 2 was completed in January 2007, in which key subsystem

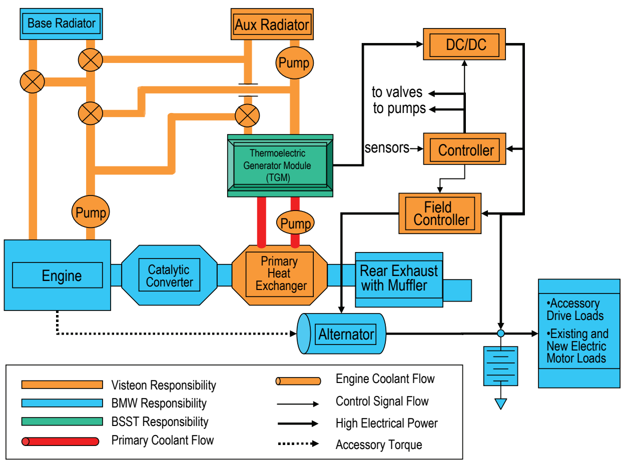

FIGURE 1. Initial System Architecture

components were built and tested and the system model updated to provide revised performance predictions.

Engine exhaust gas passes through the PHX where thermal energy is extracted and transferred to a gaseous working fluid (preliminarily designated as 75% He, 25% Xe). Wide variations in exhaust gas mass flow, which result in correspondingly wide variations in thermal flux, are managed by means of a pump which circulates the working fluid between the PHX and TGM's hot side. The use of this working fluid loop enables optimal usage of the TE material in the TGM as well as providing a dense, minimally sized hermetic enclosure for the TE material. Heat rejection from the cold side of the TGM can be facilitated by either the vehicle's powertrain cooling system or a supplemental cold-side cooling loop. TGM electrical power is linked to the vehicle electrical bus via a load matching DC/DC converter in the PCS. Fuel efficiency is increased by off-loading the vehicle alternator by use of power generated in the TGM.

Approach

A key element in BSST's approach to building TGMs for the WHRS is in the application of proprietary high density design and construction for joining TE materials to substrates. TE subassemblies based on traditional and BSST high density principles are shown in Figure 2.

TGMs will be built using the BSST configuration (with variation in the TE elements and geometry of the "Y" substrates) to better accommodate TE material compatibility, coefficient of thermal expansion mismatches and to significantly reduce the amount of TE material required.

An incremental approach is being followed in which low-temperature TGM subassemblies are built and tested prior to building high-temperature systems. This approach includes validation of TE material properties

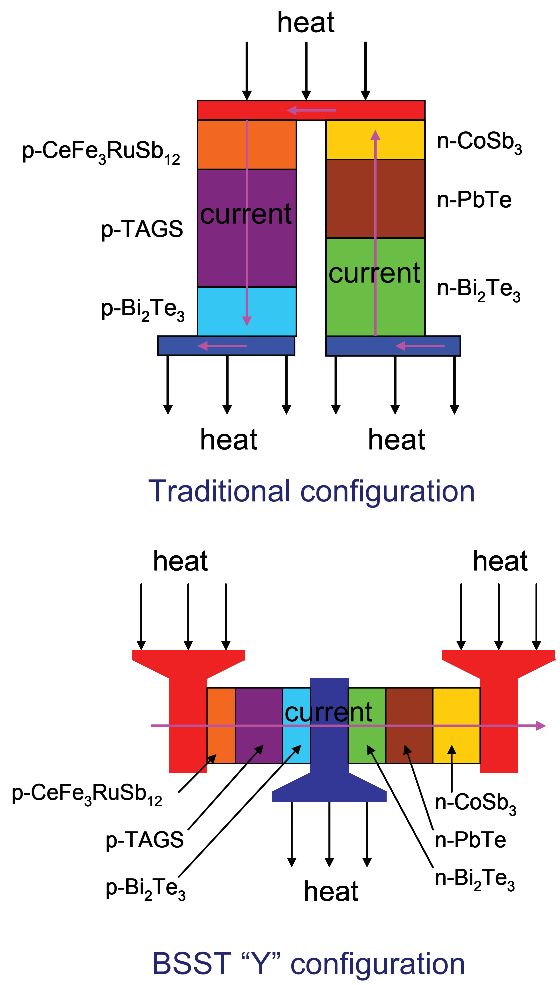

FIGURE 2. Traditional and BSST High Density TE Subassemblies

and performance models at the subassembly and subsequently at the full-scale level.

Results

Low-Temperature TGM Results

A low-temperature fractional TGM using BiTe TE material was modeled, built and tested. A TE subassembly of the BiTe TGM is shown in Figure 3 (heat exchangers not shown).

N and p type TE material was soldered to copper substrates which were placed in close contact with cold and hot heat exchangers. Current flows through the substrates and TE material as shown in Figure 3.

One partial layer of the fractional BiTe TGM is shown in Figure 4. BiTe subassemblies were arranged on a liquid heat exchanger through which hot oil flows. The hot heat exchanger is anodized aluminum to prevent electrical shorting of the subassemblies and thermal grease is used to promote heat transfer. A similar cold-

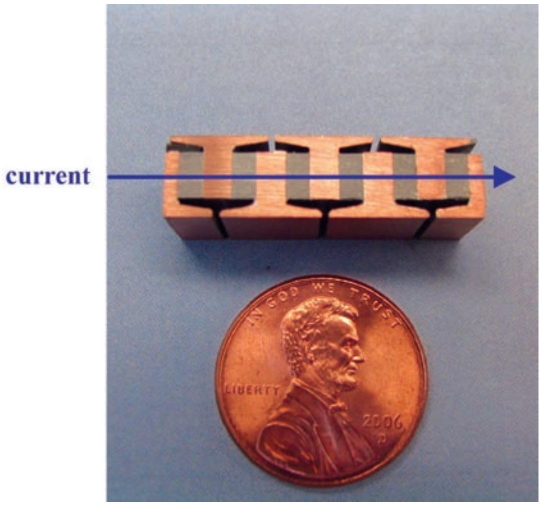

FIGURE 3. BiTe Subassembly

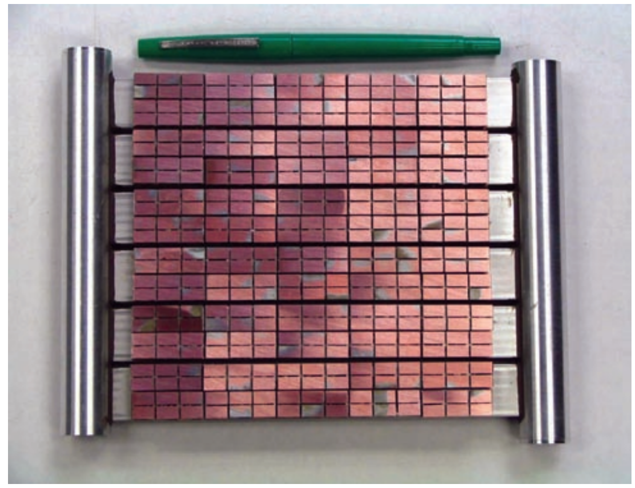

FIGURE 4. BiTe Fractional TGM

side heat exchanger (not shown) is set atop the BiTe subassemblies to complete the TGM. Another layer of BiTe subassemblies and additional cold heat exchanger is placed on the opposite side.

Test results for the fractional BiTe TGM operated over a range of cold- and hot-side temperatures are shown in Figure 5. As shown in the data, 130 watts of electric power was generated at a peak ΔT of 205°C.

Additional layers were then built and a full-scale BiTe TGM was assembled. Five hot and six cold heat exchangers were used in the full-scale TGM. The full-scale BiTe TGM is shown in Figure 6.

The full-scale BiTe TGM was operated over a range of cold and hot side temperatures. Data are shown in Figure 7 that depicts the performance of the full-scale BiTe TGM with the oil inlet temperature at 210°C and

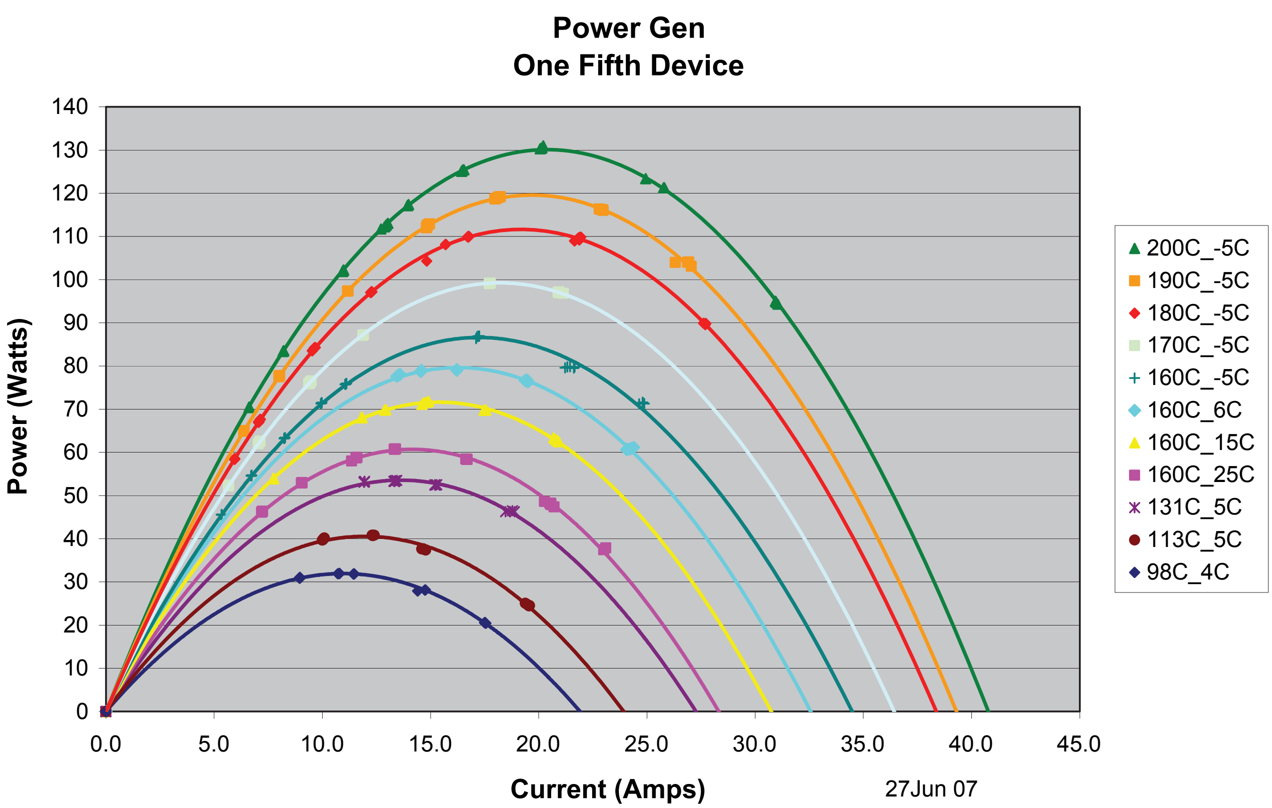

FIGURE 5. Fractional BiTe TGM Test Results

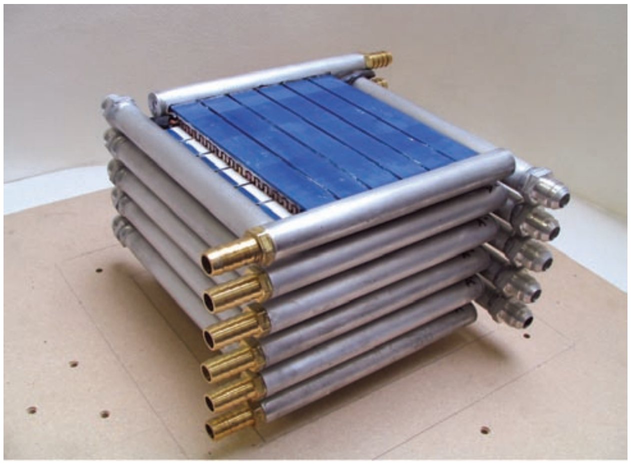

FIGURE 6. Full Scale BiTe TGM

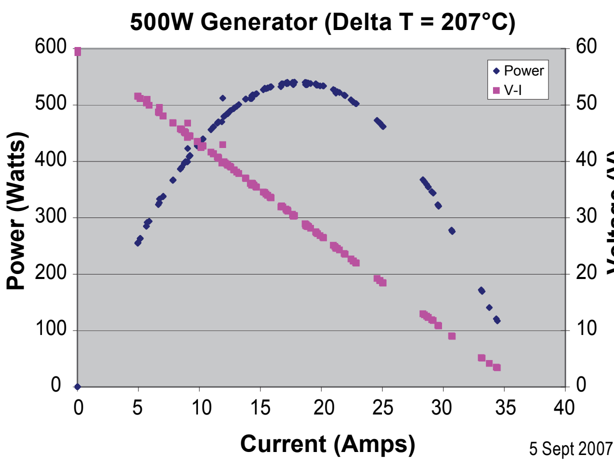

FIGURE 7. Full Scale BiTe TGM Test Results

the water inlet temperature at 2.5°C. For this condition ($\Delta T = 207°C$) over 500 watts of electric power was produced.

High-Temperature TGM Results

Fractional, 20 watt TGM

A fractional high temperature TGM was built using PbTe/TAGS TE material with cartridge heaters providing the thermal power. A portion of the fractional PbTe/TAGS TGM is shown in Figure 8 (cold side liquid heat exchangers not shown).

Three hot side TE subassemblies were built, each having eight total TE elements (four n-type PbTe and four p-type TAGS). The hot-side TE subassemblies were placed between cruciform shaped copper parts which were set between liquid heat exchangers through which a cold fluid was circulated.

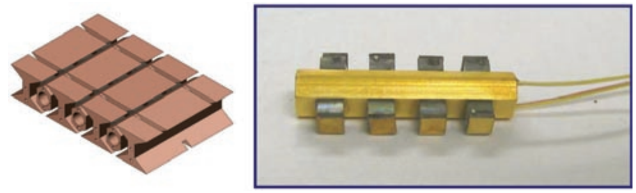

FIGURE 8. Fractional Pb/TSAGS TGM Isometric Drawing and Hot-Side Subassembly (Substrate with Interior Cartridge Heater and TE Elements)

Test results for the fractional PbTe/TAGS TGM are shown in Figure 9. Over 20 watts of electric power was generated for the test condition in which the average hot side temperature was 472°C and the cold side average temperature was 33°C.

Fractional, 10% efficient TGM

A 10% efficient fractional TGM was built and tested using PbTe and TAGS TE material segmented with BiTe. The design and construction of the fractional TGM was similar to the 20 watt PbTe/TAGS TGM, with the exception that BiTe material was joined to each n and p type PbTe and TAGS element, respectively and only one hot-side TE subassembly was used. A cartridge heater was used to generate thermal power which enabled precise measurement of power into the device.

The PbTe/BiTe and TAGS/BiTe segmented elements are shown in Figure 10.

A converter efficiency of 10% was measured when the device was operated with a hot-side temperature of 500°C and cold-side at 20°C. The calculation of efficiency was made inclusive of all electrical and thermal parasitic losses. Segmented couple TGM performance is shown in Figure 11.

System Modeling Status

The migration of the steady-state bumper-to-bumper system simulation model from the AVL Advisor platform to Gamma Technologies GT Cool was completed in early 2007. The steady-state system model was validated by comparing predicted and measured values of exhaust gas mass flow, temperature and fuel consumption for various driving conditions and found to show good agreement. Preliminary fuel efficiency predictions were made showing fuel efficiency improvement from 0% to over 8% based on driving conditions.

A transient system model was developed and is currently being evaluated. The transient vehicle model was coupled with a transient TEG model and provides a large variety of parameters for optimization, e.g. working fluid (exhaust or primary coolant such as He/Xe), heat exchanger design, TE leg design and other parameters.

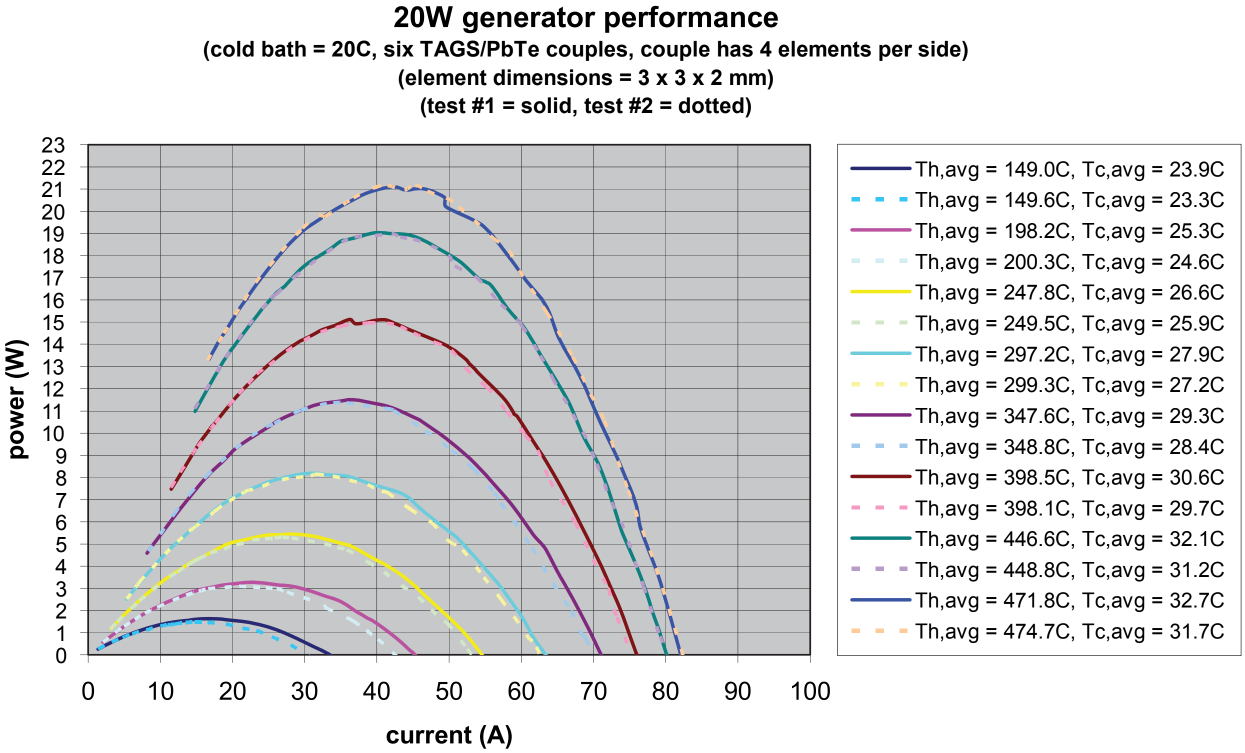

FIGURE 9. Fractional Pb/TSAGS TGM Test Results

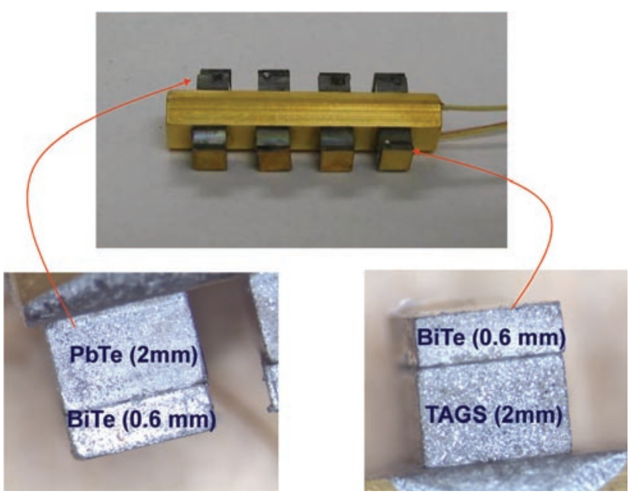

FIGURE 10. 10% Efficient Pb/TSAGS/BiTe Fractional TGM Hot Subassembly

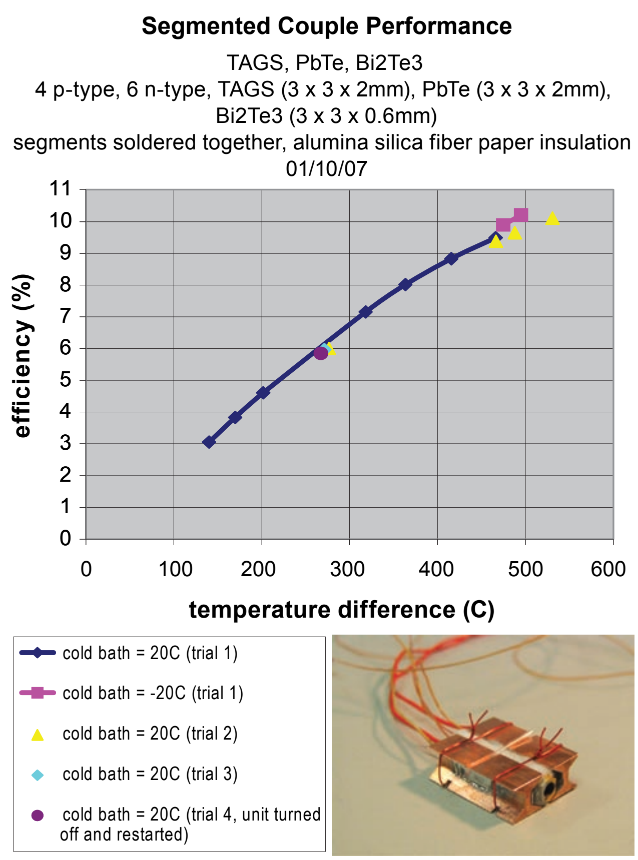

FIGURE 11. 10% Efficient Pb/TSAGS/BiTe Fractional TGM Test Results

The transient system model is being used to evaluate the performance of two system architectures. The initial system architecture, shown in Figure 1, features a secondary loop that moves exhaust gas heat to the TGM. A second architecture is simplified and does not feature the secondary loop, but does provide a means for managing the variation in exhaust gas flow to optimize TGM efficiency. These results are in review and will be provided in the near future.

Conclusions

BSST has effectively demonstrated the viability and performance of TGMs based on proprietary high density design and construction principles using low- and high-temperature TE materials.

The system performance model has been migrated from AVL ADVISOR to Gamma Technologies GT Cool. As a result, the model more closely reflects the baseline performance of the vehicle platform and therefore more accurately models the performance of the WHRS. In addition, the model has been updated to predict transient performance.

Future Directions

- Use of segmented elements to maximize ZT over the entire temperature range.
- Adjustment of segment thicknesses to combat TE material incompatibility within each element.
- Adjustment of element thicknesses to combat TE material incompatibility in the direction of flow.
- Use of alternative “Y” connector configurations to accommodate differing element thicknesses and to combat differing thermal expansion coefficients.
- Use of non-rigid joints to continue to combat thermal expansion mismatch.
- Use of advanced modeling and optimization concepts to maximize the benefits of the above mentioned design concepts.

FY 2007 Publications/Presentations

1. 2007 DEER Conference
2. 2007 DTEC Conference
3. 2007 Semi-Annual Mega Merit Review

III.3 Thermoelectric Conversion of Waste Heat to Electricity in an IC Engine Powered Vehicle

Harold Schock (Primary Contact),
Eldon Case, Adam Downey, Tim Hogan,
Mercouri Kanatzidis, James Novak, John Miller,
Fang Peng, Fei Ren, Ed Timm
Michigan State University (MSU)
East Lansing, MI 48864

DOE Technology Development Manager:
John Fairbanks

NETL Project Manager: Samuel Taylor

Subcontractors:
- Jeff Sakamoto, NASA Jet Propulsion Laboratory, Pasadena, CA
- Tom Shih, Iowa State University (ISU), Ames, IA
- Todd Sheridan, Cummins Engine Company, Columbus, IN
- Charles Cauchy, Tellurex, Traverse City, MI

Objectives – Phase II (approximately half of the effort has been completed)

- Using thermoelectric (TE) energy recovery from the exhaust system, determine material performance needed to produce a 10% improvements in brake specific fuel consumption for an over-the-road (OTR) truck operating under cruise conditions.
- Evaluate currently available TE materials to determine engineering developments required for their implementation in a thermoelectric generator (TEG) for an OTR truck, which can be demonstrated within five years.
- Determine requirements for a heat exchanger needed in this application.
- Determine power electronic and control requirements for this application.
- Assemble the equipment needed to conduct the necessary material synthesis, fabrication and hardware necessary for a scaled demonstration.
- Determine if Phase II results warrants a prototype engine. TEG final design in Phase III.

Accomplishments in Phase II

- Systems for material synthesis, powder processing, hot pressing, leg preparation, material mechanical and TE property characterization, and couple fabrication have been demonstrated at MSU. Systems are in place to produce a 40 W module in one week.
- Using the measured properties of known materials for the temperature range of operation we estimate that a segmented couple can provide a conversion efficiency of over 12%.
- The first batch of Skutterudite material has been synthesized at MSU.
- Advantages of power impedance load matching experiments were demonstrated.
- Analytical studies show potential improvement of up to 6.2% in fuel economy for a Class 8 OTR truck operating at cruise conditions using current materials.

Future Directions for Phase II

- Conduct design and analysis of the power conditioning system to optimize thermoelectric system performance, including fault remediation.
- Refine leg fabrication methods (e.g. wet milling/dry milling, hot pressing) for improving mechanical properties and microstructural characteristics.
- Refine fabrication techniques for scaleable couple/thermoelectric (TE) modules.
- Finalize analytical studies on the full engine system including coupling current simulations to the 3-D heat transfer studies to provide efficiency gains for the optimum TEG-engine configurations.
- Improve the thermoelectric figure of merit (ZT) by exploring several more promising thermoelectric material compositions with emphasis this period on PbTe systems, with S doping, as well as Skutterudite synthesis.
- Extensive mechanical, thermal cycling and thermoelectric property testing of segmented hot-pressed legs including Bi_2Te_3 and lead-antimony-silver-tellurium (LAST)/(T).
- Continue development of module fabrication methods.

✧ ✧ ✧ ✧ ✧

Introduction

At peak efficiency, current diesel engines are capable of converting 40 percent of fuel energy to useful work. When a Class 8 diesel truck is loaded, the engine might deliver 300 kilowatts of power to drive the wheels, while at the same time, another 300-400 kilowatts of energy goes out through the exhaust stack as wasted energy. This research project is attempting to find ways to capture that wasted energy and convert it to back into useful energy. A reasonable long-term goal would be to increase the diesel power plant efficiency to greater than 50%.

This unique project requires input from a number of researcher collaborators within the College of Engineering at MSU, as well as experts from outside of MSU. The aim of the research is to use a direct conversion device, fabricated out of TE materials, to recover waste heat from the exhaust of internal combustion engines and turn it into useful electricity. The team is working with TE materials that have already been developed and are assessing them to see if they can be implemented into a powertrain in a cost-effective manner. The team is also developing new high efficiency TE materials that will permit a 10% improvement in fuel economy of OTR Class 8 trucks. We expect that completion of the project through Phase 4 will result in a scaled demonstration of the internal combustion (IC) engine and TE energy recovery system.

Approach

This MSU led multidisciplinary research effort is to evaluate the entire system and identify the required processes needed to bring TE technology to a cost effective commercial product for OTR trucks. The Phase II analysis involves an exploratory analysis and feasibility study, which includes system design, new TE material synthesis, power electronics design, material thermoelectric and mechanical property characterization, heat exchanger design, TE material fabrication methods, module fabrication and evaluation of system performance. To date, about half of the Phase II effort has been completed.

Results

1. Property Characterization - Experimental Procedure

The elastic moduli measurements at Oak Ridge National Laboratory (ORNL) and at MSU were performed using resonant ultrasound spectroscopy (RUS) (Figure 1) to evaluate the elastic moduli both before and after thermal cycling.

The acoustic resonant spectrum induced in a mechanically driven specimen is a function of the elastic moduli, geometry, dimensions and mass density of the specimen.

It is important to note that this equation not only describes the thermal fatigue behavior of LAST, but Case *et al* [1], has shown that it also describes the strain versus # of cycles thermal fatigue behavior of a wide variety of brittle materials including unreinforced ceramics, whisker-, fiber- and platelet- reinforced ceramics, metal matrix composites, and polymeric composites.

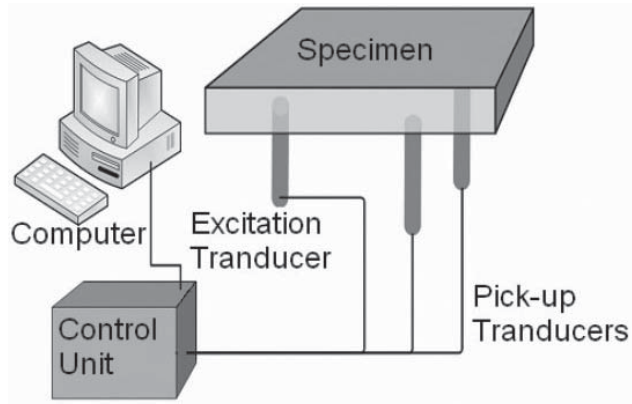

FIGURE 1. Resonant Ultrasound Spectroscopy Apparatus used for Young's Modulus Measurements

Although much more thermal fatigue work needs to be done to characterize the evolution of thermal fatigue damage in LAST materials, this work shows that the evolution of thermal fatigue damage in LAST can be described in terms of the same equation describing thermal fatigue damage in a wide range of brittle materials, which aids our overall understanding of the damage process in LAST TE legs.

Additional thermal fatigue testing at both ORNL and MSU will involve a greater range of ΔT values and a greater number of thermal fatigue cycles. In addition to performing fatigue tests on individual legs, we will conduct thermal fatigue tests on unicouples. Also, we will work toward designing experiments that more closely approximate in-service thermal cycling conditions.

2. TEG Design Alternatives for Heat Transfer

The proposed efforts are as follows:

1. Design and analyze geometrical configurations needed for transferring heat from the high temperature exhaust gases to the hot side of the thermoelectric generator.
2. Design and analyze geometrical configurations needed for transferring heat from the cold side of the thermoelectric generator to ambient surroundings.
3. Design, analyze, and select method and working fluids necessary to perform intermediate heat transfer within the thermoelectric generator.

During this past quarter, a series of 3-D computational fluid dynamics (CFD) analyses were made to understand how heat transfer from the hot gas to the TE legs could be increased, so that heat transfer rate and hence electric generation can be increased. Three design concepts were examined. The first design concept is to add advanced heat-transfer enhancement techniques on the hot-gas sidewall (e.g., inclined rounded ribs) to increase the heat transfer rate through the thermoelectric couples. The second design concept is to use heat-transfer enhancement techniques plus exposing the thermoelectric legs (with a protecting coating) to the hot gas in regions where the heat-transfer coefficient is the highest. The third design concept is a combination of design concepts one and two described above plus using the wall that separates the hot gas from the thermoelectric couples as a heat reservoir to store thermal energy.

The key findings from the CFD results generated are as follows:

1. Design concept 1 can be quite effective. Since the Biot number is quite low, the wall temperature is nearly constant across the wall and that temperature is higher when the heat transfer coefficient is higher. Thus, considerable heat can be transferred directly from the wall to the thermoelectric legs, provided that the contact resistance is not high and thermal stress issues can be resolved.
2. Design concept 2 can also be quite effective. Since the thermoelectric leg is in direct contact with the hot gas, the temperature on the surface of the thermoelectric leg in contact with the hot gas is the highest possible for a given heat-transfer coefficient. The advantage of this design concept is that it has the potential to minimize thermal stresses.
3. Design concept 3 can be highly effective when used with either design concept 1 or 2. If the maximum amount of heat that can be transferred to the wall that separates the hot gas and the thermoelectric couples is higher than the amount of heat that can be transferred from the wall to the thermoelectric couples and the Biot number of the wall is low, then the temperature in the wall will keep rising until is it reaches some maximum value close to the hot gas temperature. Thus, the wall behaves like a heat reservoir at nearly constant temperature (analogous to a flywheel) to transfer heat from the hot gas to the thermoelectric couple. The advantage of this approach is that the wall temperature can be very high even when the heat-transfer coefficient is low.

Efforts are still underway to quantify design concept 3, in order to better understand the maximum wall temperatures that can be achieved and the number of thermoelectric couples that can be packed per unit area.

3. Power Electronics - Demo and Test Results of the Power Electronics (PE) Circuit for Maximum Power Point Tracking

A heat exchanger capable of 100 W electrical power output has been developed in the last quarter and explained in a previous report. The installed 20 TE modules (G1-1.4-219-1.14) are grouped into two sets and each one is connected in series. Previous test results showed that those two sets of TEG modules can output electric power of 50.6 W and 48.4 W, respectively, if a resistive load of 40 ohms was applied.

Based on the understanding of TEG module characteristics, a PE circuit capable of 60 W was designed and fabricated in our lab to interface the TEG modules with real loads. The first set of the TEG modules were directly connected to a 50 W light bulb, and the second set was connected to a 50 W light bulb via the power electronics circuit. The light bulbs have variable and non-linear resistance, which is close to most real loads. Three thermal conditions were tested and the electrical output power vs. ΔT (T_{Hot}-T_{Cold}) curves were drawn in Figure 2. We found that TEG module set 2 (with PE interface circuit) can output as much as twice of the electric power of set 1 (directly connected to the light bulb) under same heat flux. Under the thermal condition of $\Delta T = 150°C - 31°C$ (T_{Hot}-T_{Cold}), TEG set 1 can only output electric power of 23 W, although it is capable of 50.6 W output. This is due to the heavily mismatched load impedance. However, the TEG set can still output electric power of 47 W, which is the maximum output power that can be provided from set 1. In summary, the PE circuit can extract the maximum electric power from the TE modules and feed it to loads regardless of TE module's heat flux and load impedance or conditions.

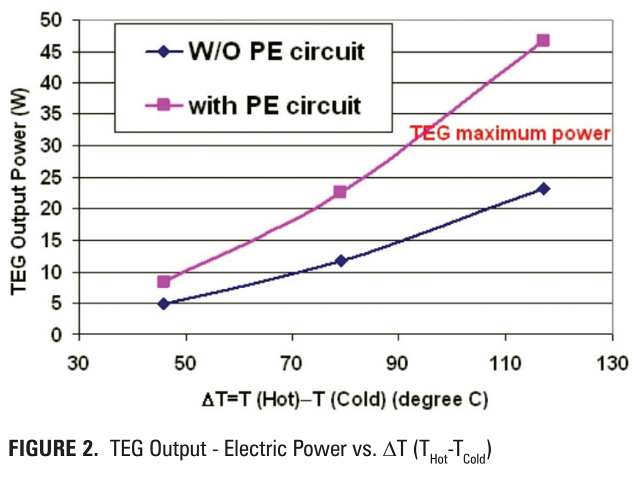

FIGURE 2. TEG Output - Electric Power vs. ΔT (T_{Hot}-T_{Cold})

4. Skutterudite Module Fabrication

Previous reports have described the results of our LAST synthesis efforts. Concurrently, an effort has been underway with the Jet Propulsion Laboratory (JPL) to fabricate Skutterudite thermoelectric modules. The primary focus is on fabricating and testing 40 W thermoelectric modules operating at greater that 12% thermal-to-electric conversion efficiency (Figure 3). The first generation modules will consist of n and p-type Skutterudite legs. The cold side of the module will share a common substrate where electrical contacts consist of copper pads patterned on an aluminum oxide substrate. The Skutterudite legs are pre-metallized (metallized during hot pressing). Bonding the cold side of the metallized legs is achieved with standard soldering techniques and leg alignment is achieved with precision graphite egg-crate tooling (designed and fabricated in house). The hot side metal interconnects are made using a brazing or diffusion bonding technique developed by Dr. Sakamoto, while at JPL. It is important to note that the hot side of the 40 W modules does not involve bonding the legs to a common hot side heat exchanger. Instead, the hot side interconnects are free-standing or free to expand and contract laterally/independently, thus significantly reducing shear stress on the legs and hot side metallization addition. The proposed design could enable the placement of the hot side interconnects/heat collectors directly into the exhaust stream to gain access to the hottest exhaust gas temperatures. In this paradigm, thermal management is key, thus we propose the integration of aerogel-based thermal insulation (Figure 4). Because aerogel is a highly porous form (99% porous) of silica, it has extremely low thermal conductivity. In particular, pores within aerogel are nano to sub nano in scale, thus gas conduction in aerogel is lowest of any material.

5. Engine Thermoelectric System Modeling

The second phase of this study involves modeling of the full six-cylinder Cummins ISX engine with integrated TEG units and including the turbocharger, intercooler, and exhaust gas recirculation bypass systems. This is necessary to understand the balance of exhaust energy flow split between the TEG and the variable geometry turbocharger in order to meet the engine's power output demands. Figure 5 shows the new system model illustrating the interconnected on this engine. On the left side of the figure the cloud represents the intake air after the air cleaner which feeds into the compressor side of the turbocharger. Likewise, the cloud on the right side of the figure represents the outlet of an exhaust pipe connected to the outlet of the turbocharger turbine. Various alternatives for extracting energy using the TEG while increasing fuel economy and maintaining performance are being investigated.

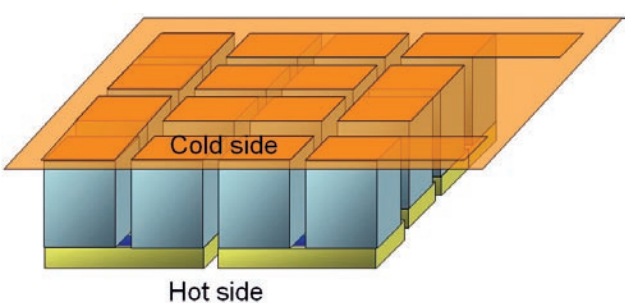

FIGURE 3. Free Standing Hot Shoe Module Design; Produces 40 W and Consists of 16 Skutterudite Legs 7mmx7mmx6mm Long

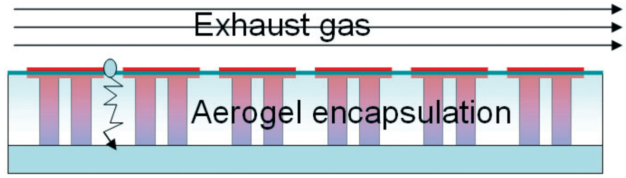

FIGURE 4. Aerogel-based thermal insulation could enable TE devices integrated directly in to the exhaust stream. Gas transport through the aerogel is significantly impeded by the highly-tortuous, nanoscale porosity, thus providing effective thermal insulation.

6. Summary

Completion of the Phase II effort will provide the following results:

- Preliminary TEG design will be completed using the most promising TE materials.
- Demonstrate the viability of a module which can produce between 20 and 40 W of power with a temperature difference of less than 800 K on the hot side and 300 K on the cold side.
- Accurately quantify the bulk mechanical properties for the LAST/tellurium material for use in the finite element analysis (FEA) studies of the thermoelectric generator.
- Complete selection of appropriate TE materials, metallization for segmented couples, voltage insulators and required sublimation suppression.
- Couple detailed Iowa State University heat transfer models to WAVE and FEA models of thermoelectric generator. Perform comparison of system efficiency for various options.
- Estimate potential TEG-engine performance gains using demonstrated materials with measured mechanical and thermoelectric properties.

Results to date suggest that using TEG technology, a 5% improvement in brake specific fuel consumption for an OTR truck is a reasonable 5 year goal - 10% improvement possible with advanced designs and new TE materials.

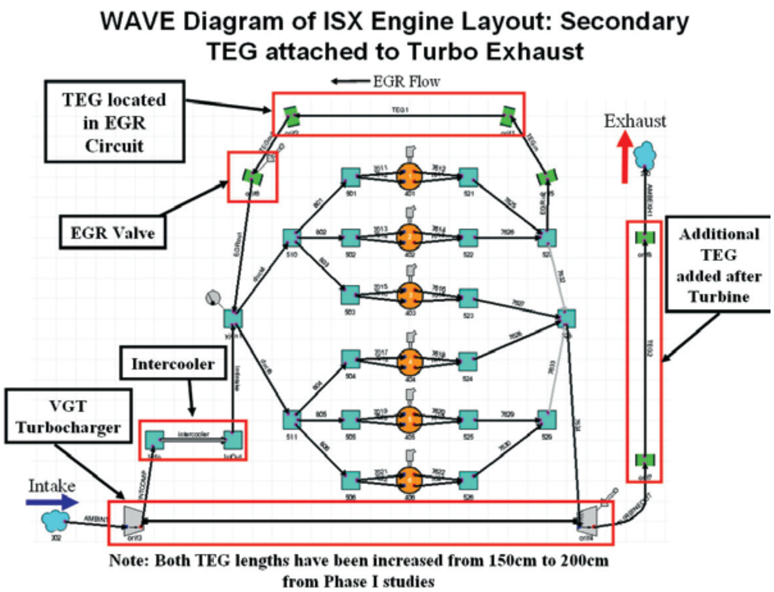

FIGURE 5. WAVE Diagram of Cummins ISX Engine Layout: Secondary TEG attached to Turbo Exhaust - Note: Both TEG lengths have been increased from 150 cm to 200 cm from Phase I studies.

References

1. E. D. Case, The Saturation of Thermomechanical Fatigue in Brittle Materials, Thermo-Mechanical Fatigue and Fracture, WIT Press, Southampton, UK, editor M. H. Alibadi, 2002, pp. 137 – 208.

FY 2007 Publications and Presentations

1. Characterization of Dry Milled LAST (Lead-Antimony-Silver-Tellurium) Thermoelectric Material, Pilchak, A., Ren, F., Case, E., Timm, E. and Schock, H., submitted to Philosophical Magazine, Spring 07.

2. Nanostructured Thermoelectric Materials and High Efficiency Power Generation Modules, Hogan, T., Downey, A., Short, J. et al., prepared spring 07.

3. The Young's Modulus and Poisson's Ratio of Lead-Telluride Based Thermoelectric Materials as a Function of Temperature, Ren, F., Case, E., Timm, E., Schock, H., Lara-Cuzio, E., Trejo, R., Lin, C.H., Kanatzidis, M., submitted to International Journal of Applied Ceramics Technology, Spring 07.

4. Hardness as a Function of Composition for N-Type LAST Thermoelectric Materials, F. Ren, E.D. Case, E.J. Timm, and H.J. Schock, Journal of Alloys and Compounds, (2007) doi:10.1016/jallcom.2007.01.086.

5. Young's Modulus as a Function of Composition of N-Type Lead-Antimony-Silver-Telluride (LAST) Thermoelectric Materials, F. Ren, E.D. Case, E.J. Timm, and H.J. Schock, submitted to Philosophical Magazine, Spring 07.

6. Weibull Analysis of the Biaxial Fracture Strength of a Cast P-Type LAST-T Thermoelectric Material, F. Ren, E.D. Case, E.J. Timm, M.D. Jacobs and H.J. Schock, Philosophical Magazine Letters, Vol. 86, No. 10, Oct. 2006, 673-682.