NSF-DOE Thermoelectrics Partnership:

Automotive Thermoelectric Modules with Scalable Thermo- and Electro-Mechanical Interfaces

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Automotive Thermoelectric Modules with Scalable Thermo- and Electro-Mechanical Interfaces

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Leveraged Support:
Precourt EEC, Northrop Grumman, AMD/SRC, ONR, AFOSR
Fellowships from NSF, Sandia National Labs, Stanford DARE

Program Managers: John Fairbanks, Tom Avedisian (DOE). Arvind Atreya (NSF)
Key Challenges for Thermoelectrics in Combustion Systems

*Improvements in the intrinsic ZT of TE materials are proving to be very difficult to translate into efficient, reliable TEG systems.*

**Major needs include…**

…Low-thermal-resistance interfaces with tailored electrical properties, which are stable under thermal cycling.

…High-temperature TE materials that are stable and promise low-cost scaleup.

…Characterization methods that include interfaces and correlate better with system performance.

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Thermoelectric Interface Challenge

“Nanostructured Interfaces for Thermoelectrics,”
Pettes, Hodes, Goodson, Trans. Advanced Packaging, 2009

- Combustion systems experience enormous stresses at interfaces due to large temperature differences.
- Interfaces must offer low thermal resistance, targeted electrical performance, mechanical compliance.

LeBlanc, Gao, Goodson, Proc. IMECE 2008

Clin et al., J. Electronic Materials, 2009

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Automotive Thermoelectric Modules with Scalable Thermo- and Electro-Mechanical Interfaces

GOALS

Develop, and assess the impact of, novel interface and material solutions for TEG systems of interest for Bosch.

Explore and integrate promising technologies including nanostructured interfaces, filled skutterudites, cold-side microfluidics.

Practical TE characterization including interface effects and thermal cycling.

METHODS

Multiphysics simulations ranging from ab-initio (band structure) to system scale.

Photothermal metrology including Pico/nanosecond TDTR, cross-sectional IR.

MEMS-based mechanical characterization.

System impact assessment considering the interplay of thermal, fluidic, mechanical, electrical, and thermoelectric phenomena.


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<table>
<thead>
<tr>
<th>Interfaces</th>
<th>Nanostructured films &amp; composites, metallic bonding Ab initio simulations and optimization</th>
<th>Stanford Bosch</th>
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<tbody>
<tr>
<td>Metrology</td>
<td>(ZT)$_{\text{eff}}$ with independent $k$&amp;$c_p$, thermal cycling High temperature ZT</td>
<td>Stanford USF/NIST</td>
</tr>
<tr>
<td>Materials</td>
<td>Filled skutterudites and half Heusler intermetallics Ab initio simulations for high-T optimization</td>
<td>USF Bosch</td>
</tr>
<tr>
<td>Durability</td>
<td>In-situ thermal cycling tests, properties Interface analysis through SEM, XRD, EDS</td>
<td>Stanford Bosch</td>
</tr>
<tr>
<td>Heat sink</td>
<td>Gas/liquid simulations using ANSYS-Fluent Novel cold HX using microfluidics, vapor venting</td>
<td>Bosch Stanford</td>
</tr>
<tr>
<td>System</td>
<td>System specification, multiphysics code Evaluation of research impacts</td>
<td>Bosch Stanford</td>
</tr>
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<td>Outreach</td>
<td>TE for vehicles competition, UG Lab, K-12 outreach</td>
<td>Stan&amp;USF</td>
</tr>
</tbody>
</table>
Bulk TE Materials for Automotive Applications


• Skutterudites with partial filling using heavy, low valence “guest” atoms

Heavy-ion Filling Yields Lower Thermal Conductivity. Low Valence Filling Facilitates Optimization of Power Factor and ZT.

George S. Nolas
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University of South Florida

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Bulk TE Materials for Automotive Applications


• *Skutterudites with partial filling using heavy, low valence “guest” atoms*

Partial Filling – Optimization of mobility & thermal conductivity

• *Half-Heusler alloys: from small grain size towards the disordered state*

George S. Nolas
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University of South Florida

La$_x$Co$_4$Sb$_{12-y}$Sn$_y$
Ab-initio/BTE computations will assist the optimization of TE material stoichiometry.

Past work at Bosch predicted the effect of Ba filling on CoSb$_3$ skutterudites using DFPT.

Collaborative optimization with Nolas group will focus on filled skutterudites, mobility, seebeck, and interfaces with metallics.
Simulations examine thermodynamic stability of TE material phases and assess potential for interdiffusion.

Simulations examine interface electrical conduction and optimize resistance considering band structure.

Mechanical & thermal simulations will focus on the expansion coefficients and transport through low-dimensional contacts.
Conduction Physics in CNT Films

Nanoscale metal-CNT interface resistance (phonons)

Partial nanotube engagement

Individual CNT conductance

Inter-tube contact

Spatially varying alignment

Growth interface resistance

Thermal and Mechanical Characterization of Aligned CNT Films

Nanosecond Thermoreflectance

Probe laser for thermometry
Pulsed Laser Heating
Metal Coating
Sample Film
Heat Sink (Si or metal substrate)

Picosecond Thermoreflectance

CNT
CNT Catalyst
Metal Coating
Transparent Substrate (e.g. quartz)

Cross-sectional IR Microscopy

Heater
500 μm
CNT Film
growth substrate

Mechanical Characterization

Laser Doppler Velocimeter
Vibrometer, ω

Temperature (°C)
Distance (μm)

ΔT → R_b

$k \propto \left( \frac{dT}{dx} \right)^{-1}$

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Metallization and CNT Thermal Resistance using Nanosecond Thermoreflectance


\[
\varphi = \frac{C_{\text{eff}}}{C_{\text{v, individual}}}
\]

Potential Performance

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Mechanical Behavior of CNT Films

Students: Yoonjin Won, Yuan Gao, Matt Panzer. Collaborators: Prof. Wei Cai, Stanford ME

<table>
<thead>
<tr>
<th>Material</th>
<th>Thickness (μm)</th>
<th>Modulus (MPa)</th>
<th>Density (kg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNT_{Top}</td>
<td>0.4</td>
<td>140</td>
<td>&gt;29</td>
</tr>
<tr>
<td>CNT_{Middle}</td>
<td>0-150</td>
<td>7</td>
<td>29</td>
</tr>
<tr>
<td>Si</td>
<td>8.7</td>
<td>155e3</td>
<td>2330</td>
</tr>
</tbody>
</table>

Maruyama Lab Samples (SWNT), 95 kg/m³

Monano Samples (MWNT), ~30 kg/m³

Wardle Lab Samples/MIT (MWNT), 45 kg/m³

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Thermal & Mechanical Requirements at Interfaces

Thermal Resistivity (m K / W)

Elastic Modulus (MPa)

- Metallic Alloys
- Adhesives
- Organic Phase Change
- Greases & Gels
- Nano-gels

Lifetime thermal cycling

Research Goal

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Thermal & Mechanical Requirements at Interfaces

<table>
<thead>
<tr>
<th>Material Type</th>
<th>Thermal Resistivity (m K / W)</th>
<th>Elastic Modulus (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Greases &amp; Gels</td>
<td>1.0</td>
<td>10^1</td>
</tr>
<tr>
<td>Organic Phase Change</td>
<td>0.1</td>
<td>10^2</td>
</tr>
<tr>
<td>Metallic Alloys</td>
<td>0.01</td>
<td>10^3</td>
</tr>
<tr>
<td>Adhesives</td>
<td></td>
<td>10^4</td>
</tr>
</tbody>
</table>

Lifetime thermal cycling

Our Latest CNT Data

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Thermal Cycling of CNT-SiGe Composite


Resistances for 1.5, 2.5, and 40 micron thick CNT films varied between 0.035 and 0.055 cm$^2$ °C/W, with evidence of decreasing engagement with increasing film thickness.

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(ZT)_{eff} Characterization with Electrical Heating & Cross-Sectional IR Thermometry

Heating/thermometry Setup
AC current source
Lock-in Amp.

Resistive Heater
Th = 300-700 K
Connecting metal
Ceramic plate
n-type Pellet
p-type Pellet

Normalized temp. Amplitude
Phase (deg)
Frequency (Hz)

Sapphire IR Transparent window
Spatial resolution ~ 2 mm
Temp. range 300-700 K

Cross-sectional IR Microscopy

IR microscope system
QFI

Heater
growth
substrate
CNT Film

k
\frac{dT}{dx} \propto \frac{1}{k}

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HX and System-Level Simulations

- Bosch-lead system simulations explore impact of improved parameters on system efficiency
- Multiphysics simulations of thermal/thermoelectric transport in TE material, and interface transport incorporating ab initio results.
- HX design and optimization accounts for novel pressure drop designs including Stanford Vapor Escape technology

Research and Technology Center North America
Educational Engagement

Thermoelectrics for Vehicles Challenge: Multi-University Competition

Long-term vision: Teams of undergraduates work with commercial TE components and heat sinks to extract waste heat from demo vehicle exhaust.
✓ Connects classroom education and research & development.
✓ Links students with industry, graduate & faculty advisors.

Undergraduate Thermoelectrics Lab

Stanford’s heat transfer course (ME131A) will include a thermoelectrics laboratory experience.
✓ Connects theory and practical applications.
✓ Recruits undergraduates for research experiences in thermoelectrics with graduate student mentoring.

K-12 Educational Outreach

High school students and teachers will conduct energy-conversion research in Stanford’s Microscale Heat Transfer Laboratory.
Interactions and Flow of Samples & Information

Stanford
- Prepares CNTs samples on TE materials
- Transport property measurements of CNT-TE pellet combination, thermomechanical reliability tests on interface (300-800 K)
- Process development for CNT TIM tape

Bosch
- Ab-initio simulations of transport properties of TE materials and interfaces.
- System-level simulation and optimization

USF
- Develops high-T, high efficiency TE materials
- Transport properties (ρ, S and κ) and Hall measurements (10 - 300K)
- Structural, morphological and thermal (DTA/TGA) analyses

NIST
- Transport properties (ρ, S and κ) and Hall measurements (1.8-390K)
- Specific heat, Power Factor measurement at 300 K.
- Custom-designed precision TE properties measurement system (300 – 1200 K)