Nanoscale Materials and Devices for Enhanced Energy Transport and Conversion
An Overview of the Nanoscale Transport Research Group at Purdue

Timothy S. Fisher
Professor of Mechanical Engineering
Birck Nanotechnology Center
Purdue University
29 January 2008
*currently Visiting Professor, Jawaharlal Nehru Centre for Advanced Scientific Research
Background & Acknowledgments

• My Background
  – Born and raised in Aurora, IL USA
    • 1991-1993, Design Engineer, Motorola Automotive Group
  – 1998-2002, Assistant Professor, Vanderbilt University
  – 2002-present, Associate Professor and now Professor, Purdue
  – Jan-May 2008, Visiting Professor, JNCASR

• Special Thanks
  – Prof. C.N.R. Rao and Prof. G.U. Kulkarni for agreeing to my visit and for so kindly making arrangements for me, my family, and my student (Kyle Smith)
  – Faculty and staff of JNCASR for such a warm welcome
  – Dr. Pankaj Sharma (Purdue, Discovery Park) for coordinating activities with JNCASR and other Indian institutions
Outline

Group Research Topics

Subjects
- Heat, mass and charge transfer at small scales
- Energy conversion and storage
- Nanomaterials

Methods
- Material synthesis and characterization
- Functional characterization
- Atomistic-to-continuum modeling

Applications
- Electronics cooling
- Hydrogen storage
- Nanoelectronics
- Direct energy conversion devices
- Sensors

Carbon Nanotube (CNT) Arrays for Enhanced Interfacial and Convective Heat Transfer

CNT-based Electron Emission for Energy Conversion

Green's Function Modeling of Phonon and Electron Transport

Templated Single-Wall CNT Nanoelectronics

Hydrogen Storage with Metal and Chemical Hydrides

Nanoscale Transport Research Group

T.S. Fisher, Feb-08
Slide 3
Computer Power and Cooling Trends

- Shrinking volume
- Quieter
- Yet, High Performance
  - Thermal budget decreasing
  - Higher heat sink volume
  - Higher air flow rate

Courtesy of R. Mahajan, Intel
Thermal Contact Resistance in Electronics

- Resistance across a Thermal Interface Material (TIM) comprises a significant fraction of the total thermal budget in modern microprocessor packages.
- Substantial technological progress has been achieved to date in improving conductivity and process control.
- Polymer, hybrid and solder TIM’s have helped accomplish ~10x reduction in resistance (from 100 mm²K/W to 10 mm²K/W) in the past decade.
- Accompanied by major metrology improvements.
- nano-TIMs being actively explored to move toward 1 mm²K/W.
What is Contact Resistance?

• Contact resistance is resistance to heat transfer across a real interface.
• The interface poses a resistance to the heat flow, which is seen as a temperature drop across the interface.

Source: Williamson & Majumdar, 1992
Factors that Affect Thermal Contact Resistance

- **Contact geometry**
  - Surface roughness and waviness
  - Flatness of contact

- **Thermal/physical properties**
  - Contacting members
  - Gas gap (or filler material)

- **Applied pressure**
  - Elastic or plastic surface asperity deformation

- **Interface temperature**
  - Properties change
  - Change in phonon scattering at contact spots

Thermal resistance of filler material

\[
R = \frac{L_{\text{filler}}}{k_{\text{filler}}} \quad \text{bond line thickness}
\]
Heat Flow Through a Real Interface

- Hence, total is the sum of the solid spot and the interstitial gap conductances.
**Thermal Contact Conductance / Resistance**

- Thermal contact conductance (TCC) is the ratio of heat flux to the temperature drop
  \[
  h = \frac{Q}{A\Delta T} = \frac{q''}{\Delta T} \left( \frac{W}{\text{mm}^2\text{K}} \right)
  \]

- Thermal contact resistance (TCR) is just the inverse of TCC, therefore
  \[
  R = \frac{1}{h} = \frac{A\Delta T}{Q} = \frac{\Delta T}{q''} \left( \frac{\text{mm}^2\text{K}}{W} \right)
  \]

- Alternate definition of TCR
  \[
  R' = \frac{\Delta T}{Q} = \frac{1}{hA} \left( \frac{K}{W} \right)
  \]

Note that contact resistance at a joint is not a physical property of the interface.
Carbon Nanotube (CNT) Interfaces

- CNTs are highly conductive
  - Room temperature thermal conductivity ≈ 3000 W/mK (8X copper, Kim et al. 2001)
  - Ballistic electron conductor, $R = 6500 \Omega$, independent of length up to ~0.1 μm at RT (Frank et al., 1998)
- CNTs have high aspect ratios
  - Length more than 1000 x diameter
- CNTs are mechanically resilient
  - Young’s modulus ~ 1 TPa (5X steel, Treacy et al. 1996)
- CNTs have strong van der Waals interactions
  - Increased nanotube-substrate contact area (Hertel et al., 1998)
- CNTs are chemically stable in a large temperature range (in air up to ≈ 450 °C)
Microwave Plasma CVD

Process gases:
- H₂ – 1000cm³/min
- CH₄ – 10cm³/min
- N₂ – 10cm³/min
- Other – O₂, Ar

Substrate Bias:
- 0 – 600 V; 0 – 1.7 A

Stage Temperature Control with Heating up to 1000°C

External Interlocks for Safe Operation

1.5kW@2.5GHz Microwave Generator
Vacuum Chamber
Dual Wavelength Pyrometer
75 mm of Stage Translation
Seki Technotron Corp. AX5200 Series
Some Growth Substrates for CNT Arrays

- silicon/SiO₂
- copper
- quartz
- sapphire
- diamond
- stainless steel
- iron
- nickel
- silicon carbide
- aluminum
- titanium
- and more...
General Characteristics of CNT Arrays

- Full multi-walled CNT coverage over the sample (macroscopic)
- Uniform CNT layer thickness for each array (array heights up to 100μm)
- Strong CNT-substrate bonding
- Dense and vertically oriented CNT ‘forest’
  - Density ≈ several hundred million to more than one billion CNTs/mm²
  - MWCNT diameters can range from 5 to 90 nm

Broken stems of CNTs after scratching

Purdue University Discovery Park

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CNT Array Thermal and Electrical Interfaces

One-sided interface

- Solid 2
- Solid 1

Two-sided interface

- Solid 2
- Solid 1

CNT/foil interface

- Solid 2
- Cu foil
- Solid 1

One-sided (post test)

- 5 μm

Copper

- 5 μm

Silicon

- 5 μm

100 μm
Thermal Interface Results: Summary

silicon/copper substrates at room temperature

References:


Resolving Component Resistances: One-Sided

- Resolution enabled by photoacoustic measurement

Results: Two-sided CNT Interfaces

silicon/copper substrates at room temperature

- 1-D reference bar measurement
- Photoacoustic measurement

Thermal resistance (mm²K/W)

Pressure (MPa)
Resolving Component Resistances: Two-Sided

- Resolution enabled by PA measurement

Contact Conductance Model: CNT Array Mechanics

CNT arrays deform similarly to wool fibers

C.M. Van Wyk, J. Textile Inst. 37, T285 (1946)

\[ P \approx c E_{\text{cnt}} \left( \frac{V_{\text{cnt}}}{tA} \right)^3 \]

- \( c \) – constant that depends on CNT orientation, quality, aspect ratio, and packing density
- \( E \) – Young’s modulus
- \( t \) – CNT array height
- \( V \) – volume of CNTs in array
- \( A \) – substrate area

Recently measured, nonlinear bulk modulus, \( B \), of CNF arrays

Y. Zhang et al., J. Mater Res. 21, 2948 (2006)

\[ B = -t \frac{dP}{dt} \]
CNT Array Contact Mechanics

- Aluminum
- Silicon

Force application shows a change in the contact mechanics, with a decrease in contact area from 5 μm to 2 μm.
Contact Conductance Model for CNT Array Interfaces

CNT growth substrate (Si)

Opposing substrate (Ag)

Silicon

Ag

$R_{D,\text{Si}}$

$R_{B,\text{Si-CNT}}$

$R_{C\text{NT array}}$

$R_{B,\text{CNT-Ag}}$

$R_{D,\text{Ag}}$

$R_{B,\text{Si-CNT}}$

$R_{D,\text{Si}}$

…….$N$……..
**Diffusive Heat Flow**

- For steady, continuum heat flow, the critical characteristics are thermal conductivity \( k \) and contact spot size \( a \)
- Thermal conductivity can be expressed as \( k = C v_g \lambda / 3 \), where
  - \( C \) is the volumetric heat capacity of the energy carriers
  - \( v_g \) is the group velocity of the energy carriers
  - \( \lambda \) is the mean free path of the energy carriers

\[
R_{\text{diffusive}} = \frac{1}{4ka}
\]

(see Carslaw and Jaeger, 1959)
Ballistic Heat Flow

- When the carrier mean free path becomes comparable to the contact spot size, sub-continuum effects become significant.
- As a result, the Knudsen number ($Kn = \lambda/a$) becomes an important parameter, in addition to $k$ and $a$ alone.
Phonon Ballistic Transport

- Contact size \( a < \lambda \), phonon ballistic transport
  - \( \lambda \), phonon mean free path
  - \( v_g \), frequency independent phonon group velocity
  - \( C_v \), Debye volumetric specific heat
  - \( \Gamma \), average transmissivity
- Heat flux through the \( a \)-contact

\[
q'' = \frac{\Gamma_{1\to2} \cdot C_{v1} \cdot T_1 \cdot v_{g1} - \Gamma_{2\to1} \cdot C_{v2} \cdot T_2 \cdot v_{g2}}{4}
\]
Thermal Constriction 
Resistance: Total

If interface materials are the same, then, \( R_{\text{PBT}} = \frac{4Kn}{3k \cdot \pi \cdot a} \) where, \( Kn = \frac{\lambda}{a} \)

\[ R_{\text{Total}} \approx R_{\text{diffusive}} + R_{\text{PBT}} \]

Continuum

as \( Kn \to 0 \) : \( R_{\text{PBT}} \to 0 \) and as expected, \( R_{\text{Total}} \sim R_{\text{diffusive}} \)

Sub-continuum

if \( Kn \sim 10^2 \) then \( R_{\text{PBT}} \sim 10^2 \cdot R_{\text{diffusive}} \) thus, \( R_{\text{Total}} \sim R_{\text{PBT}} \)

(typical of nanocontacts)
Preliminary Results

Lines: Model with two adjustable parameters (c and $t_0$)

Points: Experimental Data
Electrical CNT Interfaces to Thermoelectrics

Motivation
• Parasitic electrical contact resistance can strongly degrade the efficiency of thermoelectric devices
• Direct electrodeposited thermoelectric (Bi$_2$Te$_3$) on CNTs shows dramatically reduced interface resistance

Mishra et al., MRS Fall Meeting (2007)
Summary of Pool Boiling from CNT Arrays

Faculty: Issam Mudawar
Students: Sebastine Ujereh, Vikash Khanikar

Copper block with stacked components for silicon wafer adhesion.

- Silicon Wafer
- Indium Foil
- Oxygen-Free Copper Block
- Thermocouple Hole
- Solder
- Thick Film Resistor
- Power Leads

Boiling chamber
Patterned CNT Arrays on Si

"Island" Pattern

"Grid" Pattern

All dimensions in mm
Pool Boiling from an Si Substrate with FC-72

Enhancement Hypothesis

Bare Si

Coated with CNTs

(a) heated substrate

(b) parting of nanotubes

(c) departing bubble

replacement liquid

Vapor embryo

q'' = 1.3 W/cm²
ΔT_{sat} = 16.1 K

q'' = 5.1 W/cm²
ΔT_{sat} = 26.5 K

q'' = 1.3 W/cm²
ΔT_{sat} = 8.6 K

q'' = 4.9 W/cm²
ΔT_{sat} = 9.8 K
Ionic Winds for Electronics Cooling

- Macroscale corona discharges require high voltages (>2 kV)
- Field emission in micro-gaps require much lower voltage (~100V)
  - Nanostructured carbon field enhancement shows potential of lowering voltage to ~10V → suitable for microelectronics

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Slide 33
SWCNT Transistors


Javey et al., Nano Lett, 5, 2005
Challenges in SWCNT Device Fabrication

- Placement and addressability
  
- \textit{In situ} ohmic contact metallization
  - Lithography (photo or electron beam)
  - Focused ion beam

- Chirality / diameter control
  - CVD parameter variation for chirality control
Templated Vertical Growth of SWCNT Devices

Faculty: Tim Sands, David Janes
Students: Aaron Franklin, Matt Maschmann

- Start with Fe (SWCNT catalyst) embedded in Al film stack
Templated Vertical Growth of SWCNT Devices

- Film anodized to create porous anodic alumina (PAA), exposing Fe catalyst within pores

Templated Vertical Growth of SWCNT Devices

- SWCNTs grown from Fe catalyst using microwave plasma-enhanced CVD

Contacting SWCNTs *in situ*

- Pd electrodeposited into pores, contacting SWCNTs with Pd nanowires

Gating/Device Approach

Selective etchback of Al₂O₃ and deposition of gate metal to coat dielectric pillars

Gate metal etch to define channel length

Passivation layer deposition (Al₂O₃), planarization and top contact definition
Faculty: K.-S. Choi

- Pd nanowires contact SWCNTs, adding them to the cathodic electrode during electrodeposition
- Defect sites have been shown to serve as nucleation points for contact metals


Addressable ‘Fields’ of Templated SWCNTs

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CNT-based Thermal and Bio Sensors
Bioconjugation of Au/Pd-CNT Arrays

Research Associate: Ghanashyam Acharya
Student: Jonathan Claussen

Pd crystals on CNTs

Au/Pd-CNTs

Ligand (Biotin-SH)

Analyte (Streptavidin-Fluorescent)

Bright Field Image

Fluorescence Image

Manuscript in preparation
Biosensing with MWCNT Arrays

dc Bias During Synthesis

Student: Sungwon Kim

Catalyst Calcination Temperature

0V  -100V  -200V  -300V

250°C

550°C

700°C

900°C
Glucose-Glucose Oxidase Reaction

- Three electrode cell
  - Ag/AgCl electrode (reference)
  - Platinum electrode (counter)
  - CNT/CNF substrate (working)
- 4mL of diluted glucose (1000mg/50mL)
- Cyclic Voltammetry: Initial potential 0V, switching potential 800mV, final 0V
- Scan rate of 100mV/sec
- Total CNT areas estimated from SEM images

Manuscript in preparation
Important Issues in Biosensing with CNT Arrays

• Reduction of sensor size and detection time
• Elimination of target labeling/signal amplification and complicated/expensive fabrication protocols
• Optimization of CNT array sensors
  – Correlation of growth conditions to nanostructure
  – Influence of quality and morphology of CNTs/CNFs on degree of enzyme adsorption
    • More defect sites $\rightarrow$ better adsorption of enzyme?
  – Biofunctionalization of CNTs for different assays
  – Effects of tethered vs. immobilized receptors
**Noise Thermometry with CNTs**

- **Motivation**
  - Measuring the temperature is nanostructures is extremely difficult, yet critically important to many applications.
  - Noise thermometry offers the possibility of a self-calibrating, primary thermometer.

- **Applications**
  - Atomic-scale thermal interface resistances.
  - Self-heating in nanoelectronics.
  - Thermal energy exchange in field emission processes.
  - Convective boiling processes.

Noise Spectral Density (combined Johnson and shot noise)

\[
S_{I,J+s} = 2eI \coth\left(\frac{eV}{2k_BT}\right)
\]  

Modification to include self-heating \((T \to QR_0 + T_\infty)\)

\[
S_{I,J+s} = 2eI \coth\left(\frac{eV}{2k_B(QR_0 + T_\infty)}\right)
\]
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Nanomaterials Applications
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Outline
Atomistic Green’s Function (AGF) Modeling of Phonon Transport

• Motivation
  – More efficient atomistic simulation tools are needed to address problems at practical scales
  – Include effects of bulk contacts through self-energy matrices
  – Suitable for ballistic transport
    • Low temperature and/or very small dimensions (~10 nm)

• Required inputs
  – Equilibrium atomic positions
  – Inter-atomic potentials
  – Contact temperatures
The AGF Algorithm

- Establish atomic positions and interatomic potential parameters

- Assemble harmonic matrices ($H$)
  
  \[ H = \{ H_{ij} \} = \frac{1}{\sqrt{M_i M_j}} \begin{cases} \frac{\partial^2 U}{\partial u_i \partial u_j}, & \text{if } i \neq j \\ - \sum_{m \neq j} \frac{\partial^2 U}{\partial u_j \partial u_m}, & \text{if } i = j \end{cases} \]

- Calculate the Green’s function ($g$) of uncoupled contacts

- Calculate device $G$ and phonon transmission ($\Xi$)

- Integrate ($\Xi$) over phonon frequencies and $k_||$ to obtain the thermal conductance

\[ \Xi \left( \omega, \vec{k}_|| \right) = \text{Trace} \left[ \Gamma_L G_{LD,RD} \Gamma_R G^\dagger_{LD,RD} \right] \]

\[ J = \frac{1}{s} \int_0^\infty \int_{\vec{k}_||} \frac{\hbar \omega}{2\pi} \Delta \bar{N} \left( \omega, \vec{k}_|| \right) \Xi \left( \omega, \vec{k}_|| \right) \frac{d\vec{k}_||}{(2\pi)^2} d\omega \]
Results for Simple Atomic Chains

Homogeneous chain density of states

Homogeneous vs heterogeneous

Contacted Si Nanowire

Effect of Diameter

Electron Green’s Functions: Modeling of the Nottingham Effect

Student: Tyler Westover

Electron Emission:
Electrons cross over vacuum barrier (thermionic emission) or tunnel through barrier (field emission)

Cooling Mechanism:
Emitting electrons carry net energy from emitter to collector (heat sink)
Cooling by Vacuum Electron Emission?

Compare to Thermoelectric Refrigeration

- Theory indicates possibility of large local cooling rates (> 100 W/cm²)
- No lattice thermal conductivity
- Reduced ohmic resistance
- Large area interfaces

Challenges

- Very low work function electrodes are necessary
- Vacuum gap must be small
- Emission area must be large enough to produce necessary current

Non-Equilibrium Green’s Function Model

• Vacuum discretized with a one-band effective mass model
• Energy levels described by a Hamiltonian matrix $[H]$
• Coupling at interfaces described by self-energy matrices $[\Sigma_i]$

\[
\Gamma_i = i\left[\Sigma_i - \Sigma_i^+\right] \quad i = 1, 2
\]

\[
G = \left[EI - H - \Sigma_1 - \Sigma_2\right]^{-1}
\]

\[
I = \frac{2q}{h} \int_{-\infty}^{\infty} \left[T\right] \cdot \left[f_1(E) - f_2(E)\right] dE
\]

\[
f_i(E) = \frac{1}{1 + \exp\left[(E - \mu_i) / k_B T\right]}
\]

\[
[T] = Trace\left[\Gamma_1 G \Gamma_2 G^+\right]
\]

Theory based on work of S. Datta:
• NEGF simulation yields accurate results
• WKB approximation overpredicts cooling
• Maximum cooling density $\approx 80$ W/cm$^2$
• But, COP $\sim 0.001$, Electronic Coefficient of Performance (cooling power to power input ratio)


Applied field, $F$ (V/nm)

- Not practical in a cooling device
- Need a lower work function, $\phi$
Effect of Gap Spacing

COP = Electronic Coefficient of Performance
(ratio of cooling power to electrical power input)

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Outline
Thermionic Power Generation

Students: Tyler Westover, Vance Robinson
Faculty: Ron Reifenberger, Chuck Lukehart (Vanderbilt)

• Alluring direct power generation scheme because vacuum separation minimizes parasitic thermal losses.

• At a surface, excited electrons may escape the material if their energy exceeds a surface potential barrier, or work function $\phi$.

• Additional potential barriers exist due to space charge and/or generated voltage, $qV_0 = \mu_2 - \mu_1$. For these cases, the sum of all such barriers and the work function is denoted by $\Phi$.

Electron motive diagram for a thermionic power generation diode, with $T_1 > T_2$. 
Thermionic Electron Energy Distributions from Nanomaterials

- Experiments on arrays of graphitic carbon nanofibers with and without potassium intercalation

Li et al., *Nanotechnology*, 18, 325606 (2007)
Concept for Solar Thermionics

- Basic (highly idealized) theory predicts ultra-high efficiency (Ross, Nozik, J Appl Phys 53 3813 (1982))
- Concentrated solar irradiation provides some photoemission, perhaps amplified by CNT-induced field concentration and low scattering rates in CNTs
- Solar energy that does not directly produce photoemission heats the CNT absorber, promoting thermionic emission
- New modeling tools are needed that incorporate quantum considerations and accurate electron-phonon scattering models to explain measured performance
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US DoE 2010 Targets for Hydrogen Storage

- Specific energy: 6 wt% H$_2$ or 2 kWh/kg
- Energy density: 0.045kgH$_2$/L or 1.5 kWh/L
- Cost: $133/kgH$_2$ or $4/kWh

- These are for the system: fuel + tank + BOP

- Storage system for a compact car
  - Hydrogen: 5.6 kg
  - System weight: 93.3 kg
  - System volume: 124.4 liters
  - Cost: $745
  - Fueling rate: 1.5 to 2.0 kg H$_2$/min

Storage Approaches

• Compressed gas and liquid hydrogen
  – 700 bar, 300K: 143.5 liters
  – LH₂: 78.9 liters (fuel only)

• Material-based storage (adsorption or absorption)
  – Hydrogen itself can occupy much less space
  – Adds extra volume and weight from additional chemical species
  – Complex system: Useful hydrogen + material + tank + thermal management subsystem + BOP

• So far, no system has been demonstrated to meet the 2010 targets
• Reviewed heat transfer in on-board hydrogen storage technologies using compressed \(H_2\), \(LH_2\), chemical hydrides and metal hydrides

• Sodium borohydride (SBH) systems
  – Heat of reaction measurements
  – Kinetics measurements
  – Sub-scale (1-kW\(_e\)) system design, construction and tests
  – Sub-scale (1-kW\(_e\)) system modeling

• High-pressure metal hydride systems
  – Sub-scale (1/50) system design, construction and tests
  – Sub-scale (1/50) system modeling
  – Vehicle-scale facilities and testing
Hydrogen Storage Using NaBH₄

\[ \text{NaBH}_4 + 2\text{H}_2\text{O} \xrightarrow{25^\circ\text{C}} \text{RuCl}_3(\text{cat.}) \rightarrow \text{NaBO}_2 + 4\text{H}_2 \]

Heat of Reaction for SBH Hydrolysis

- Commonly accepted: 300 kJ/mol NaBH$_4$
- Measured: 210 kJ/mol ± 11 kJ/mol

Schematic of a 1 kW$_e$ NaBH$_4$ System
Effects of Flow Rate

High-Pressure Metal Hydride Research

Students: Jinsong Zhang, Varsha Velagapudi, Kyle Smith, Avanthi Boopalan, Scott Flueckiger, Andrew Steiner, Yen Yu, Casey Porta, Tyler Voskiulen, Aaron Sisto

Faculty: Issam Mudawar, Timothee Pourpoint, Yuan Zheng

Funding: General Motors
**Safety**

- **Most important rule at the Hydrogen Systems Lab:**
  
  “Safety comes first.”

- **Significant effort placed on:**
  
  - **Training:**
    - High Pressure Lab procedures and safety training followed by all students involved in project
    - Linde Gas training on high pressure systems
  
  - **Procedures:**
    - Careful development of test procedures for safe and repeatable testing
  
  - **Safety:**
    - Safety measures and evacuation procedures developed with the Purdue Fire and Safety Department
    - Emergency alarm system:
      - 3 sirens (122 dB at 10 feet) with amber flashing lights installed to notify all personnel in ZL1 of an emergency situation
      - To be activated in case of uncontrolled fire, catastrophic test article failure
    - **Event tree** developed to assess and solve emergency situations
Heat Transfer Systems for Metal Hydrides

• Introduction
  – Reversible metal hydrides used for hydrogen storage generate a large amount of heat (20-30 kJ/mol H₂) during the hydrogen absorption process
  – Practical on-board hydrogen refueling rate of 2 kg H₂/min leads to extremely high heat release rates (Q ≈ 0.5 MW over 3 minutes)

• Key Technical Issues
  – High heat release rates require active convective cooling
  – High-pressure systems for gases and coolants
  – Low thermal conductivity of nanoparticulate hydride bed
  – Adequate storage capacity and reversibility
Experimental Objectives

• Design and implement a heat exchanger with an integrated metal hydride containment system ensuring thermostructural integrity of the tank and its contents
• Modular design for flexibility of scaling: scale range extends from 1/50th to full-size vehicle-scale metal hydride hydrogen storage tank
• Measure filling-dependent thermal performance of a well instrumented subscale tank
• Verify thermodynamic model with operation of vehicle-scale reacting system at desired hydriding and dehydriding rates
Pressure Vessel and Tank Inlet Connections

- GH₂ Inlet
- Thermocouple Probes
- Coolant Loop

PRESSURE VESSEL
Test Article Installed in Pressure Vessel

Preliminary Experimental Results

Temperature [°C] vs Time [min]

MH Temp Test 5, 03/06/07
MH Temp Test 6, 03/15/07
MH Temp Test 7, 03/20/07
Pressure*10⁻¹ bar
Heat Conduction and Reaction Rate

- Conduction is the most significant contributor to heat dissipation.
- Reaction progress and conduction are coupled due to temperature-dependent kinetics.
- Conduction limits reaction progress for kinetically good materials.

\[
\left( \rho C \right)_{\text{eff}} \frac{\partial T}{\partial t} = \varepsilon \frac{\partial p}{\partial t} + k \nabla^2 T + \dot{q}
\]

Contribution of volumetric energy rates as a function of time:

- Sensible Energy
- Conduction
- Gas Compression
- Reaction Generation

Volumetric Power [W/m^3]

Time [min]
Conduction Modeling

Unactivated $\rightarrow$ cycles of low and high temperature hydriding $\rightarrow$ Activated

- Packing Configuration
- Nano-scale constrictions at contacts
- Ballistic/diffusive gas between particles
- Thermal & Elastic Properties
- Density Functional Theory
- Plane Wave Lattice Dynamics
- Boltzmann Transport Equation (BTE)
Conclusions

• Many opportunities exist for improved understanding of energy and charge transfer processes at the nanoscale
• Spatial confinement may enable the engineering of higher-efficiency energy transfer and conversion processes in carbon nanotubes
• Promising results for early ‘benchtop’ CNT applications
  – Weld-like heat transfer with ‘thermal velcro’
  – Ideal boiling behavior
  – Exceptional electrical transistor behavior
  – Large work function reduction of carbon nanofibers for direct energy conversion, possibly solar
  – Major breakthroughs needed in hydrogen storage, thermal issues paramount
• Progress generally requires coordinated efforts in a variety of disciplines and skills
  – Material synthesis and scale-up
  – Transport property characterization
  – System-level scaling/engineering
  – Health, safety, and environmental impact
Acknowledgments

• Collaborators
  – As listed in the slides

• Funding
  – General Motors
  – Cooling Technologies Research Center
  – National Science Foundation
  – US Air Force Research Laboratory
  – NASA
  – Creare
  – Intel Corp.
  – Nanoconduction, Inc.
THANK YOU