Nanomaterials for space exploration applications

NanoMaterials Group
NASA Johnson Space Center
ES4/Materials and Processes Branch

E-Mail: padraig.g.moloney@nasa.gov
NASA’s Strategic Vision

Deep Space Exploration

Mars Robotic

Crew Exploration Vehicle

Lunar Robotic

ISS Complete

Lunar Manned

Mars Manned

2005

2010

2015

2020

2035
Technology Readiness Levels (TRL)

- **TRL 9**: Actual system “flight proven” through successful mission operations
- **TRL 8**: Actual system completed and “flight qualified” through test and demonstration (Ground or Flight)
- **TRL 7**: System prototype demonstration in a space environment
- **TRL 6**: System/subsystem model or prototype demonstration in a relevant environment (Ground or Space)
- **TRL 5**: Component and/or breadboard validation in relevant environment
- **TRL 4**: Component and/or breadboard validation in laboratory environment
- **TRL 3**: Analytical and experimental critical function and/or characteristic proof-of-concept
- **TRL 2**: Technology concept and/or application formulated
- **TRL 1**: Basic principles observed and reported
Nanomaterials: Fundamentals to Applications

Growth/Production
Laser and HiPco
Production and Diagnostics

Characterization
Purity, Dispersion, Consistency, Type
SWCNT Load Transfer
Single Fiber Diffusivity

Processing
Purification
Functionalization
Dispersion
Alignment

Collaboration
Academia, Industry, Government

Applications For Human Spaceflight

<table>
<thead>
<tr>
<th>APPLICATION</th>
<th>PARTNERS</th>
<th>TRL</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
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<tr>
<td>Ultracapacitors</td>
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<td>Proton Exchange Membrane – PEM - Fuel Cells</td>
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<td>RCRS - Regenerable CO₂ Removal System</td>
<td>EC, Ames, Industry</td>
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<tr>
<td>Active / Passive Thermal Management Materials</td>
<td>EC, Rice, ORNL, Industry</td>
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<tr>
<td>Nanofiltration for Water Recovery</td>
<td>EC, Industry</td>
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<tr>
<td>Electromagnetic Shielding Materials (ESD/EMI)</td>
<td>EV, Rice, LaRC, Industry</td>
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<td>Radiation Dosimeter</td>
<td>NX, Rice, PV, LaRC, Ames</td>
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<td>Nanotube-Based Structural Composites</td>
<td>ES, Rice, UH, LaRC</td>
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</table>

Ceramic Nanofibers (TPS)
High Thermal Conductivity Fabrics
Electromagnetic Shielding
Electrostatic Discharge (ESD) Protection
JSC Nanomaterials Group Collaborations

Government

- NASA Langley Research Center
  - Production / purification (JSC) for use in SWNT composites (Giochi, Pan, Smith)
- Central Intelligence Agency
  - Nanotube characterization (Carr)
- Oak Ridge National Lab
  - CNF production, purification and characterization (Geoghegan)
  - Thermal characterization (Wang)
- NASA-Ames Research Center
  - Nanotubes (JSC) for sensors / modeling of HiPco (Meadur, Gray)
- National Renewable Energy Lab
  - Composites, characterization, purification (Maruyama, Strong)
- Air Force Research Lab
  - Composites, characterization, purification (Mikhal, Pedireddy)
- NASA Marshall Space Flight Center
  - Nanotubes, MMICs (Gil, Hudson)
- Les Alamos National Lab
  - Puriﬁcation (O’Connor)

National Institute of Standards and Technology

- Development of nanoscale measurement standards (Kremer)

Academia

  - Nanotube characterization
  - Radiation protection
  - Mechanics / composites
- Michigan Tech
  - Summer Faculty Fellow - Composites (Canada)
- UCRiverside
  - Purification / characterization (Hodgson)
- University of Houston
  - Advanced Nanotechnology Mat’s and Applications (Barnes, Tsur, Barnera)
  - Computational Materials Sci. (Yakobson)
  - Nanoshells (Hassan)
- University of Pennsylvania
  - GSEP: year 3 of 3 - Polymer dispersion, composites (Michell, Krishnamurthy)
- University of Paris 11
  - Ans process (Facetti)
- University of Florida
  - Isolated SWNTs (Rondinier)
- Northwestern
  - Nanomechanics (Ruff)
- LeTourneau University
  - Summer Faculty Fellow - Nanoscale growth processes (Davies)
- University of Houston
  - Nanodentistry Penumadu
- University of Tennessee, Knoxville
  - Nanomechanics (Penumadu)
- University of California - Davis
  - Nanocrystalline Ceramics (Mehreria)
- University of Oklahoma
  - Nanoscale growth processes (Rasras)
- Penn State
  - Ceramic / characterization (Eklund)
- University of Texas - Tyler
  - Summer Faculty Fellow - CFD of Laser process (Greenberg)
- Wake Forest
  - Characterization of nanotubes (Carroll)
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C₆₀
DC₆₀ = 10.18Å
DFe = 2.52Å
DCo = 2.50Å
DNi = 2.50Å
DC = 1.54Å

Size Comparison – C₆₀, Nanotubes, and Atoms

Unique Properties
- Exceptional strength
- Interesting electrical properties (metallic, semi-conducting, semi-metal)
- High thermal conductivity
- Large aspect ratios
- Large surface areas

Possible Applications
- High-strength, light-weight fibers and composites
- Nano-electronics, sensors, and field emission displays
- Radiation shielding and monitoring
- Fuel cells, energy storage, capacitors
- Biotechnology
- Advanced life support materials
- Electromagnetic shielding and electrostatic discharge materials
- Multifunctional materials
- Thermal management materials

Current Limitations
- High cost for bulk production
- Inability to produce high quality, pure, type specific SWCNTs
- Variations in material from batch to batch
- Growth mechanisms not thoroughly understood
- Characterization tools, techniques and protocols not well developed

Nanomaterials: Single Wall Carbon Nanotubes
Objective: Ensure a reliable source of single wall carbon nanotubes with tailored properties (length, diameter, purity, chirality)

High Pressure CO (HiPco)

CO + CO  Fe, Ni Catalysts  900-1200°C  10-40 atm
CO₂ + SWCNT + impurities

- Continuous process
- 10-100’s g/day
- Small diameters (0.9nm)
- Company spin-off (CNI)

Rice Univ.  & NASA  Carbon Nanotechnologies, Inc.

Laser Ablation

Graphite  Co, Ni Catalysts  4000-5000 K  argon
fullerenes + SWCNT + impurities

- Batch process
- ~1g/day
- Large diameters (~1.4nm)

Modeling, Diagnostics, and Parametric Studies
Standard Nanotube Characterization Protocol

New Purity Reference Standard

Haddon, 2003

NASA/NIST 2nd Characterization Workshop January 2005 Gaithersburg, MD

Areppalli, et al., Carbon, 2004
Applications for Human Space Exploration

Power / Energy Storage Materials
- Proton Exchange Membrane (PEM) Fuel Cells
- Supercapacitors / batteries

Advanced Life Support
- Regenerable CO₂ Removal
- Water recovery

Multi-functional / Structural Materials
- Primary structure (airframe)
- Inflatables

Thermal Management and Protection
- Ceramic nanofibers for advanced reentry materials
- Passive / active thermal management (spacesuit fabric, avionics)

Electromagnetic / Radiation Shielding and Monitoring
- ESD/EMI coatings
- Radiation monitoring

Nano-Biotechnology
- Health monitoring (assays)
- Countermeasures
Electrical Power / Energy Storage Systems

- Shuttle: 3x Alkaline Fuel Cells
- ISS: Photovoltaics & NiH₂ batteries
- ISS: NiMH, Li-MnO₂, and Ag/Zn batteries
- Pistol Grip Tool (PST) Battery Nickel Metal Hydride (NiMH)
- Helmet Light (HIL) Battery Nickel Metal Hydride (NiMH)
- Increased Capacity Battery (ICB) for EMU Silver-Zinc (Ag/Zn)
- Rechargeable EVA Battery Assembly (REBA) Nickel Metal Hydride (NiMH)
- Simplified Aid For EVA Rescue (SAFER) Battery Lithium Manganese Dioxide (Li-MnO₂)
Advanced Power Generation: Hybrid Systems

Fuel Cell
- Continuous energy supply
- High energy density
- Low power density

Battery
- Smaller, lighter, longer life with hybrid
- Intermediate power density
- Intermediate energy density

Supercapacitor
- Pulse power source
- Fast charge/discharge
- Very high power density
- Virtually unlimited cycle life

Energy-power tradeoff

Specific Power (W/kg) vs. Specific Energy (Wh/kg)
Advanced PEM Fuel Cells – Nanotube Electrodes

- Carbon nanotube electrode assemblies for proton exchange membrane (PEM) fuel cells
- Membrane Electrode Assembly (MEA) formed from a Nafion™ membrane sandwiched between nanotube electrodes with Pt catalyst

- Increased surface area of the electrodes
- Enhanced thermal management
- Reduce Ohmic losses – increase efficiency
- Higher power density
- Small diameter HiPco tubes may enhance H₂ dissociation – optimized porosity
- More uniform current density

Source: www.eere.energy.gov
# Advanced PEM Fuel Cells - Characterization

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Technique/Instrument</th>
<th>Destructive</th>
<th>When</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amount of Pt, Fe, Co, Ni</td>
<td>X Ray Photoelectron/Fluorescence Spectroscopy</td>
<td>no</td>
<td>After BP is baked (Part 5)</td>
<td>Quan</td>
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<tr>
<td>Platinum Dispersion</td>
<td>Scanning Electron Microscopy (SEM)</td>
<td>yes</td>
<td>After BP is baked (Part 5)</td>
<td>Qual</td>
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<tr>
<td>Platinum Dispersion</td>
<td>Transmission Electron Microscopy (TEM)</td>
<td>yes</td>
<td>After BP is baked (Part 5)</td>
<td>Qual</td>
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<tr>
<td>Electrical Conductivity</td>
<td>Probe Meter</td>
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<td>After MEA is made (Part 7)</td>
<td>Qual</td>
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<tr>
<td>Surface Area &amp; Porosity</td>
<td>Brunauer, Emmett, and Teller Analysis (BET)</td>
<td>yes</td>
<td>After BP is (1) made and (2) baked (Part 4 and Part 5)</td>
<td>Quan</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
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<th>Technique/Instrument</th>
<th>Destructive</th>
<th>When</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass</td>
<td>Scale</td>
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<tr>
<td>Thickness</td>
<td>Randall&amp;Stickney Dial Gauge</td>
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<td>After BP is (1) made and (2) baked (Part 3 and Part 5)</td>
<td>Quan</td>
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<tr>
<td>Interface and Thickness</td>
<td>Freeze Fracture then SEM</td>
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<td>After MEA is made (Part 7)</td>
<td>Qual/Quan</td>
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<tr>
<td>Interface</td>
<td>Flash IR Thermography</td>
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<td>After MEA is made (Part 7)</td>
<td>Qual</td>
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<tr>
<td>Interface</td>
<td>Current Voltage Curve</td>
<td>no</td>
<td>During Fuel Cell Testing</td>
<td>Quan</td>
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</table>
Prototype Membrane Electrode Assembly

Carbon Fiber Gas Diffusion Layer (GDL)

Single Wall Carbon Nanotube (SWCNT) Electrode

Nafion™ Membrane

SWCNT Electrode

Carbon Fiber (GDL)

SWCNT interface in MEA

Nafion™ interface in MEA
• EDX data does not indicate the presence of Fe (would show up at about 6.4 keV).

• EDX does indicate the presence of Pt, therefore we presume that the visible nanoparticles are composed of Pt.

• TEM shows a range of Pt particle sizes between 2nm and 10nm.

• XPS data indicates that Pt is metallic. This indicates complete decomposition of the precursor.
Characterization PEMFC: TEM of Electrodes

Ultramicrotomy

TEM Ultramicrotomy Study to characterization interface between GDL, electrodes and Nafion
• Developed Characterization protocol
• Test capability at NASA JSC
• Achieving catalyst size and performance
• Higher performance at lower current loading – increased PEMFC kinetics
Water Purification

• NASA JSC Structural Engineering and Crew & Thermal Systems Divisions

• Use light induced production of singlet oxygen by fullerenes to destroy harmful microbes in water supplies

• Developing process for attaching fullerenes to fiber optic cables

• CDDF 2005 – Report Due December 2005
Air Revitalization: CO$_2$ Removal

- Remove CO$_2$ from cabin air in order to extend the use of cabin air supplies
- Only a small amount of CO$_2$ can contaminate a large amount of cabin air
Lithium Hydroxide: Not suited for long duration missions since it is non regenerable

\[
2 \text{LiOH} \cdot \text{H}_2\text{O}(s) + \text{CO}_2(g) \rightarrow \text{Li}_2\text{CO}_3(s) + 3 \text{H}_2\text{O}(g)
\]

\[\Delta H^\circ = +3.8 \text{ kcal/mol LiOH},\]

Zeolite 5A: Physisorption of CO\(_2\)
- Requires 200°C to renew the adsorbent – high power consumption
- Lower surface area to volume ratio
- Non selective

MetOx – Metal Oxide (AgO) reacts with CO\(_2\) to form a carbonate.
- Large system mass – not optimal for PLSS
- Also requires high temperature

\[
\text{Ag}_2\text{O} + \text{CO}_2 \overset{\text{H}_2\text{O}}{\rightarrow} \text{Ag}_2\text{CO}_3
\]

\[
\text{Ag}_2\text{CO}_3 \overset{\Delta}{\rightarrow} 220\text{C} \rightarrow \text{Ag}_2\text{O} + \text{CO}_2
\]
Catalyzed by moisture

Depending on their bonding amines have varying degrees of affinity for CO₂ capture and desorption

Primary binds CO₂ tightly, thus inhibiting desorption while tertiary amines bind CO₂ poorly

Secondary amines are preferred for pressure swing
Advanced solid amine bed system flown in mid-1990’s (pressure swing)
- Volume constraints, thermally inefficient, amine volatility
- Not suited for planetary use (need temperature swing)
- Surface area ~100 m²/g

Need for new material: high surface area, high thermal conductivity, ability to be coated with amine system

*Carbon nanotubes may offer a thermally conductive high surface area light weight support material for this application*
Initial Results and Technology Assessment

Results

• Carbon Nanotubes have high surface area: bucky pearls, fibers, bucky paper
• TGA experiment: the amine is reactive with the CO₂ gas stream
• Poor adherence to nanotube surface - requires a specific pore size and shape
• We need a better way to integrate the support phase with the amine
Materials Development and Testing

- Collaborations for functionalization of SWCNTs
  - Dr. W. E. Billups group (Rice University)
  - Dr. J. Tour group (Rice University)
  - Collaboration with Dr. T. Filburn (University of Hartford)
    - Determine the types of amines that would be suitable for spaceflight needs
    - Testing methods for equilibrium adsorption and desorption and well as cyclic behavior
Functionalization of SWCNTs with Amine Groups

• Since amines are volatile the coating would be prone to degradation during repeated thermal or vacuum driven renewal of the adsorbent.

• Chemically bonding of the amine to the support phase was a solution to this problem.

Hirsch et al.
The argument for functionalization

- **Amenable to repeated cycling**
  - Materials are thermally stable up to 100 C. (Thermal desorption takes place at 50 – 60 C)
  - Chemical bonding of the amine to the support ensures these materials will be amenable to repeated vacuum desorption

- **We have the tools and capability to manufacture materials**
  - Collaborators at Rice (Tour and Billups) are experts in the area of nanotube functionalization
  - Chemistry is repeatable and reliable.
  - High amine loadings are possible especially with long branched amine polymers
Active / Passive Thermal Management Materials

- SWNT thermal properties are extremely anisotropic; SWNT axial conductivity is comparable to that of diamond (2150 W/m-K)
- Nylon Spandex/SWNT fabric improves crew member’s thermal comfort and increases heat transfer rate to EMU sublimator (SBIR)
- Active heat acquisition and transport applications in concept stage (advanced coldplate, interface, fluids)
- New single-fiber thermal diffusivity tool developed by JSC Nano Team and ORNL

Nylon Spandex/SWNT Fabric for Spacesuits

Single Fiber Thermal Diffusivity (JSC and ORNL)
ESD and EMI Materials with Nanotubes

• Application
  – SWNTs in a polymer at low concentrations to shield electronics from electromagnetic interference (EMI) and for electrostatic discharge (ESD) protection of sensitive electronics components.
  – Advantages – lightweight, humidity independent, flexible, ideal for coatings

Conducting Polymers from Nanotube Fillers

- Testing plan in work with EV (EMI)
- Industry-produced composites tested in RITF (ESD)

Surface Resistivity (ohm/sq) vs. Concentration in weight %

- Insulating
- ESD range
- ABS/SWNT’s
- EMI range

E.V. Barrera et al., Rice University
Carbon Nanotube Radiation Dosimeter

Compelling need to directly measure the radiation environment of spacecraft and compare to models for safety to humans for EVA and future space travel

- SWNTs respond at the particle level—radiation particle bombardment may be quantitatively detectable
- Fly initially as a passive experiment to gather real-time radiation dose on orbit
- Applicable for commercial usage by Medical, Nuclear industries
Summary

- Overview of NASA JSC NanoMaterials Project
  - Need
  - NanoMaterials Growth
  - NanoMaterials Characterization
  - NanoMaterials Processing
  - NanoMaterials Application

- NanoMaterials for PEMFC
- Presented work for developing solid-supported amine adsorbents based on carbon nanotube materials
  - Materials testing
  - Functionalization of SWCNTs

- Briefly: Other Application areas
Nanomaterials for space exploration applications

Questions?
• TGA/DSC experiment: Measure the weight change of a sample upon exposure to CO₂ +H₂O stream – DSC shows heat flow indicative of amine/ CO₂ reaction
• Recent upgrade: Residual gas analyzer measures the change in CO₂ concentration
Characterization of Functionalized SWCNTs

TGA for PEI functionalized SWCNTs

XPS Spectrum of L-PEI functionalized SWCNTs

Raman Spectrum (780 nm) of:
- a) Purified SWCNTS
- b) Dodecylated SWCNTS as synthesized
- c) Dodecylated SWCNTS after heating – the groups have been removed

Liang et al. 2004
TGA/XPS study of removal of functional groups

• Heat samples to various temperature and observe weight loss
• Examine XPS peaks characteristic of groups of interest
• Correlate weight loss to loss of functional group
Active / Passive Thermal Management Materials for Space

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![Graph showing thermal diffusivity](image)

Nylon Spandex/SWNT Fabric for Spacesuits

Heat Acquisition
Heat Transport

Single Fiber Thermal Diffusivity (JSC and ORNL)
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• Industry-produced composites tested in RITF (ESD)

E.V. Barrera et al., Rice University
Nanoshells for Thermal Control Coatings

- Nanoshells offer possibility of designing thermal control coatings
- Thermo-optical properties manipulated by nanoshell geometry
  - ratio of silica core to shell thickness
  - independent of overall organization of nanoshells
- Interested in nanoshell design with low solar absorptivity and high emittance

Courtesy of NanoSpectra
Carbon Nanotube Dosimeter

Compelling need to directly measure the radiation environment of spacecraft and compare to models for safety to humans for ISS and future space travel

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• Fly initially as a passive experiment to gather real-time radiation dose on orbit
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Nanotechnology & Human Spaceflight

Key Enabler to Human & Robotic Exploration

Nano-Engineered Materials
- Truly multi-functional materials
- Best known mechanical, thermal, and electrical properties exist now at the nanoscale
- Highest possible surface area

Technology Needs for Long-Duration Human Spaceflight
- Reduced mass / volume
- Greater reliability of materials/systems
- System health monitoring & repair
- Air revitalization
- Water recovery
- Human health diagnosis & treatment
- Radiation protection & detection
- In-space manufacturing

Human Spaceflight applications will drive unique advances in…
- Safety and Toxicology
- Reliability and Durability

Current Nanoscale R&D on Human Spaceflight Applications
- Electromagnetic Shielding Materials
- Proton Exchange Membrane – PEM - Fuel Cells
- Nanotube-Based Structural Composites
- RCRS - Regenerable CO₂ Removal System
- Ceramic Nanofibers for Thermal Protection Materials
- High Thermal Conductivity Fabric for Spacesuits
- Radiation Resistance/Protection
- Passive Radiation Dosimeter
- Active Thermal Control Systems for Space
- Nanoshells for Thermal Control Coatings