Nanomaterials for space exploration applications

NanoMaterials Group
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ES4/Materials and Processes Branch

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NASA’s Strategic Vision

- **Deep Space Exploration**
  - Mars Robotic
    - ISS Complete
    - Crew Exploration Vehicle
    - Lunar Robotic
  - Lunar Manned
  - Mars Manned

Timeline:
- 2005
- 2010
- 2015
- 2020
- 2035
Technology Readiness Levels (TRL)

- **TRL 1**: Basic principles observed and reported
- **TRL 2**: Technology concept and/or application formulated
- **TRL 3**: Analytical and experimental critical function and/or characteristic proof-of-concept
- **TRL 4**: Component and/or breadboard validation in laboratory environment
- **TRL 5**: System/subsystem model or prototype demonstration in a relevant environment (Ground or Space)
- **TRL 6**: System prototype demonstration in a space environment
- **TRL 7**: Actual system completed and “flight qualified” through test and demonstration (Ground or Flight)
- **TRL 8**: Actual system “flight proven” through successful mission operations
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>
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</thead>
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<tr>
<td>Ultracapacitors</td>
<td>EP, Glenn, Industry</td>
<td>X</td>
</tr>
<tr>
<td>Proton Exchange Membrane – PEM - Fuel Cells</td>
<td>EP, Glenn, Industry</td>
<td>X</td>
</tr>
<tr>
<td>RCRS - Regenerable CO₂ Removal System</td>
<td>EC, Ames, Industry</td>
<td>X</td>
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<tr>
<td>Active / Passive Thermal Management Materials</td>
<td>EC, Rice, ORNL, Industry</td>
<td>X</td>
</tr>
<tr>
<td>Nanofiltration for Water Recovery</td>
<td>EC, Industry</td>
<td>X</td>
</tr>
<tr>
<td>Electromagnetic Shielding Materials (ESD/EMI)</td>
<td>EV, Rice, LaRC, Industry</td>
<td>X</td>
</tr>
<tr>
<td>Radiation Dosimeter</td>
<td>NX, Rice, PV, LaRC, Ames</td>
<td>X</td>
</tr>
<tr>
<td>Nanotube-Based Structural Composites</td>
<td>ES, Rice, UH, LaRC</td>
<td>X</td>
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</table>

Ceramic Nanofibers (TPS)

High Thermal Conductivity Fabrics

Electromagnetic Shielding

Electrostatic Discharge (ESD) Protection
Nanomaterials: Single Wall Carbon Nanotubes

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

Size Comparison – $C_{60}$, Nanotubes, and Atoms

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

High Pressure CO (HiPco)

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

Graphite $\rightarrow$ fullerenes + SWCNT + impurities

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

Modeling, Diagnostics, and Parametric Studies
Standard Nanotube Characterization Protocol

Arepalli, et al., Carbon, 2004

New Purity Reference Standard

Haddon, 2003

NASA/NIST 2nd Characterization Workshop January 2005 Gaithersburg, MD
## Applications for Human Space Exploration

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

### Advanced Life Support
- Regenerative CO₂ Removal
- Water recovery

### Multi-functional / Structural Materials
- Primary structure (airframe)
- Inflatable

### 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

EVA NiMH, Li-MnO₂, and Ag/Zn batteries
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)
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
<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>
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<td>After BP is baked (Part 5)</td>
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<tr>
<td>Platinum Dispersion</td>
<td>Scanning Electron Microscopy (SEM)</td>
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<tr>
<td>Platinum Dispersion</td>
<td>Transmission Electron Microscopy (TEM)</td>
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<td>Electrical Conductivity</td>
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<td>After MEA is made (Part 7)</td>
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<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>

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</tr>
</thead>
<tbody>
<tr>
<td>Mass</td>
<td>Scale</td>
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<td>After BP is (1) made and (2) baked (Part 3 and Part 5)</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/Qu</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>
</tr>
<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>
Advanced PEM Fuel Cells - Characterization

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
Characterization PEMFC: TEM of Electrodes Made with Purified SWCNTs

TEM provides particle size distribution and EDX Shows elemental composition.

- 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: CO₂ Removal

- Remove CO₂ from cabin air in order to extend the use of cabin air supplies
- Only a small amount of CO₂ 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\textsubscript{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\textsubscript{2} to form a carbonate.
- Large system mass – not optimal for PLSS
- Also requires high temperature

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

\[
\text{Ag}_2\text{CO}_3 \xrightarrow{\Delta 220^\circ\text{C}} \text{Ag}_2\text{O} + \text{CO}_2
\]
Supported Amines for Air Revitalization

\[ R_1R_2NH + CO_2(aq) \rightleftharpoons K \rightarrow R_1R_2NH \cdot CO_2^- \] (1)

\[ R_1R_2NH + R_1R_2NH \cdot CO_2^- \rightleftharpoons K \rightarrow R_1R_2NH^- + R_1R_2NCO_2^- \] (2)

\[ R_1R_2R_3N + H_2O + CO_2(aq) \rightleftharpoons K \rightarrow R_1R_2R_3NH^- + HCO_3^- \] (3)

Catalyzed by moisture

Depending on their bonding amines have varying degrees of affinity for CO\(_2\) capture and desorption

Primary binds CO\(_2\) tightly, thus inhibiting desorption while tertiary amines bind CO\(_2\) poorly

Secondary amines are preferred for pressure swing

N-aminoethylpiperazine
The State of the Art in Amine Systems

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
Results

- Carbon Nanotubes have high surface area: bucky pearls, fibers, bucky paper
- TGA experiment: the amine is reactive with the CO$_2$ 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
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

![Graph showing surface resistivity vs. concentration in weight %]

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

E.V. Barrera et al., Rice University
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 the Thermal Stability of Functionalized SWCNTs

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

XPS Data Spectra at 200C, 400C and 600C

TGA Weight Loss

Aniline
Active / Passive Thermal Management Materials for Space

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Nylon Spandex/SWNT Fabric for Spacesuits

Heat Acquisition
Heat Transport

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

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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

![Graph showing extinction spectra for nanoshells of different core-shell ratios and wavelength](image)

**Reflectance vs. Wavelength**

- **AJ** - 0.067 mg/ml
- **AG** - 0.2 mg/ml
- **AD** - 0.6 mg/ml
- **AB** - 1.8 mg/ml

*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

- 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
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

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

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