Nanomaterials for space exploration applications

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

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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
- **TRL 9**: System Test, Launch & Operations
### 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>
<tbody>
<tr>
<td><strong>Ultracapacitors</strong></td>
<td>EP, Glenn, Industry</td>
<td>X X X X</td>
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<tr>
<td><strong>Proton Exchange Membrane – PEM - Fuel Cells</strong></td>
<td>EP, Glenn, Industry</td>
<td>X X</td>
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<tr>
<td><strong>RCRS - Regenerable CO₂ Removal System</strong></td>
<td>EC, Ames, Industry</td>
<td>X X</td>
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<tr>
<td><strong>Active / Passive Thermal Management Materials</strong></td>
<td>EC, Rice, ORNL, Industry</td>
<td>X X</td>
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<tr>
<td><strong>Nanofiltration for Water Recovery</strong></td>
<td>EC, Industry</td>
<td>X X</td>
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<tr>
<td><strong>Electromagnetic Shielding Materials (ESD/EMI)</strong></td>
<td>EV, Rice, LaRC, Industry</td>
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<td><strong>Advanced Nanostructured Materials for Thermal Protection and Control</strong></td>
<td>ES3, Ames, Goddard, Industry</td>
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<tr>
<td><strong>Radiation Dosimeter</strong></td>
<td>NX, Rice, PV, LaRC, Ames</td>
<td>X</td>
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<tr>
<td><strong>Nanotube-Based Structural Composites</strong></td>
<td>ES, Rice, UH, LaRC</td>
<td>X X</td>
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</table>
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

**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

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

Size of $C_{60}$: 10.18 Å
Size of Fe: 2.52 Å
Size of Co: 2.50 Å
Size of Ni: 2.50 Å
Size of C: 1.54 Å
Objective: Ensure a reliable source of single wall carbon nanotubes with tailored properties (length, diameter, purity, chirality).
Characterization: Purity, Dispersion & Consistency

Standard Nanotube Characterization Protocol

New Purity Reference Standard

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

Arepalli, 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

EVA
NiMH, Li-MnO₂, and Ag/Zn batteries

Pistol Grip Tool (PST) Battery
Nickel Metal Hydride (NiMH)

Helmet Light (HL) 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

![Graph showing specific power and energy for Fuel Cell, Battery, and Supercapacitor](image-url)
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>
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<tbody>
<tr>
<td>Amount of Pt, Fe, Co, Ni</td>
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<tr>
<td>Platinum Dispersion</td>
<td>Scanning Electron Microscopy (SEM)</td>
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<td>Platinum Dispersion</td>
<td>Transmission Electron Microscopy (TEM)</td>
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<tr>
<td>Surface Area &amp; Porosity</td>
<td>Brunauer, Emmett, and Teller Analysis (BET)</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>baked (Part 4 and Part 5)</td>
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<tr>
<td>Mass</td>
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<tr>
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<td>baked (Part 3 and Part 5)</td>
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<tr>
<td>Interface and Thickness</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>
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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>
Advanced PEM Fuel Cells - Characterization

Prototype Membrane Electrode Assembly

Carbon Fiber Gas Diffusion Layer (GDL)

Nafion™ Membrane

Single Wall Carbon Nanotube (SWCNT) Electrode

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\(_2\)
- Requires 200C 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

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

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

\[ R_1R_2NH + CO_2(aq) \xrightleftharpoons[K_1]{K_2} R_1R_2NH\cdot CO_2^- \]  \hspace{1cm} (1)

\[ R_1R_2NH + R_1R_2NH\cdot CO_2^- \xrightleftharpoons[K_3]{K_4} R_1R_2NH^+ + R_1R_2NCO_2^- \]  \hspace{1cm} (2)

\[ R_1R_2R_3N + H_2O + CO_2(aq) \xrightleftharpoons[K_5]{K_6} R_1R_2R_3NH^+ + HCO_3^- \]  \hspace{1cm} (3)

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

N-aminoethylpiperazine
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 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
• 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.
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](image)

- Testing plan in work with EV (EMI)
- Industry-produced composites tested in RITF (ESD)
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?
Microscale Testing of Equilibrium CO$_2$ Capture

- TGA/DSC experiment: Measure the weight change of a sample upon exposure to CO$_2$ +H$_2$O stream – DSC shows heat flow indicative of amine/ CO$_2$ reaction
- Recent upgrade: Residual gas analyzer measures the change in CO$_2$ 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

- 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)
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![Diagram showing thermal diffusivity of different nanofibers](image)

**Nylon Spandex/SWNT Fabric for Spacesuits**

**Heat Acquisition Heat Transport**

**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

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

- Testing plan in work with EV (EMI)
- 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

![Graph showing extinction spectra with varying nanoshell concentrations](image)

![Diagram illustrating core-shell nanoshell structure](image)

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