Nanomaterials for space exploration applications

NanoMaterials Group
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ES4/Materials and Processes Branch

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NASA’s Strategic Vision

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

Timeline:
- 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
**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

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**Applications For Human Spaceflight**

<table>
<thead>
<tr>
<th>APPLICATION</th>
<th>PARTNERS</th>
<th>TRL</th>
<th>1</th>
<th>2</th>
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<td>RCRS - Regenerable CO₂ Removal System</td>
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<td>Active / Passive Thermal Management Materials</td>
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<td>Nanofiltration for Water Recovery</td>
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<td>Radiation Dosimeter</td>
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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
Objective: Ensure a reliable source of single wall carbon nanotubes with tailored properties (length, diameter, purity, chirality)
**Standard Nanotube Characterization Protocol**

- **SEM**
  - Characterization images
- **TEM**
  - Characterization images
- **UV-Vis Spectroscopy**
  - Characterization graphs
- **Optical Dispersion Analysis**
  - Characterization graphs
- **Raman**
  - Characterization graphs
- **TGA**
  - Characterization graphs

**New Purity Reference Standard**

- Reference graph showing absorbance vs. wavenumber (cm⁻¹)

**NASA/NIST 2nd Characterization Workshop**

- January 2005
- Gaithersburg, MD

**Characterization: Purity, Dispersion & Consistency**

- 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 & NiH$_2$ batteries

EVA
NiMH, Li-MnO$_2$, and Ag/Zn batteries
Advanced Power Generation: Hybrid Systems

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

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

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

Energy-power tradeoff

- Fuel Cell
- Battery
- Supercapacitor
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>
<td>X Ray Photoelectron/Fluorescence Spectroscopy</td>
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<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>
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<tr>
<td>Platinum Dispersion</td>
<td>Transmission Electron Microscopy (TEM)</td>
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<td>After BP is baked (Part 5)</td>
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<td>Probe Meter</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>
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</table>

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<tr>
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<th>Destructive</th>
<th>When</th>
<th>Results</th>
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<td>Mass</td>
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<td>Interface and Thickness</td>
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<tr>
<td>Interface</td>
<td>Current Voltage Curve</td>
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<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
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.
Air Revitalization: Some Current Technologies

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 \( \text{CO}_2 \)
- Requires 200C to renew the adsorbent – high power consumption
- Lower surface area to volume ratio
- Non selective

MetOx – Metal Oxide (AgO) reacts with \( \text{CO}_2 \) 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

\[
R_1R_2NH + CO_2(aq) \rightleftharpoons K[R_1R_2NHCO_2^-] 
\]  
(1)

\[
R_1R_2NH + R_1R_2NHCO_2^- \rightleftharpoons K[R_1R_2NH^+ + R_1R_2NCO_2^-] 
\]  
(2)

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

Catalyzed by moisture

Depending on their bonding amines have varying degrees of affinity for CO\textsubscript{2} capture and desorption

Primary binds CO\textsubscript{2} tightly, thus inhibiting desorption while tertiary amines bind CO\textsubscript{2} 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
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 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.
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

![Diagram of thermal diffusivity](image)
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 (ohm/sq) vs Concentration in weight % for different materials.]

- E.V. Barrera et al., Rice University

- **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\textsubscript{2} Capture

- TGA/DSC experiment: Measure the weight change of a sample upon exposure to CO\textsubscript{2} + H\textsubscript{2}O stream – DSC shows heat flow indicative of amine/CO\textsubscript{2} reaction
- Recent upgrade: Residual gas analyzer measures the change in CO\textsubscript{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
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

TGA Weight Loss

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

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

**TMJ Paint with Varying Nanoshell Concentrations**

![Graph showing reflectance vs. wavelength with varying nanoshell concentrations](image)

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

**Reflectance vs. Wavelength (nm)**

![Graph showing reflectance vs. wavelength](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

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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

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