InnoSense LLC

# REFRACTORY COATED SILICA AEROGELS: ISOTOPE CATCHERS FOR THE FAST RELEASE OF UNSTABLE LIGHT NUCLEI

Argonne NATIONAL LABORATORY

## Nuclear Physics SBIR/STTR Exchange Meeting

September 13–14, 2010

## Sponsor: Department of Energy

Phase II Contract Number: DE-FG02-07ER86315

Project Officer: Dr. Manouchehr Farkhondeh

## Contractor: InnoSense LLC

2531 West 237th Street, Suite 127

Torrance, CA 90505

**Principal Investigator:** Uma Sampathkumaran, PhD

**Telephone:** (310) 530-2011

**E-mail:** uma.sampathkumaran@innosense.us

# Outline

- Introduction
- About InnoSense LLC (ISL)
- Our Capabilities and Core Technologies
- Phase II Project Goals
- Relevance to the Nuclear Physics Program
- Schedule and Deliverables
- Project Progress
- Summary/Future Plans
- Acknowledgments

InnoSense LLC

# About InnoSense LLC


**InnoSense LLC occupies a 7,500-square-foot facility in a business park in Torrance, CA, 15 miles south of Los Angeles International Airport.**

- **Established in 2002 through private funding**
- **Limited Liability Company based in California**
- **Growth-oriented high-tech company**
- **Mantra: Innovation**
- **Eighteen employees including six PhDs, six engineers, two MBAs**

InnoSense LLC

# Key Personnel

**Kisholoy Goswami, PhD, President and Chief Technology Officer**
- Eleven relevant U.S. patents
- First commercial fiber-optic sensor
- Optical sensors
- Raising private capital

**Uma Sampathkumaran, PhD, Director of Research**
- Ormosils/sol-gels /aerogels
- Integrated optical waveguides
- Metal oxide thin films
- Self-assembled monolayers
- Nanomaterials-based sensors and nanocomposite coatings

**Tania Betancourt, PhD, Research Scientist**
- Polymer synthesis
- Polymeric nanoparticles
- Biomaterials
- Drug delivery
- Cancer imaging and diagnostics

**David Michael Hess, PhD, Research Scientist**
- Photoelectrochemical conversion of $CO_2$ to methanol
- Templating by phase separation of polymers
- Materials engineering and testing
- Biomaterials

# Key Personnel (continued)

**Thomas William Owen, Jr., PhD, Research Scientist**

- Electrochemical and microgravimetric sensors/biosensors
- Functional materials for sensor applications
- Supramolecular assemblies

**Rashmi Dalvi, PhD, Research Scientist**

- Organometallics
- Organic synthesis
- Heterocyclics
- Catalysis

**Mr. Corey Selman, BS, MBA, Senior Product Engineer**

- Commercialization
- Process chemistry and product scale-up
- Engineering design (five patents)
- Product packaging

**Mark Slaska, BS, MBA, Technology Transition Specialist**

- Commercialization
- Coating formulations
- Process engineering
- Organic synthesis

# InnoSense Core Capabilities

## Nanomaterials and Coatings

- W-coated silica aerogels and porous refractories as catchers for rare isotope production/separation
- Carbon aerogels for catchers for molecular species ($^{12}C^{15}O$, $^{12}C^{15}O_2$)
- Nanocomposite anti-fog coatings for protective facemasks
- Cryogenic insulating nanocomposite foams
- Flame-retardant materials for fabrics/structural composites
- Nanoparticle-based contrast agents for bioimaging

## Sensors

- Chemical Sensors — Optical detection of gases and liquids
- Physical Sensors — Colorimetric temperature dosimeter
- Biosensors — Electrochemical detection of biomarkers

## Energy Conversion Devices

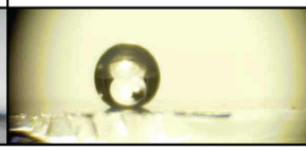
- Photoelectrochemical conversion of $CO_2$ to methanol
- Nanostructured photovoltaic devices

# Nanomaterials and Coatings

# Anti-Fog Coatings

## Anti-Fog Coating

| Clean-It | Clear-It |
|---|---|
| Superhydrophilic | Superhydrophobic |



### Features

- Conformal Optical Coatings on Plastic Lenses of Different Geometries
- Resistant to Mechanical Abrasion, Sanitizers and Cleaners
- Durable to Temperature Extremes from -60F – 160F and UV Radiation
- Full Scale, Continuous and Reliable Anti-fog Coating Process

### Commercialization Partners

- Avon Protection Systems
- Smith Optics
- Boeing
- Kollmorgen Electro-Optical
- Coating Design Group Inc.
- Lamart Corporation

## Military

| Protective Mask | All Terrain Vehicle | Periscope Windows |
|---|---|---|

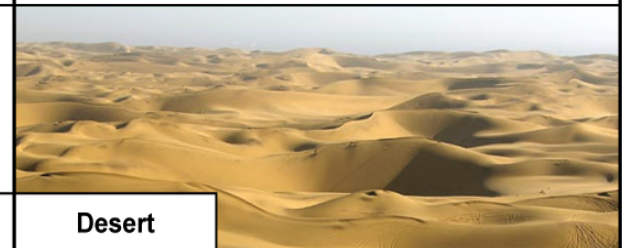
## Commercial

| Aircraft | Solar Panels | Automobiles |
|---|---|---|

## Personal Protective Eyegear

| Swimming Goggles | Motorcycle Visors | Ski Goggles |
|---|---|---|

## Environments



Desert

Arctic

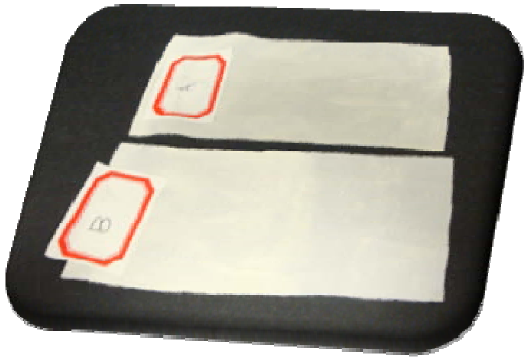
Tropic

InnoSense LLC

# Flame-Retardant Treatments for Textiles

## Features:

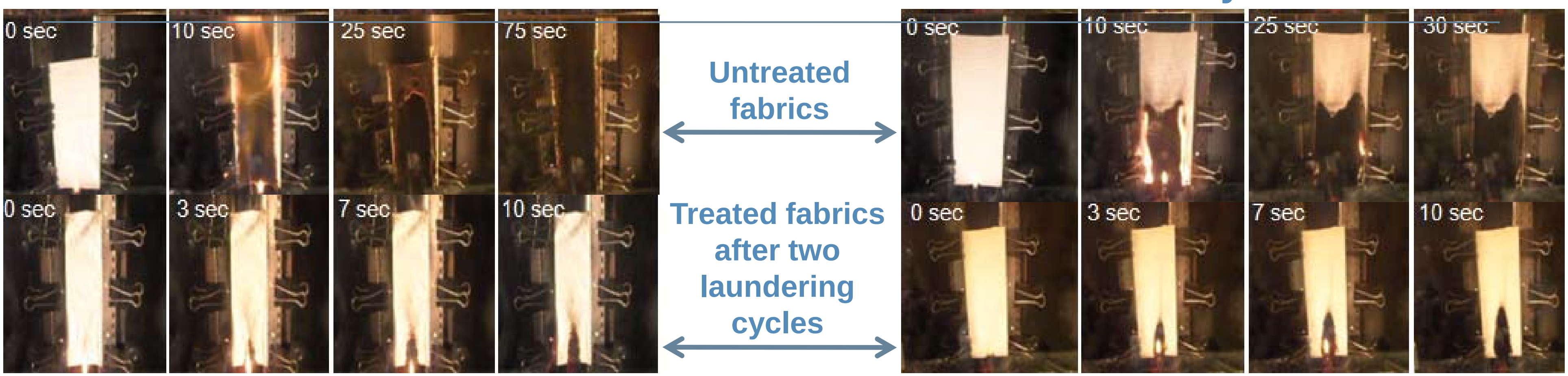
- Zero halogen content
- Phosphorus-based small-molecule and polymeric materials
- Protection offered by formation of insulating char layer
- Great process ability from solution
- Treatment durability ensured by covalent binding of flame retardant
- Applications in upholstery, bedding, protective wear, and structural components as coatings/composites



*Treated polyester fabrics maintain original color and flexibility*

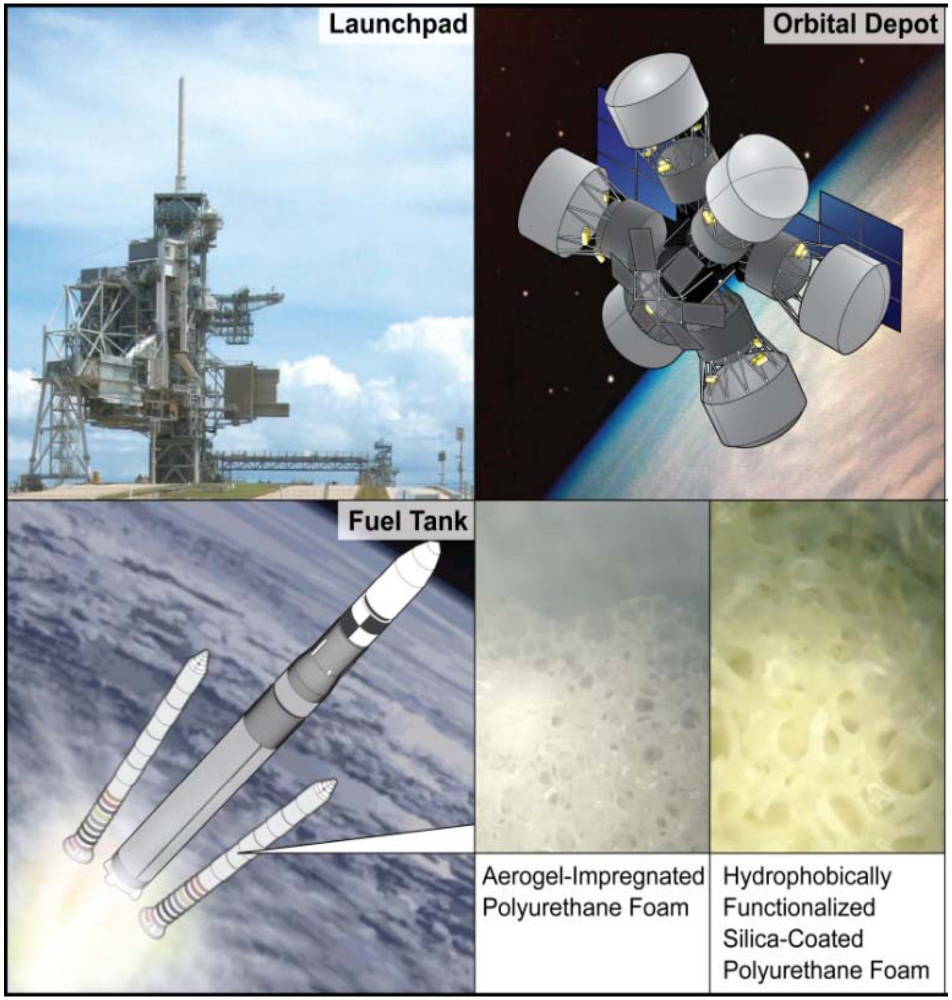
## Vertical Flame Propagation Studies in 34% Oxygen

**Cotton** **Polyester**




*Images shown at beginning of test (left), during test, and at time of ignition removal (10 sec) or end of fabric afterflame/afterglow (right).*

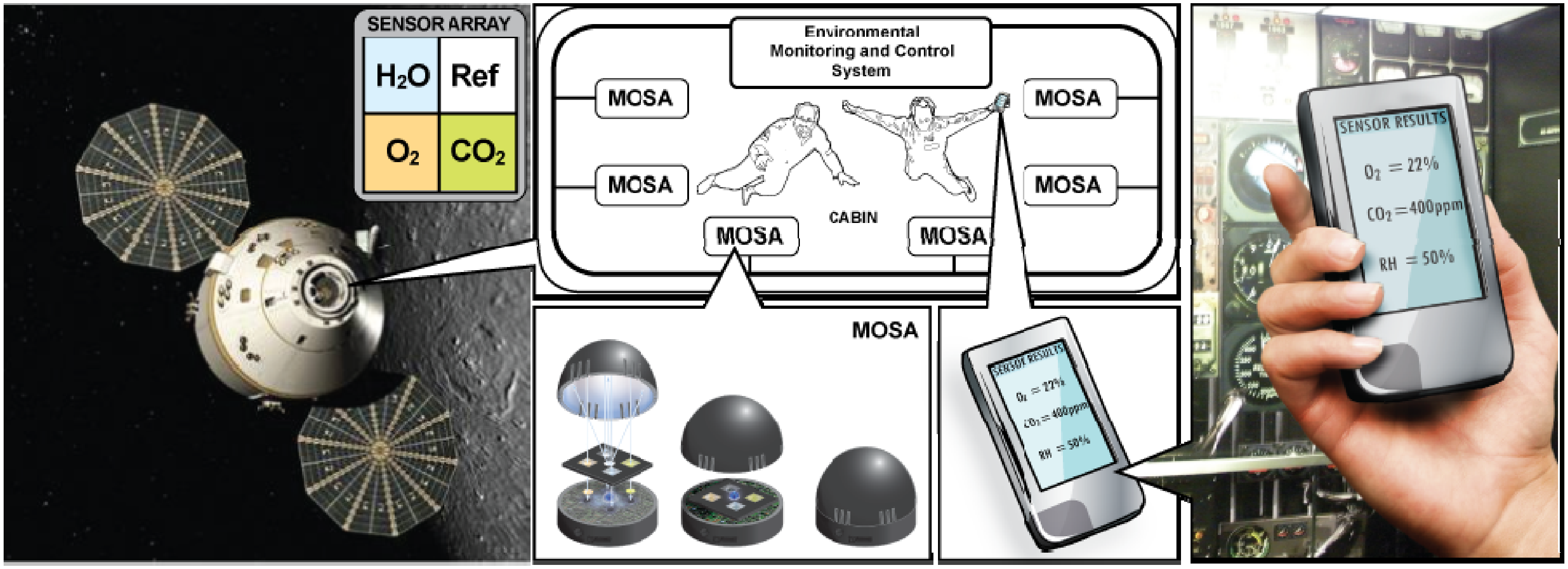
# CryoPore™ Insulation Foams




- Open cell structures suitable for a variety of applications and insulating environments.
- Hydrophobic surfaces reduce water uptake.
- Polymeric foam scaffold is configurable to a variety of mission needs.
- Compression resistant.
- Controlled porosity for tunable thermal insulation.
- Engineered for flexibility in terrestrial and space applications.

# Sensors

# Multi-Analyte Optical Sensor Array

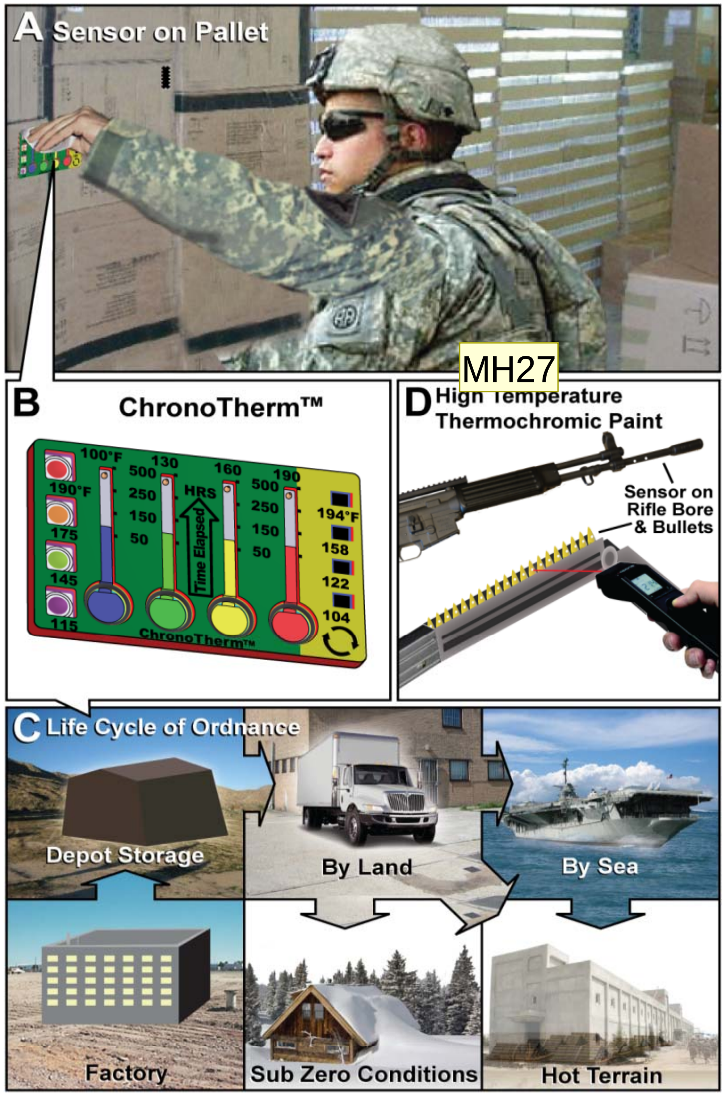



## Colorimetric and fluorescent indicators on a multi-analyte optical sensing platform

## Features/Benefits

- Versatility to customize sensors based on end use
- Reliable high-sensitivity sensors
- Lightweight, portable, and battery-powered
- Cost effective and user-friendly

# Colorimetric Temperature Dosimeter




## ChronoTherm™ time–temperature indicator

- Passive visual indicator with opto-electronic readout capability
- Reversible and irreversible records of thermal changes
- Temperature range 0–200°F for most applications
- Temperature-induced color changes
- No external power supply or batteries necessary

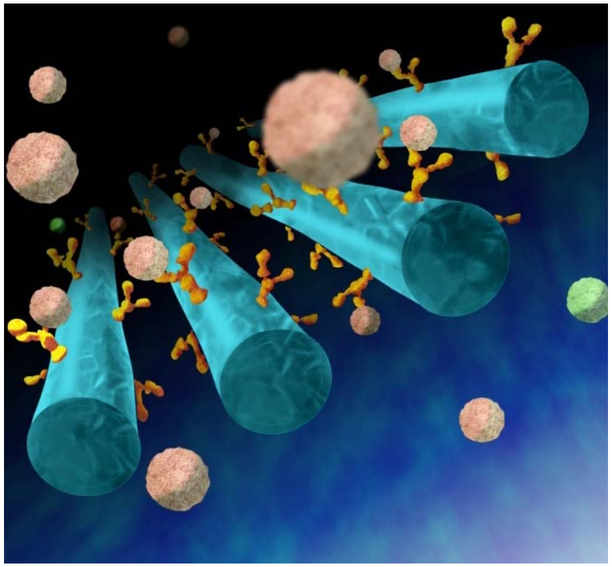
## Slide 13

**MH27** Add hyphen: High-Temperature
michael, 9/13/2010

# Nanowire-Based Chemical Sensors and Biosensors

## APPLICATIONS

- Diagnostics and prognostics
- Biotech and pharmaceutical
- Industrial process control
- Contamination detection and remediation
- Food and beverage quality/safety



## FEATURES

- Highly sensitive
- Array-formattable
- Samples analyzed within seconds to minutes
- Customizable for chemical and/or biological analytes
- Low power requirements and small size
- Cost-effective production

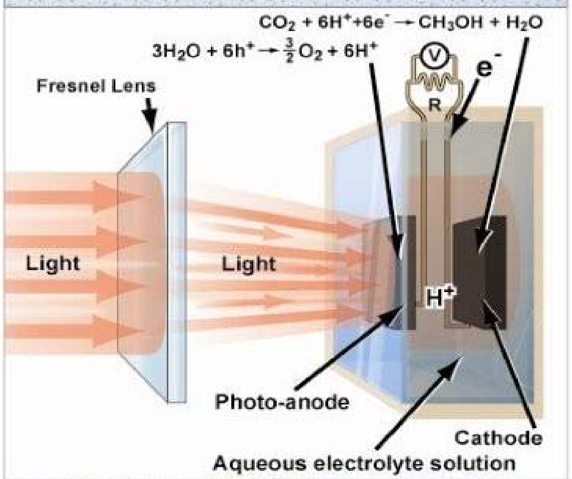
***ISL has successfully developed nanowire sensors for***

- ✓ Alzheimer’s Disease biomarkers
- ✓ Cancer-related biomarkers
- ✓ Carbon dioxide
- ✓ Chemical simulants

## Energy Conversion Devices

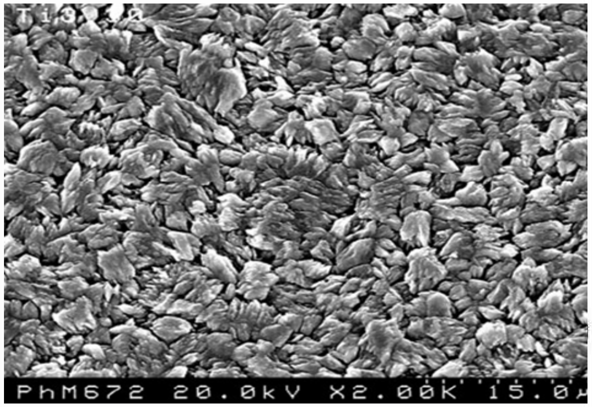
InnoSense LLC

# Direct Conversion of $CO_2$ to Methanol



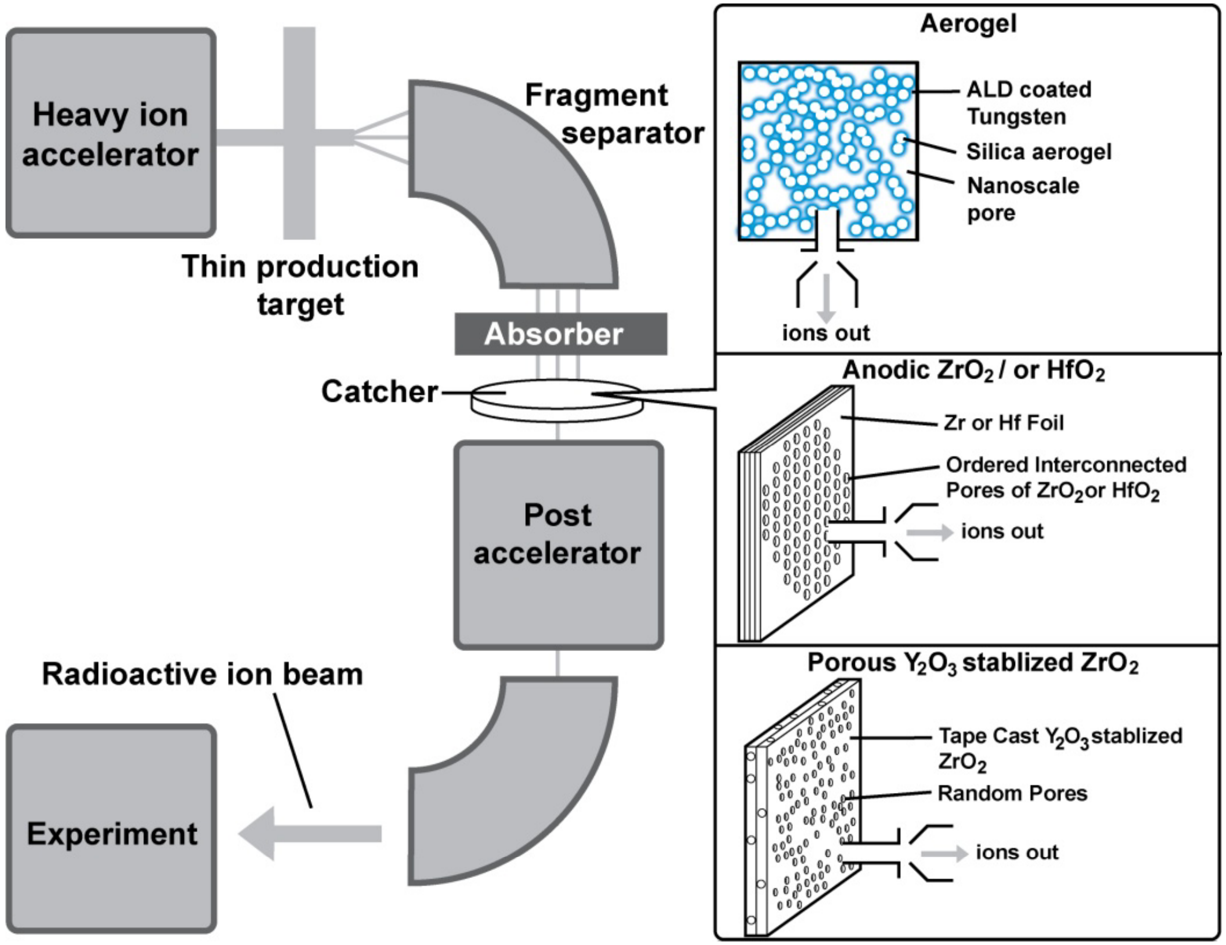

**Innovations**

- Inexpensive processing to lower electrode production costs.
- Modified titanium oxide surfaces broaden visible absorption for increased photoefficiency.
- Solar powered conversion of a green house gas to a useful end product.
- Sequestration technique for carbon dioxide capture.




# STTR Phase II Project Objective

**Optimize fabrication of refractory nanoscale materials (tungsten (W)-coated aerogels and refractory ceramic membranes) with a high degree of porosity to be used in catcher mode during radioisotope production.**



# Background on ISOL Target Materials

Isotope Separation On-Line (ISOL) used to generate radionuclides

Spallation of heavy targets by high-energy protons beams

- Target — Fast liberation of the radioactive nuclei in large amounts of target
- Combined with Ion Source — ion beam preferably of isotopes of only one chemical element
- Must be dense enough to stop energetic beam — porous enough to allow rapid diffusion of radionuclides to the accelerator source
- Targets heated to > 2000°C to increase diffusion rates

Currently used materials

- SPIRAL at GANIL, Caen, France —Solid graphite target and varying projectile (heavy ions)
- Refractory target materials like Ta or Nb foils or compressed powders of TiC, SiC
  - Diffusion time is limiting factor (sample thickness, grain size ~ 10–100 μm)
  - Release time from foils or powders scale as a square of the thickness or grain size
  - For $T_{1/2}$ of ~ 500 ms, diffusion losses can be high, aerogels could constitute a breakthrough
- HRIBF, RVC foam, 200 μm pores — 100 μm coating for useful target density
- CERN, Geneva, Anodic alumina membranes—Large number of stacked foils
- LBNL – SRI, Carbon aerogel coated in pores of RVC foam — pore size 20 nm

# Justification

- Meso- and macroporous catcher materials expected to have stopping power ~ 1000 times of He gas catcher
  - Longer ranged light isotopes and isotopes with relatively large energy spread
  - Essential for light ions like $^{11}Li$
  - Productive for $^{6,8}He$ which have zero efficiency in the He gas catcher

InnoSense LLC

# Phase II Technical Approach

**Three types of porous refractory catcher materials targeted**

1. **Nanoporous tungsten (W)-coated silica aerogels**
   - **Silica aerogel fabrication — InnoSense LLC**
   - **Atomic layer deposition (ALD) of W in the pores of the silica aerogels and their characterization — Energy Systems Division at Argonne**
2. **Nanoporous ordered zirconia and hafnia foils**
   - **Electrochemical anodization of Zr and Hf foils — InnoSense LLC**
3. **Macroporous random-porosity yttria-stabilized zirconia disks**
   - **Tape casting methods for mass fabrication — InnoSense LLC**

**Evaluation of porous refractory materials as potential catchers — Physics Division at Argonne**

- **High-temperature vacuum stability of porous refractory materials**
- **Thermal conductivity, porosity after high-temperature treatment**
- **Beam-line studies — SIRa, GANIL**

InnoSense LLC

# Phase II Target Performance Goals

- Targeted pore size of > 30 nm to 100 nm
- Silica aerogels
  - Density > 3 g/cc, open porosity; stable up to 2000°C
- Nanoporous ordered oxides of zirconia or hafnia
  - 50% of theoretical density, stable between 1500 and 2000°C
- Random-porosity yttria-stabilized zirconia
  - 50% of theoretical density, stable between 1500 and 2000°C
- Test catchers for online measurements of release times
  - Thickness of ~5 $g/cm^2$

# Benefits to the Nuclear Physics Program

InnoSense LLC

## Beneficial features of nanoporous refractory materials used in catcher mode

- Potential replacement of helium gas catcher for light ions like $^{11}Li$ that need more stopping power.
- Potential catchers for isotopes produced via heavy-ion fragmentation.
- In the catcher mode, thermal conductivity is less relevant since the beam power is deposited in the thermally separated production target irradiated with heavy ion beams.
- No radiation damage when used in catcher mode since only secondary radioisotope beams impinge on it.
- Potential targets for spallation induced by light ions in a standard ISOL-type facility.
- Extend the reach of all ISOL-based radioactive beam facilities to very short-lived isotopes by greatly reducing the release time of rare isotopes from solid target materials.

# The InnoSense–Argonne Project Team

- **Dr. Uma Sampathkumaran—**Principal Investigator, Technical Direction; Silica Aerogel Fabrication/Characterization
- **Dr. Thomas W. Owen—**Fabrication of Ordered Porous Zirconia and Hafnia Foils; Materials Characterization by SEM
- **Mr. Ray Winter—**Fabrication of Porous Refractory Yttria-Stabilized Zirconia by Tape Casting Methods
- **Mr. Mohammad Mushfiq—**Materials Processing and Optimization
- **Dr. Jeffrey Elam, Energy Systems Division, ANL—**Technical Direction for Atomic Layer Deposition (ALD) of tungsten (W) on silica aerogels
- **Dr. Anil Mane, Energy Systems Division, ANL—**W-ALD processing and characterization of W-coated silica aerogels
- **Dr. Jerry Nolen, Physics Division, ANL—**ANL Technical point of contact; Coordinate efforts to evaluate W-coated aerogels for beam-line isotope separation measurements
- **Mr. John Green, Physics Division**, **ANL—**Characterize thermal stability of W-coated aerogels in vacuum at high temperatures (1500–2000°C); thermal conductivity; porosity after high-temperature tests.

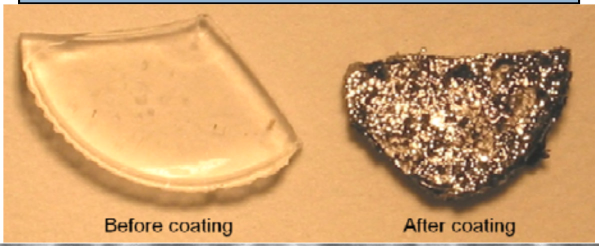
# Schedule and Deliverables

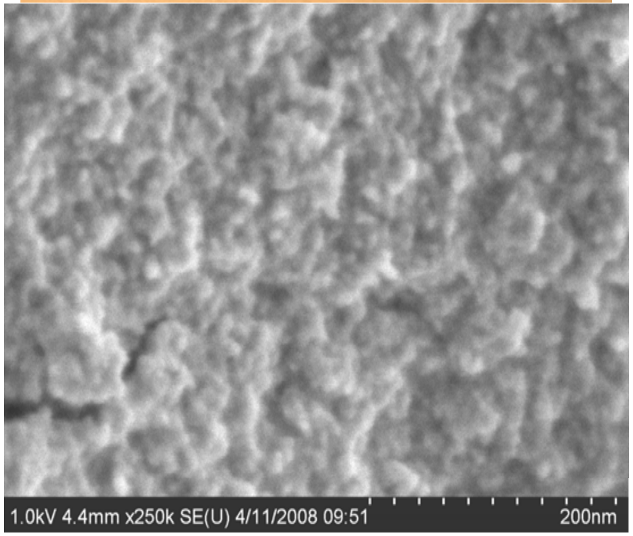
| Task ID/Description | | | Quarters after Project Initiation | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | Year 1 | | | | Year 2 | | | |
| | | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
| 3000 | Major Phase II Tasks | | | | | | | | | |
| | Task 1. Refine aerogel and ALD processes to optimize catcher properties | | | | | | | | | |
| | Task 2. Develop nanoporous refractory oxides by anodization and tape casting | | | | | | | | | |
| | Task 3. Evaluate the thermal stability and thermal conductivity of the porous catchers when heated to ~2000°C | | | | | | | | | |
| | Task 4. Evaluate prescreened test samples in the GANIL beam line | | | | | | | | | |
| | Task 5. Evaluate Phase III commercialization potential | | | | | | | | | |
| | Milestones | | | | | | | | | |
| | 1. Optimized nanoporous refractory materials developed. | | | | | | | ❶ | | |
| | 2. High-temperature evaluation of porous catchers completed. | | | | | | | | | |
| | 3. Nanoporous refractory catchers evaluated in beam line. | | | | | | | | | |
| | 4. Phase II engineering project successfully implemented. | | | | | | | | | |
| 4000 | Data/Deliverables | | | | | | | | | |
| | Annual progress reports | | | | | ♦ | | | | |
| | Final Report | | | | | | | | | |

InnoSense LLC

# Phase I - Tungsten-Coated Aerogels

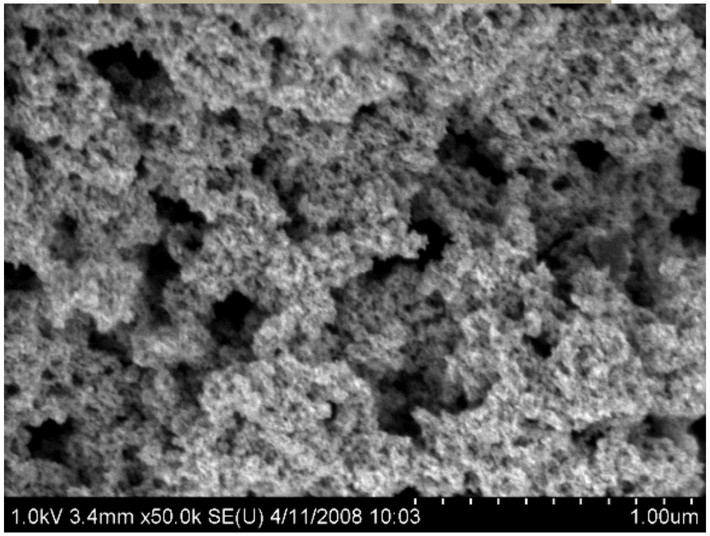
## Silica Aerogels




- Closed pores after ALD
- Pore size < 20 nm
- Density after W-ALD ~3.52 g/cc

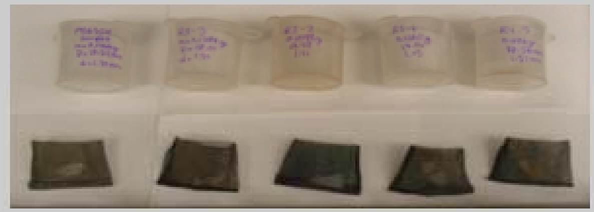
## Silica-Polymer Aerogel




- Open pores after ALD
- Pore size 10 – 1000 nm
- Density after W-ALD ~2 g/cc
- Open pores after 1300°C

InnoSense LLC

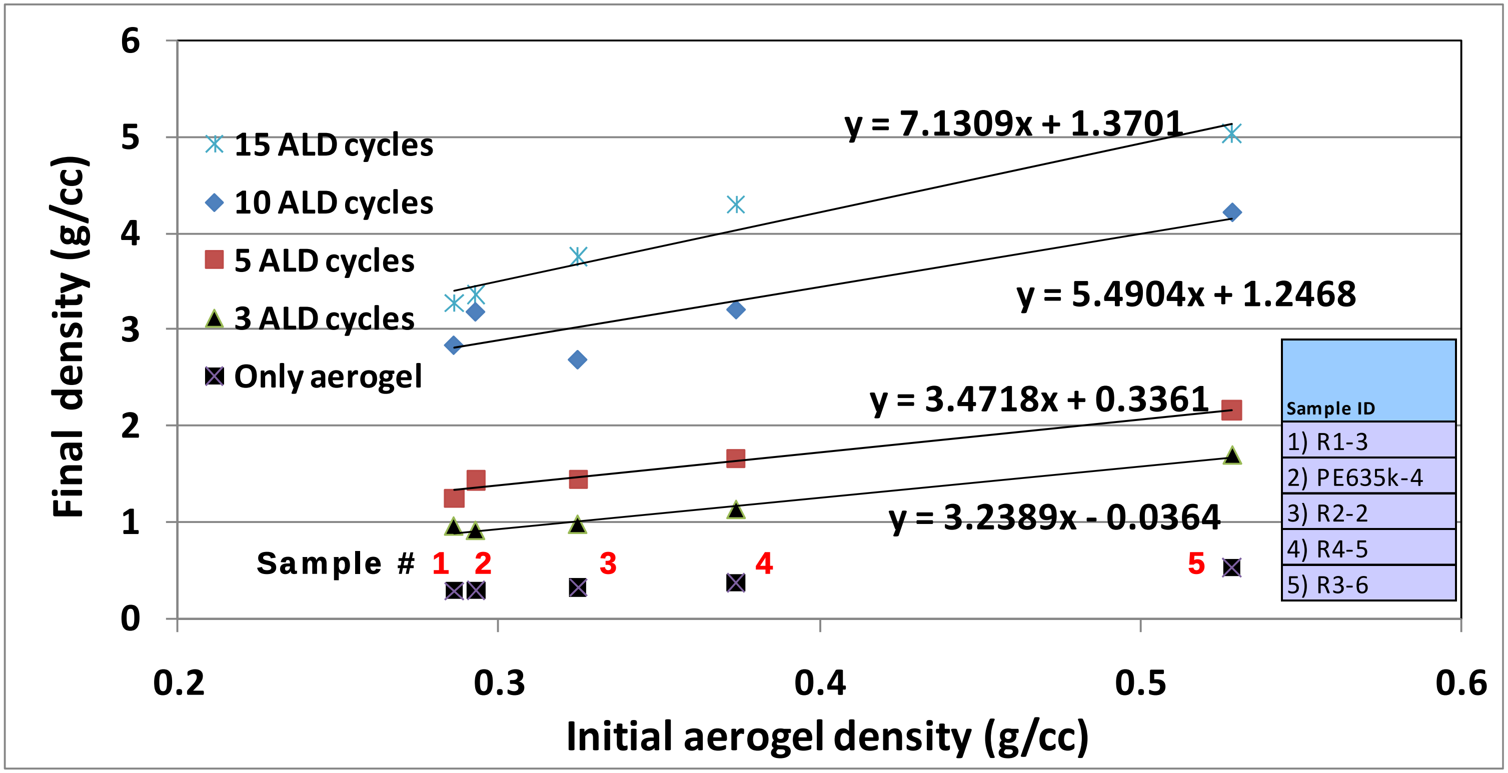
# Phase II - Aerogels Before and After W-ALD

| WALD cycles | Before Coating | After W Coating |
|---|---|---|
| 3 |  |  |
| 5 |  |  |
| 10 |  |  |
| 15 |  |  |

- **All aerogels were intact after W deposition**

InnoSense LLC

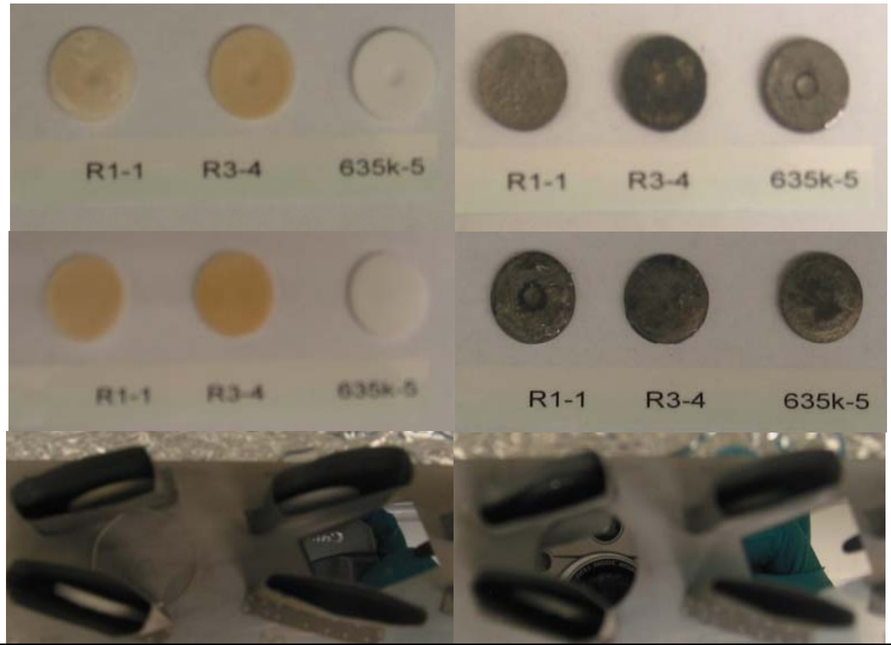
# Aerogel Density: Initial vs. Final Density




- Fractured disks of silica aerogels coated by W-ALD
- Significant density change after W deposition for all aerogels
- With 15 ALD-W cycle we can achieve target density of aerogel as high as **5 g/cc**
- Initial aerogel density influences final aerogel density

InnoSense LLC

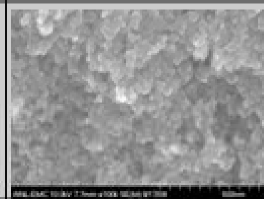
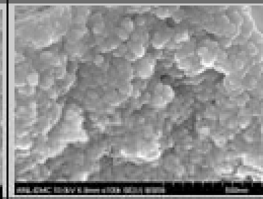
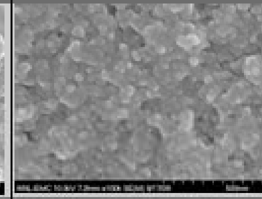
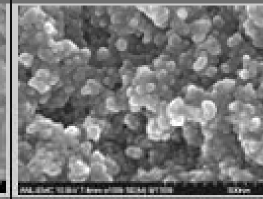
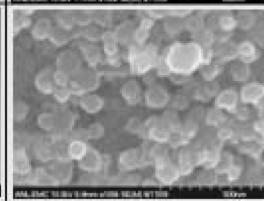
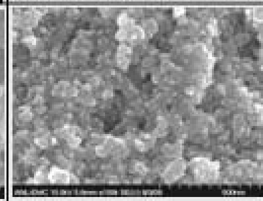
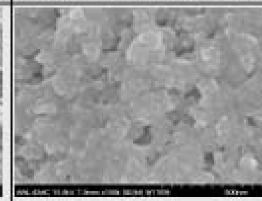
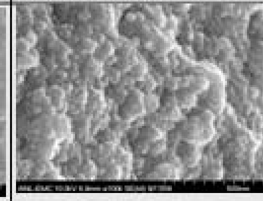
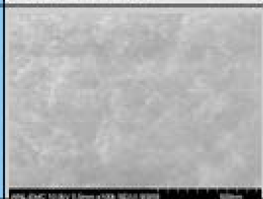
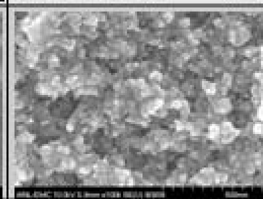
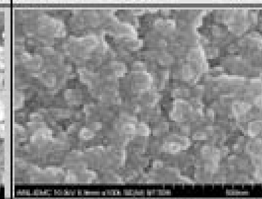
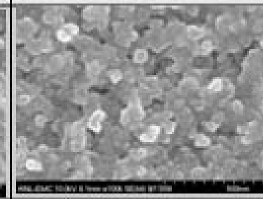
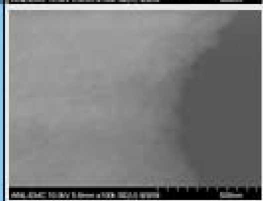
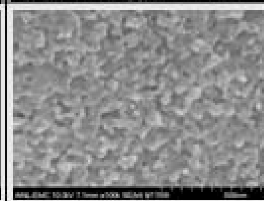
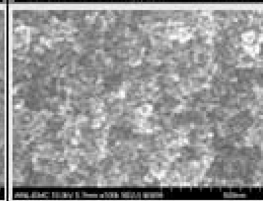
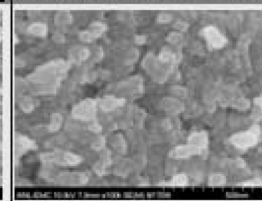
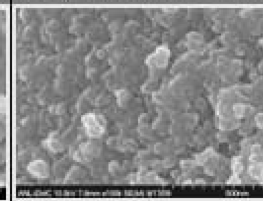
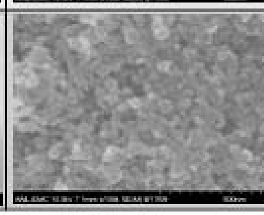
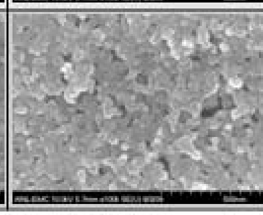
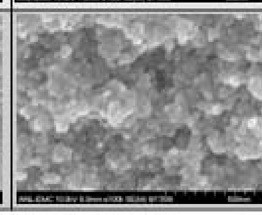
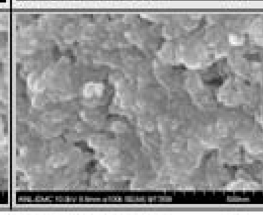
# Tungsten-Coated Monolithic Aerogels



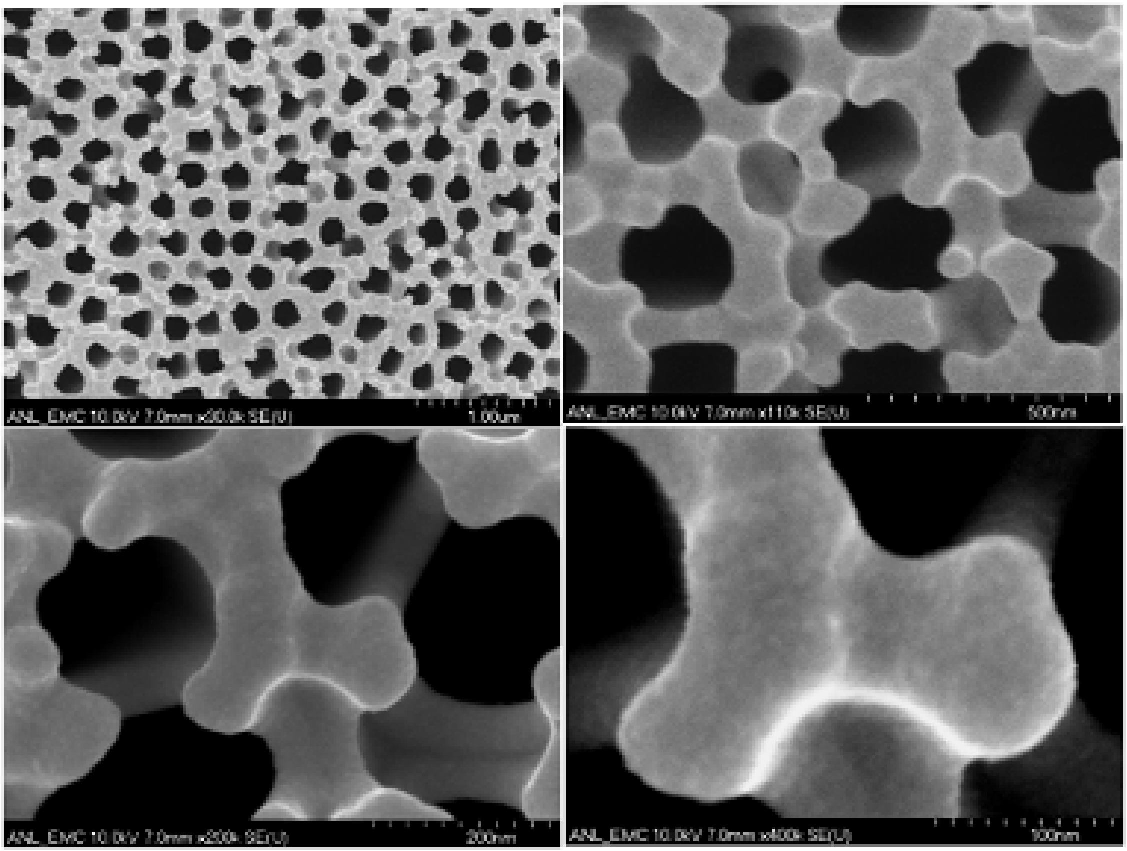

| Sample ID | Mass of disc | Initial density of aerogel (g/cc) | Comments | Final Density of (W + aerogel) (g/cc) |
|---|---|---|---|---|
| R1-1 | 0.1398 | 0.2890 | Low density, surfactant | 1.2010 |
| R3-4 | 0.1238 | 0.5173 | high density, surfactant | 2.3131 |
| PE635-5 | 0.1598 | 0.3192 | Low density, No surfactant | 1.7270 |

- **Lower density for W-coated monolithic aerogel ~2.3/g/cc**

# Overall Aerogels Summary (SEM Magnification 100k)

| Sample ID | As received | 3 W-ALD cycles | 5 W-ALD cycles | 10 W-ALD cycles | 15 W-ALD cycles | Comments |
|---|---|---|---|---|---|---|
| PE635k-4 |  |  |  |  |  | •Increase in feature size<br>•Aerogel getting denser |
| R1-3 |  |  |  |  |  | •Increase in feature size<br>•Aerogel getting denser |
| R2-2 |  |  |  |  |  | •Increase in feature size<br>•Aerogel getting denser |
| R3-6 |  |  |  |  |  | •Increase in feature size<br>•Aerogel getting denser |
| R4-5 |  |  |  |  |  | •Increase in feature size<br>•Aerogel getting denser |

# ALD-W on Anodic alumina membranes

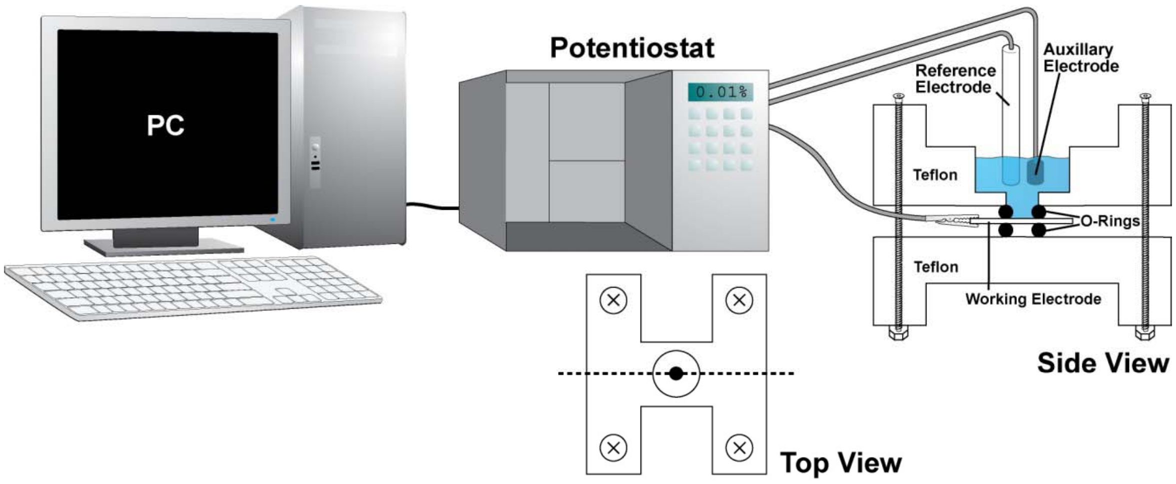



- 60 microns thick
- 0.2 microns pore size
- 13 mm diameter
- 25 nm W coating
- Density 3.32 g/cc

Challenges

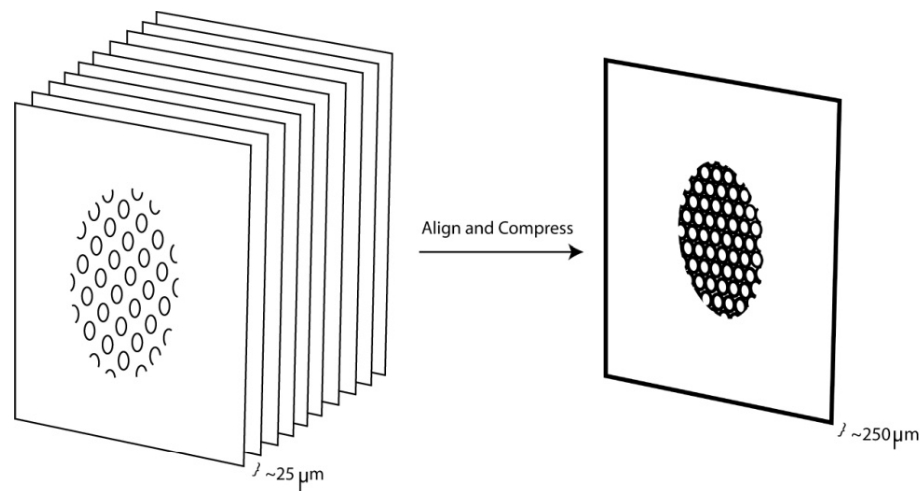
- Very fragile
- Bowing of membranes
- Cracking/shattering during cool down
- Pre-annealing $Al_2O_3$ @ 800C in Ar prevents this

# Ordered Porous Materials

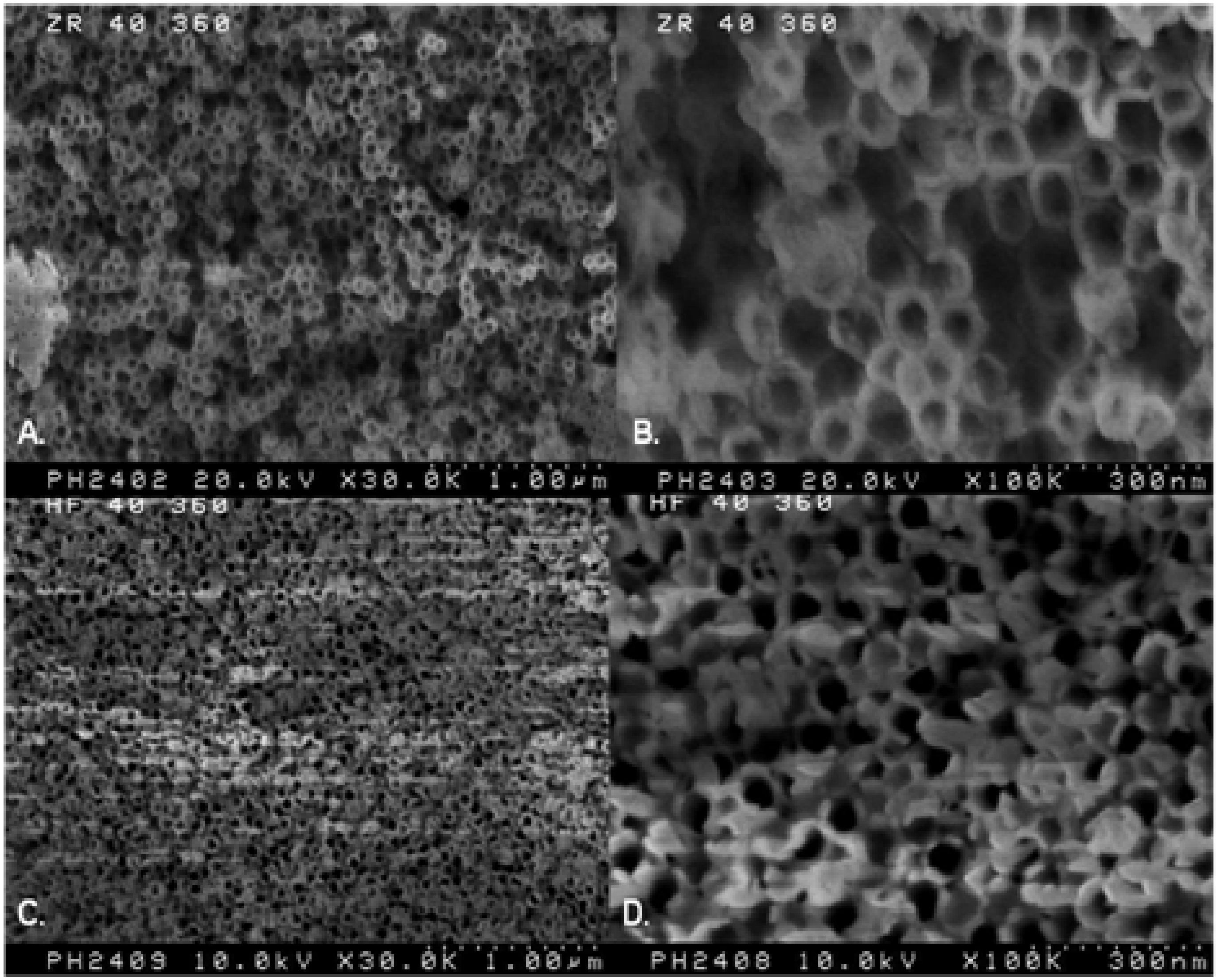



**Anodization setup**

**Stacking of anodized foils**



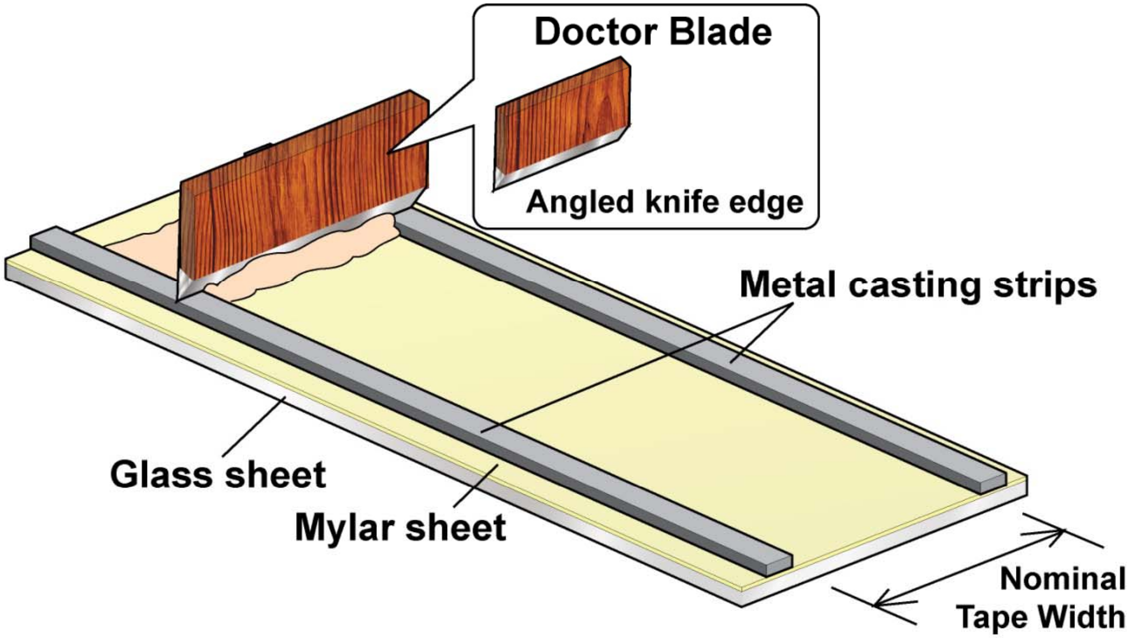
# Electrochemical Anodization of Zirconium and Hafnium Foils




**$ZrO_2$**
- **250 μm foils**
- **Ordered pores**
- **Size: 30–60 nm**

**$HfO_2$**
- **250 μm foils**
- **Ordered pores**
- **Size: 30–90 nm**

# Random Porous Materials




Tape Cast

↓

Laminate

↓

Die Punch

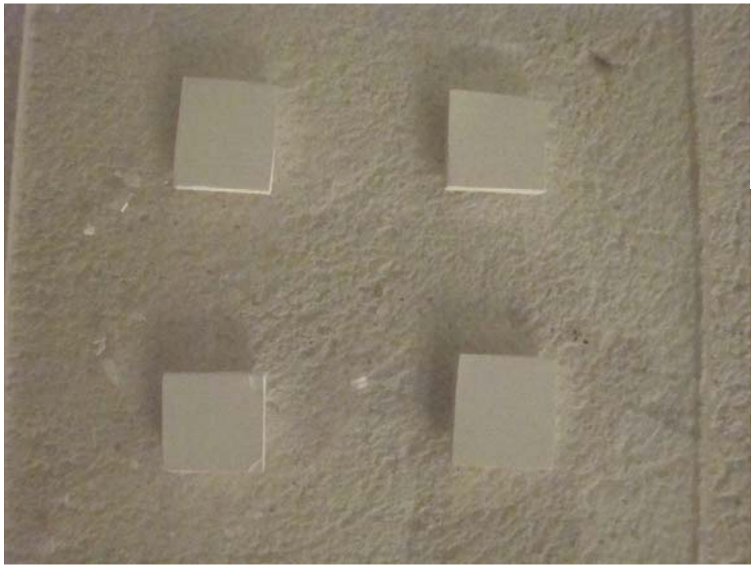
↓

Calcine

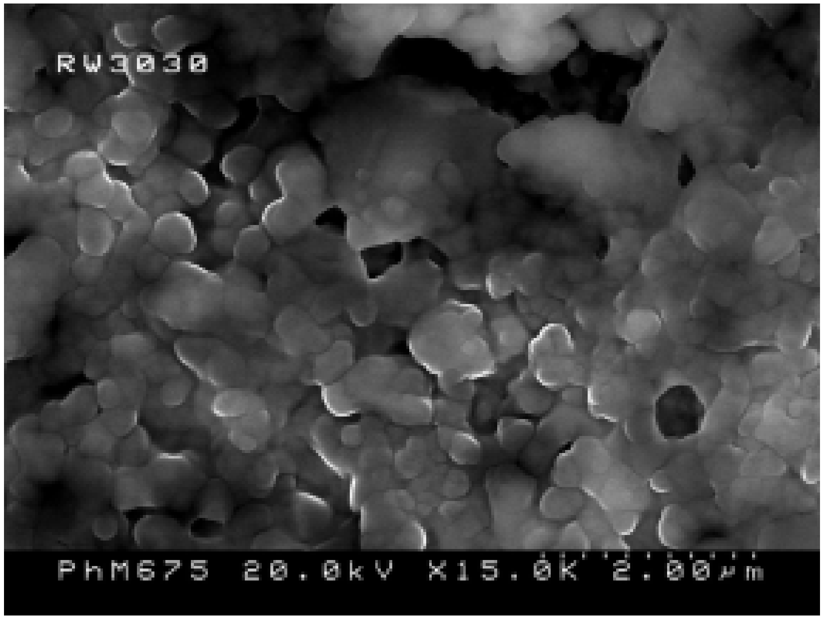
↓

Random Porous Catcher

# Random Porous Tape Cast Monoliths



- Tape cast laminated monoliths
  - Green density ~2.76 g/cc
  - Fired density ~2.22 g/cc
  - Estimated porosity ~63%




- SEM of hot-pressed monolith
  - Pore size ~0.4–4 μm
  - Particle size ~0.2–0.6 μm

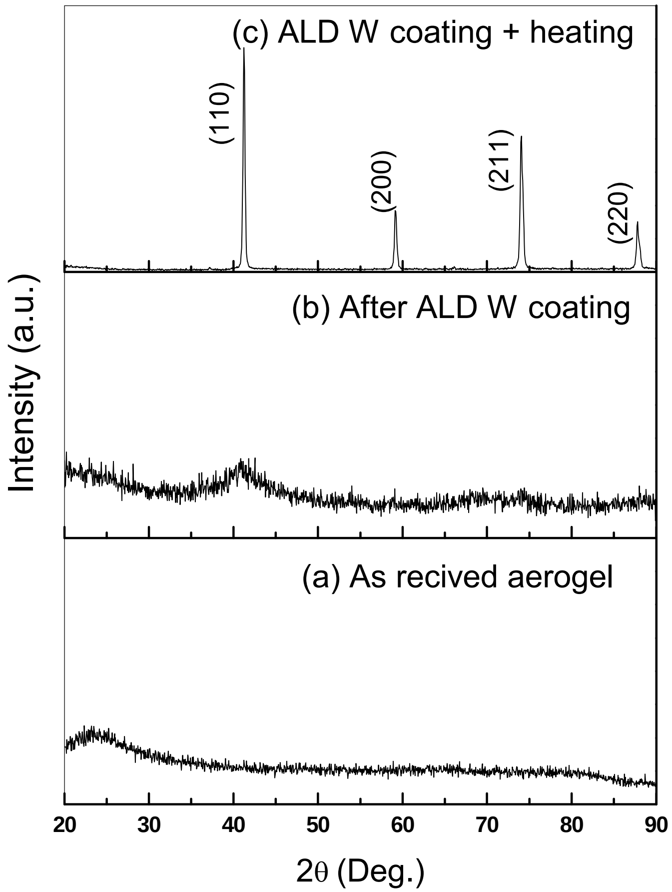
InnoSense LLC

# High-Temperature Performance of Aerogels

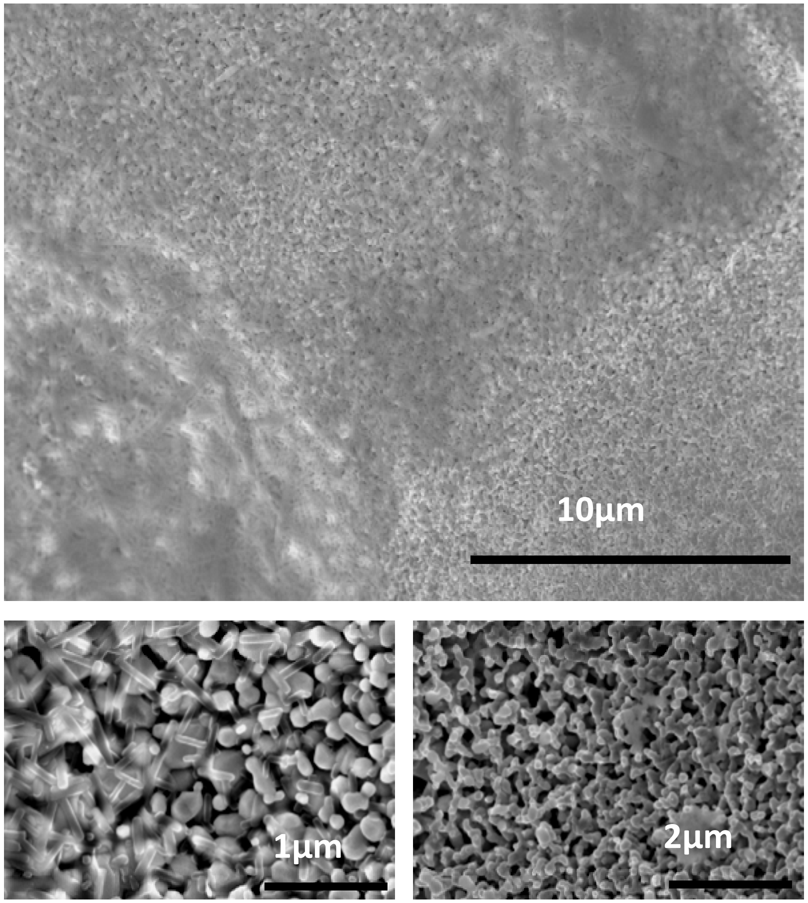
- Phase I - W-coated silica aerogels demonstrated stability up to 1300°C in vacuum
  - Heated in a bell jar
  - Out gassing at 400°C and 1100°C
  - Retained open porosity
  - Remained intact
- Phase II – Monoliths of W-coated silica aerogels
  - Heated to 1500°C
  - Some out gassing below 1500°C.
  - Remained intact
  - Weight loss equal to weight of original aerogel
  - SEM shows crystalline material
  - XRD indicates bcc W
  - Custom tantalum boats for heating to higher temperatures (1800-2000°C) required

# High-Temperature Performance of Aerogels

## XRD




## SEM after 1500°C



InnoSense LLC

# Summary / Future work

- W-coated silica aerogels – **5 g/cc and 2.3 g/cc**
  - Use supercritical $CO_2$ extraction to process aerogels for open surface pores to improve density of monoliths
- W-coated anodic alumina membranes ~ **3.3 g/cc**
  - Several hundreds of W-coated membranes stacked to achieve desired density
- Hafnia or Zirconia membranes **~ 60% porosity**
  - Same as above, fragile
- Tape cast disks ~ **65% porosity**
  - Open porosity at high temperature yet to be established
- High temperature stability tests at 1800-2000°C pending
- Beam line tests pending

InnoSense LLC

# Acknowledgments


- Program Officer: Dr. Manouchehr Farkhondeh
- Department of Energy for sponsoring this Phase II work and the new Phase I on Carbon aerogels