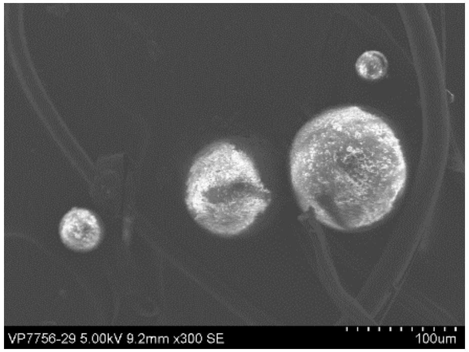
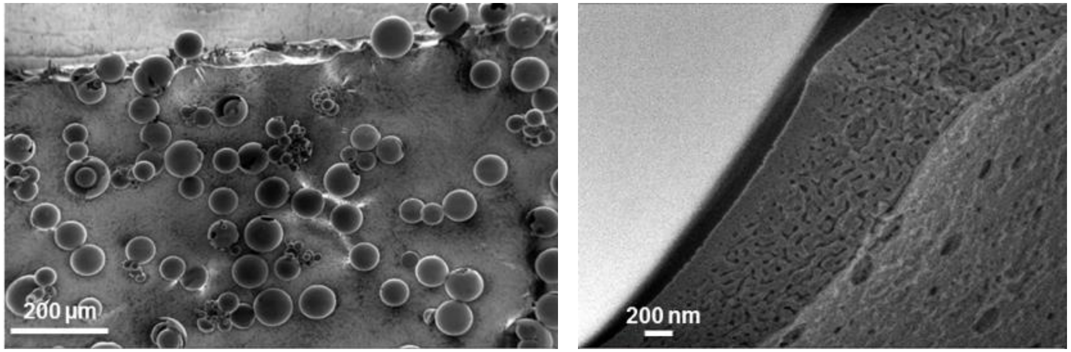
Evacuated Spheres for Closed-Cell Vacuum Insulation Systems

Polymeric Vacuum Insulation Spheres



Coated and Evacuated Insulation Spheres



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Project Summary

Timeline:

Polymeric vacuum insulation spheres

Start date: 10/1/17

Planned end date: 9/30/19

Key Milestones

1. Reduced thermal conductivity of base polymer by ≥10% by blending it w/ additives; 6/30/19
2. Produced 100 µm spheres with ≥70% void fraction using polymer w/ additives; 9/30/19

Coated and evacuated insulation spheres

Start date: 10/1/18

Planned end date: 9/30/19

Key Milestones

1. Demonstrated uniform thickness and defect-free coverage of coatings on prototype hollow spheres; 3/31/19
2. Coated and hollow spheres with demonstrated internal vacuum; 9/30/19

Budget:

Total Project $ to Date:

- DOE: $750K
- Cost Share: $0K

Total Project $:

- DOE: $750K
- Cost Share: $0K

Key Partners:

Partners will be formalized after we have proven that we can retain vacuum in the spheres. Potential future partners include:

AkzoNobel mo•sci ORCA

Project Outcome:

Develop an insulation material that has an R-value ≥ 14/in, can be manufactured cost-effectively at large scale, and is more practical for building construction than vacuum insulation panels.

Team

Polymeric Vacuum Insulation Spheres

Polymer synthesis → Sphere manufacturing → Material characterization & integration


Tomonori Saito, PhD


Bingrui Li


James Klett, PhD


Tristan Alexander


Diana Hun, PhD


Som Shrestha, PhD


Kaushik Biswas, PhD

Coated and Evacuated Insulation Spheres

Sphere evacuation & coating → Material characterization & integration


Tolga Aytug, PhD


Kai Li, PhD


Kaushik Biswas, PhD


Diana Hun, PhD

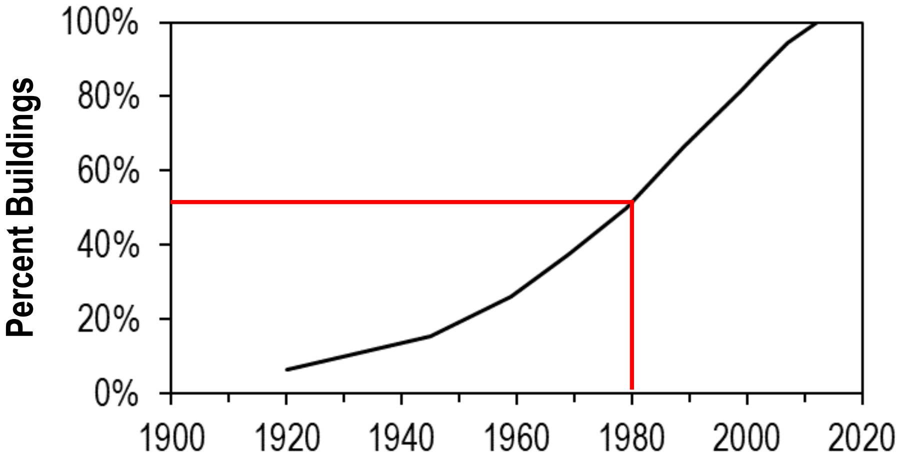
Team expertise

- Building envelopes
- Insulation materials
- Heat transport
- Polymeric chemistry
- Polymer processing
- Organic/inorganic thin film coatings

Challenge

- About 50% of existing residential and commercial buildings lack or have minimal insulation as they were built before energy codes
- The technical potential from adding 2 in. of R12/in. insulation to existing residential and commercial walls is 1.1 quads of energy by 2030*
- DOE's Building Technologies Office is seeking for cost-effective insulation materials with R-value ≥14/in. that are suitable for envelope retrofits and more practical for building construction than vacuum insulation panels.

Year of Construction of Commercial Buildings



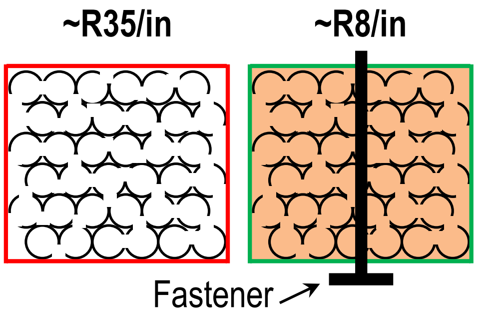
2012 Commercial Buildings Energy Consumption Survey

*2014 DOE Windows and Building Envelope Roadmap

Approach & Impact

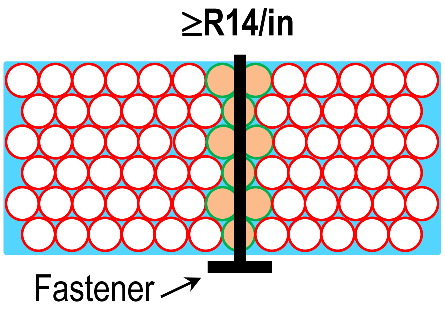
- Vacuum insulated panels (~R35/in)
  - Open-cell vacuum insulation
  - Damages diminish R-value by factor ~4
  - Not widely used in buildings
- Evacuated spheres (≥R14/in)
  - Closed-cell vacuum insulation
  - Minimal decrease in thermal performance after localized damage
  - Assembled into a board w/ binder (binder's thermal conductivity ~0.024 W/m·K)
  - Board can be cut as needed
- Proposed approaches
  - Polymeric vacuum insulation spheres (PVIS)
  - Coated and evacuated insulation spheres (CEIS)

State-of-the-art Vacuum insulation panels



○ Evacuated open cell
🟥 Air/vapor barrier
🟩 Damaged barrier
● Pores at ambient pressure

Evacuated spheres with binder



○ Evacuated hollow sphere
🟥 Spherical air/vapor barrier
🟩 Damaged barrier
● Sphere at ambient pressure
🟦 Binder

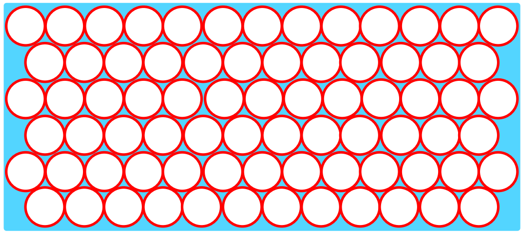
Main Parameters

- Void fraction
- Thermal conductivity of gas in spheres
  - Sphere diameter
  - Amount of air within sphere → pressure
  - Thermal conductivity of air in 100 μm sphere

Inside pressure (mbar)	Thermal conductivity of air inside sphere (W/m·K)
1.0	~0.013
0.1	~0.0025
0.01	~0.0005

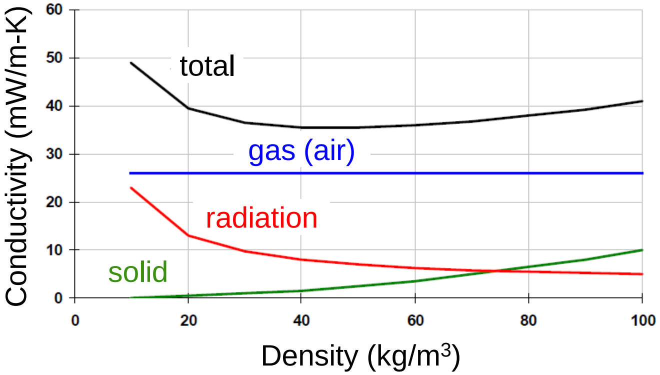
- Gas permeability of shell
- Thermal conductivity & shell thickness
- Thermal conductivity of binder

Evacuated Spheres with Binder

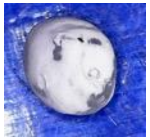


○ Evacuated hollow sphere
— Spherical air/vapor barrier
🟦 Binder

Heat Conductivity Contribution in Conventional Insulation Materials



Polymeric Vacuum Insulation Spheres: Methodology

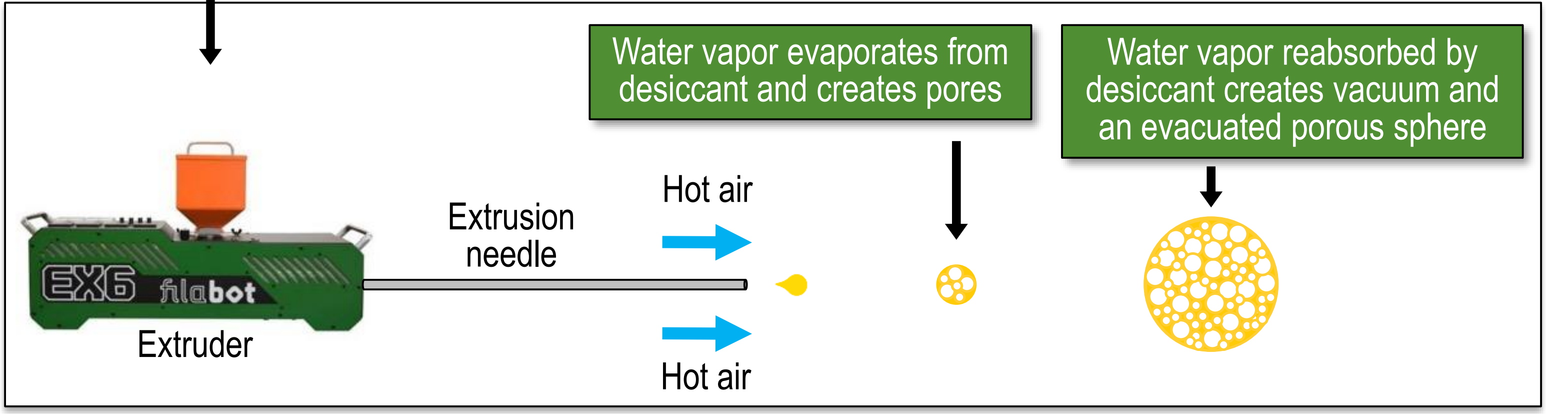


Polymer coated with desiccant particles saturated w/ water

\+

Additives to reduce polymer thermal conductivity and gas permeability

Option 1: Air assisted method



Water vapor evaporates from desiccant and creates pores

Water vapor reabsorbed by desiccant creates vacuum and an evacuated porous sphere

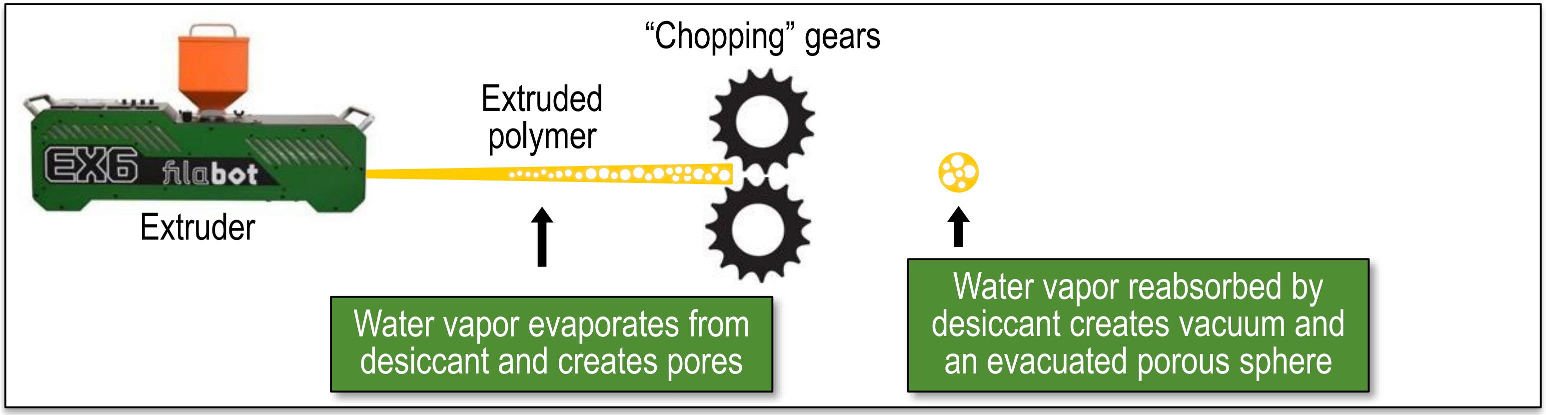
Extrusion needle

Hot air

Hot air

Extruder

Option 2: Mechanical chopping



“Chopping” gears

Extruded polymer

Extruder

Water vapor evaporates from desiccant and creates pores

Water vapor reabsorbed by desiccant creates vacuum and an evacuated porous sphere

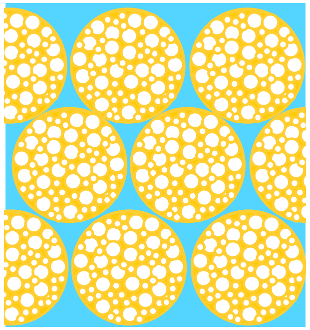
PVIS: Targets

Targets derived using equations from the literature

Parameters	FY19	Targets to achieve PVIS board w/ R-value ≥14/in
Sphere diameter (μm)	≤ 350	~200
Void fraction within sphere (%)	≥ 70	≥ 90
Void fraction within binder (%)	-	≥ 70
Pore diameter (μm)	≤ 50	10 – 20
Pressure inside pore (mbar)	≤ 100	0.1 – 1
Polymer thermal conductivity (W/m·K)	≤ 0.15	≤ 0.1
Polymer oxygen transmission rate (cm^3/m^2-day)	0.04	~0.005
Shell thickness (μm)	≤ 5	1 – 2
R-value/in without binder	≥ 5	≥ 22
R-value/in with binder*	-	≥ 14

*R-value of binder assumed to be ~6/in.

Evacuated Porous Spheres



🟨 Polymer

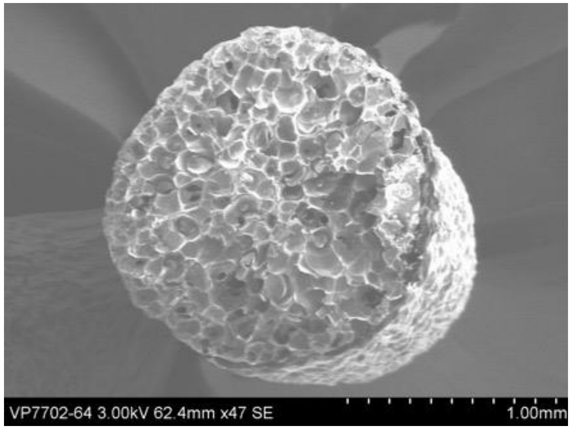
○ Evacuated pore

🟦 Binder

PVIS: Material Selection

- Polymers
  - Criteria: low cost, low thermal conductivity, modulus of elasticity ≥1.5GPa
  - Selected poly(methyl methacrylate) (PMMA) and polystyrene (PS)
  - Flammability significantly decreased with additives
- Desiccants
  - Evaluating different types of zeolites
  - Critical parameters: water saturation capacity, immiscible with polymer, loading ratio
- Inorganic additives to lower thermal conductivity and gas permeability
  - Critical parameters: miscibility with polymer, loading ratio, extrudability
  - Evaluating 200 - 300 nm nanoclay particles

SEM of Cross-Section of Extruded Polymer w/ Blowing Agent



- PMMA w/ 10 wt% water-saturated zeolite 3A
- ≥70% void fraction

PVIS: PMMA + Nanoclay Particles

- Thermal conductivity (TC) of polymer
  - PMMA baseline TC = 0.14 W/m·K
  - With 20 wt% nanoclay TC = 0.12 W/m·K
  - Target ≤ 0.1 W/m·K

~4.5 × ~4.5 × ~0.37
PMMA baseline

~4.5 × ~5 × ~0.33
PMMA w/ 20 wt% nanoclay

- Oxygen transmission rate (OTR) of polymer at 23°C and 50% RH
  - PMMA baseline (t ≅ 400 μm) = 298 cm^3/m^2-day
  - With 10 wt% nanoclay (t ≅ 400 μm) = 174 cm^3/m^2-day → 42% decrease
  - With 20 wt% nanoclay (t ≅ 400 μm) = 143 cm^3/m^2-day → 52% decrease
  - Target ≤ 0.005 cm^3/m^2-day (Guin et al. (2014) achieved this permeability w/ 4.3 μm-thick film of PET w/ 87 wt% nanoclay at 23°C and 0% RH)

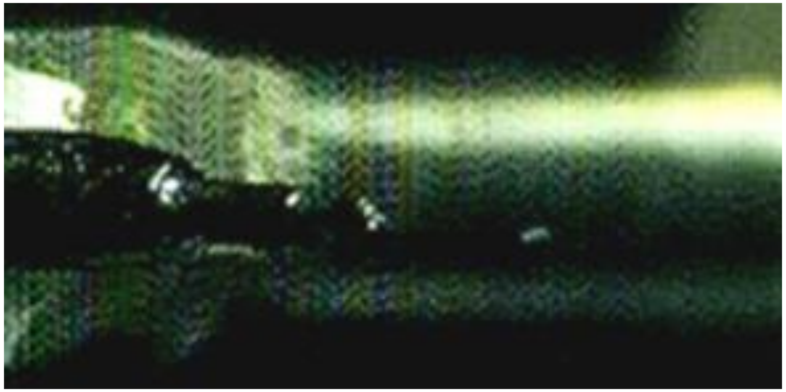
Non-optimized nanoclay layout

- Next steps
  - Increase nanoclay loading
  - Evaluate extrudability, TC and OTR
  - Study alternate method to decrease permeability: co-extrusion of coating

PVIS: Air Assisted Method

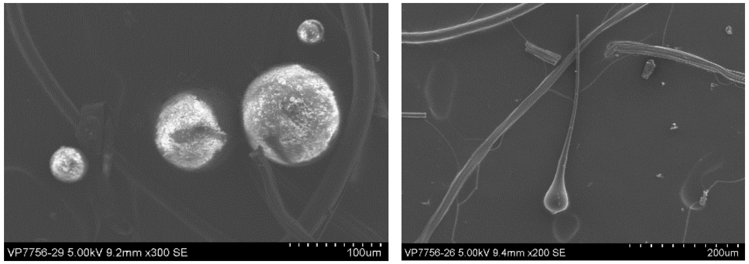
- Key parameters being evaluated
  - Extrusion temperature, speed and nozzle diameter
  - Air temperature and flow rate
  - Polymer type and nanoclay loading
  - Desiccant type, loading, and water content
- Method produces spheres but repeatability is difficult at non-optimized lab setting
  - Bench-scale proof of concept
  - Industry partner to optimize manufacturing procedure after it has been demonstrated that PVIS can attain ≥R14/in

High Throughput Rate Potential



SEM of Extruded Parts

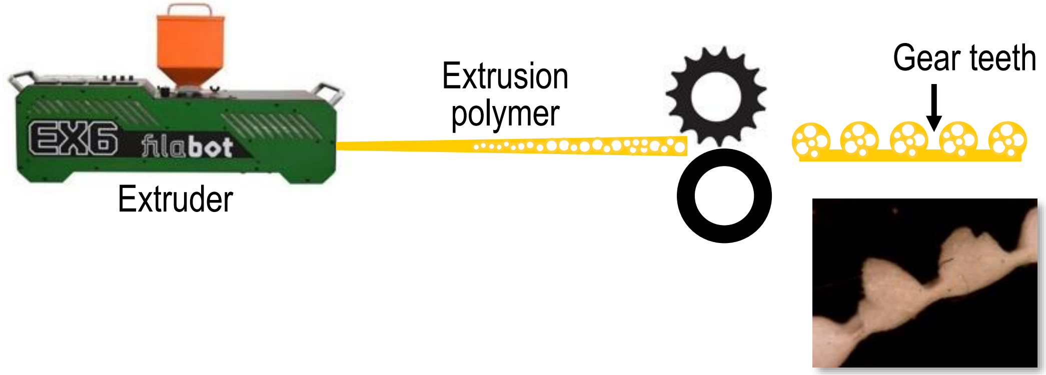
PMMA w/ 5 wt% zeolite 3A



Air temperature and flow rate highly influence the shape of the extruded part

PVIS: Mechanical Chopping Method

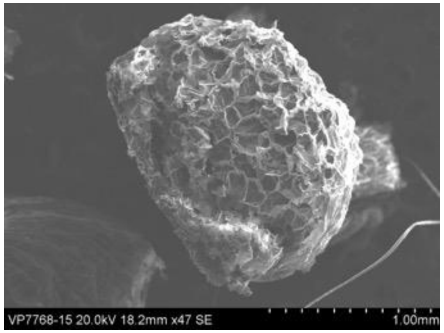
- Key parameters being evaluated
  - Most variables shown in slide 11
  - “Chopping” gear teeth size and speed
- First prototype → single “chopping” gear



See video on the right for production speed

- Next prototype: use precision machining to manufacture double “chopping” gears

SEM of Cross-Section of Extruded Part w/ Blowing Agent



- 1.2 mm diameter
  - Reduce by tailoring gear teeth size
- Void fraction > 50%

Video of High Throughput Rate Potential

PVIS: Remaining Work

- FY19
  - Measure pressure inside spheres
  - Refine steps to lower permeability of polymer
- FY20 and FY21 (PVIS only funded for FY19)
  - Feasible path to attain ≥R14/in based on results from FY19

Parameters	FY19	FY20	FY21: Target to achieve PVIS board w/ R-value ≥14/in*
Sphere diameter (µm)	≤ 350	≤ 300	200
Void fraction within sphere (%)	≥ 70	≥ 90	≥ 90
Void fraction within binder (%)	-	-	≥ 70
Pore diameter (µm)	≤ 50	≤ 30	10 – 20
Pressure inside pore (mbar)	≤ 100	≤ 10	0.1 – 1
Polymer thermal conductivity (W/m·K)	≤ 0.15	≤ 0.12	≤ 0.1
Polymer OTR (cm^3/m^2-day)	0.04	0.02	~0.005
Shell thickness (µm)	≤ 5	2 – 5	1 – 2
R-value/in without binder	≥ 5	≥ 10	≥ 22
R-value/in with binder*	-	-	≥ 14

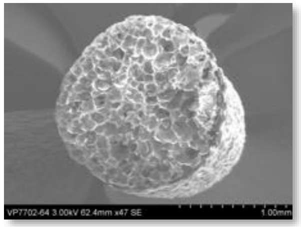
*Targets derived using equations from the literature

**R-value of binder assumed to be 6/in.

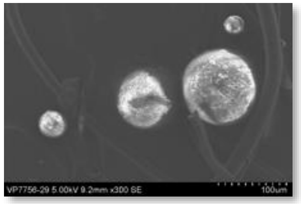
OTR: oxygen transmission rate

Example of progress to date

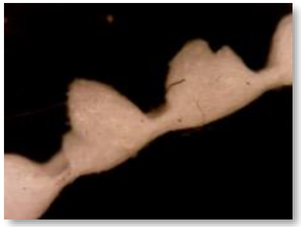
Decreased polymer thermal conductivity by 14%



Extruded part w/ ≥ 70% porosity



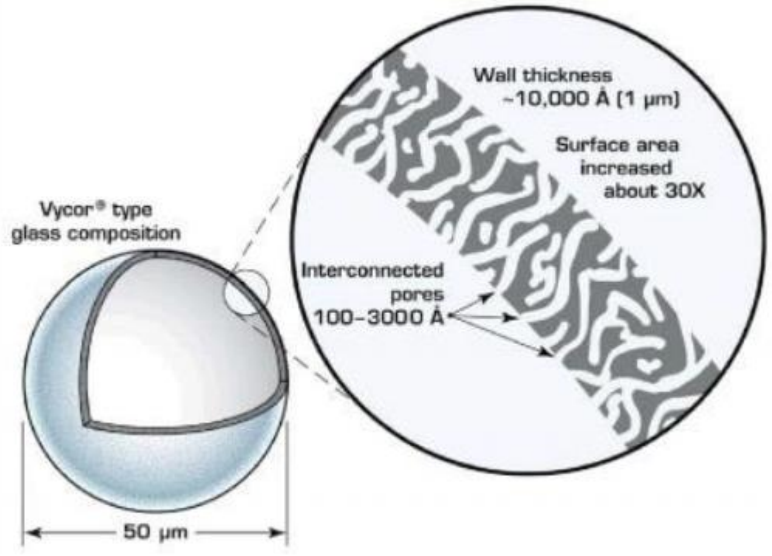
Extruded spheres w/ ≤ 350 µm diameter



Identified more robust manufacturing method w/ high throughput rate

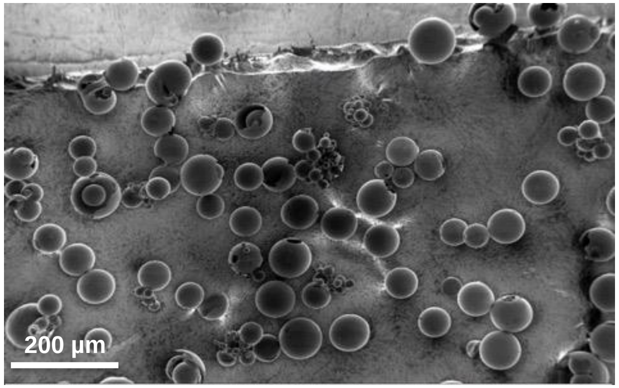
Coated and Evacuated Insulation Spheres: Methodology

- Start with naturally-occurring or synthesized hollow micro-particles/spheres with a porous shell
- Coat the porous shell, followed by post-deposition thermal processing in a vacuum furnace to create evacuated insulation spheres
- Thermal post-processing to simultaneously evacuate the hollow interior and densify the coating to impact gas impermeability
  - Processing parameters can be tailored to allow evacuation of the core (via gas diffusion through the shell) before coating densification is complete

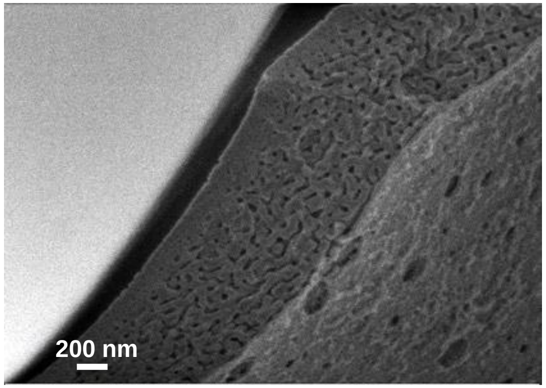


CEIS: Microspheres and Coatings

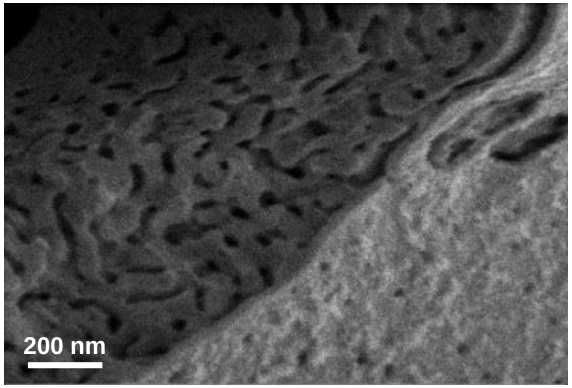
- Selection of porous walled, hollow glass microspheres
  - 30-90 µm spheres obtained from Mo-Sci
- Selection of coatings and methods
  - Low thermal conductivity
  - Conformal coating; highest physical/chemical bonding w/ particles
  - Solubility in environmentally-friendly and commercially viable solvents (e.g., ethanol, water, etc.)



Particle size: 30-90 µm



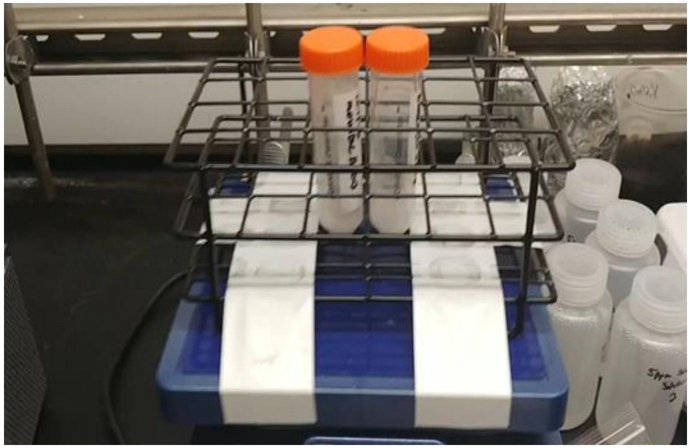
Shell thickness: ~1 µm



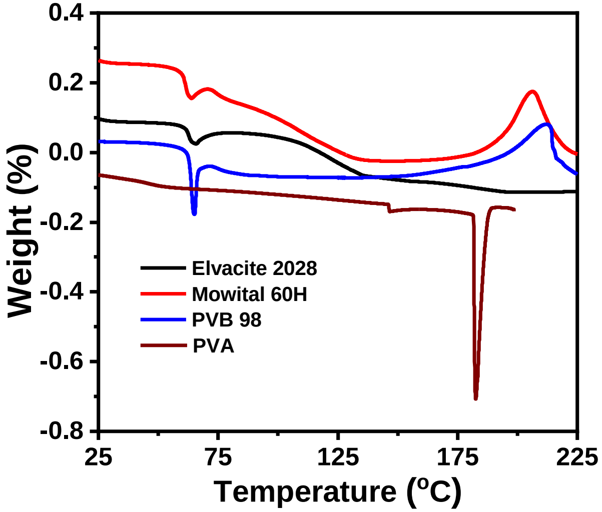
Pore size: 10-300 nm

CEIS: Polymeric Coating Agents & Methods

- Multiple polymer solutions were tested w/various solvents
- Selected coating method – Dip coating
  - Inexpensive industrial coating process, easy to scale-up
  - Microsphere and polymer solution mixed in an orbital shaker followed by separation of coated microspheres via centrifuge
- Post-coating annealing to densify the coatings and impart shell impermeability
  - Annealing temperature selected based on thermal characterization of polymers



Differential scanning calorimetry



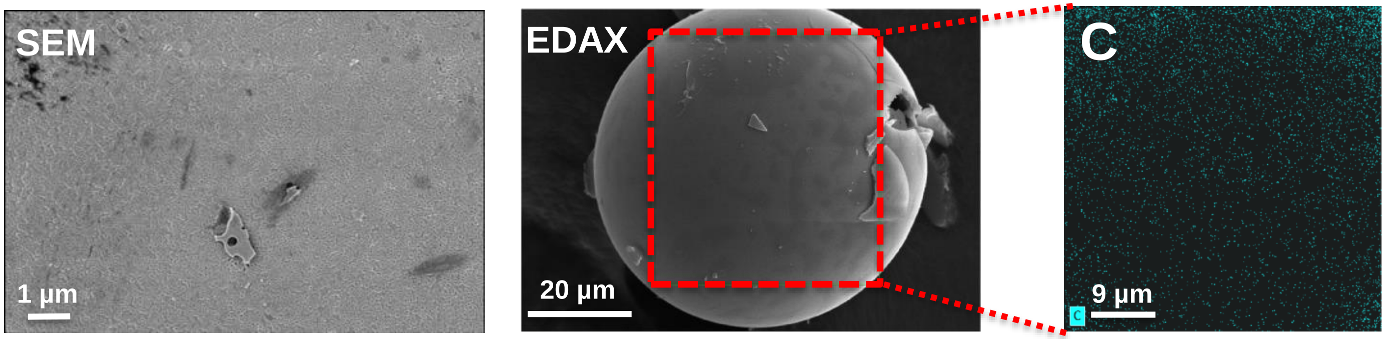
Selected polymers based on initial coating experiments

Polymers	Solvent
Polyvinyl butyral (PVB 98)	Ethanol/Toluene
Elvacite 2028	Ethanol
Mowital B60H	
Polyvinyl alcohol (PVA)	Water

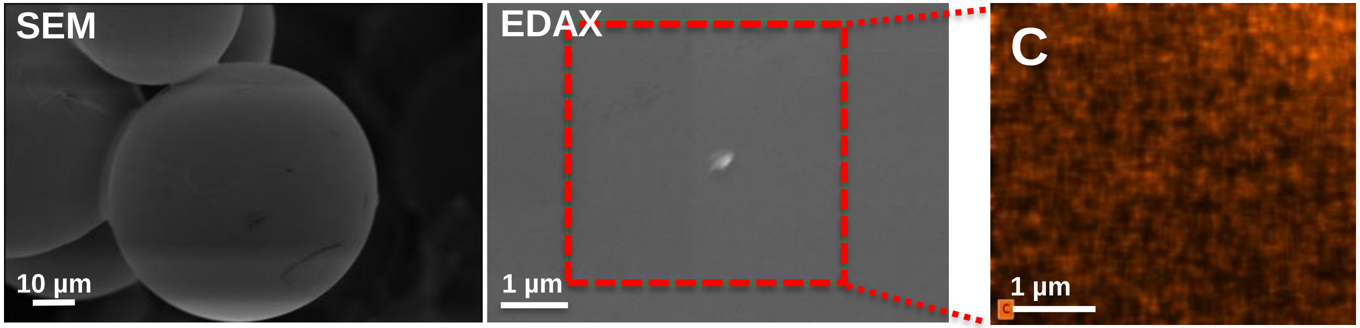
CEIS: Evaluation of Polymeric Coatings

- Scanning electron microscopy (SEM) for microstructural examination of coatings
- Energy dispersive X-ray (EDAX) is to detect signals from different elements
  - Carbon [C] from polymer coatings

Example 1 – Inhomogeneous coating w/discontinuous coverage; weak C signal

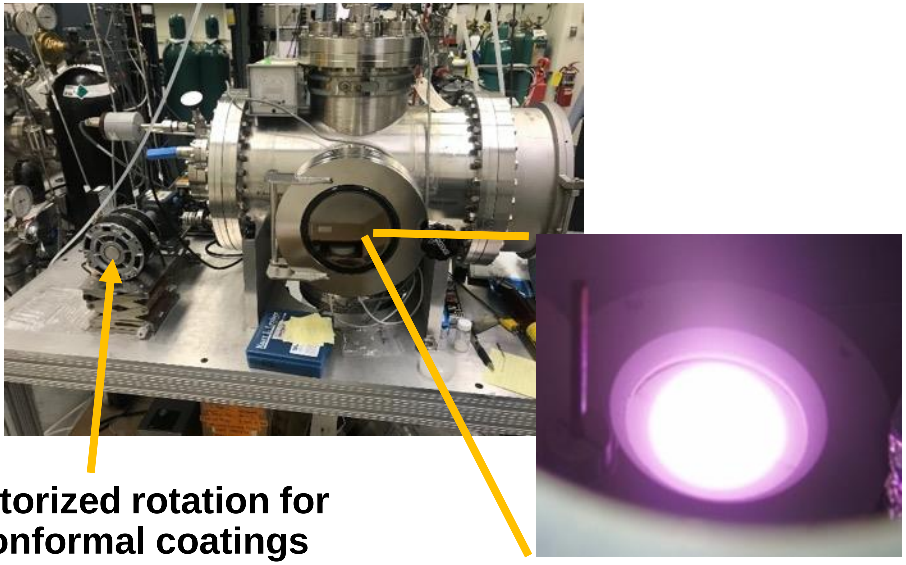


Example 2 – Dense & uniform coating; strong C signal



CEIS: Inorganic Coating Agents and Methods

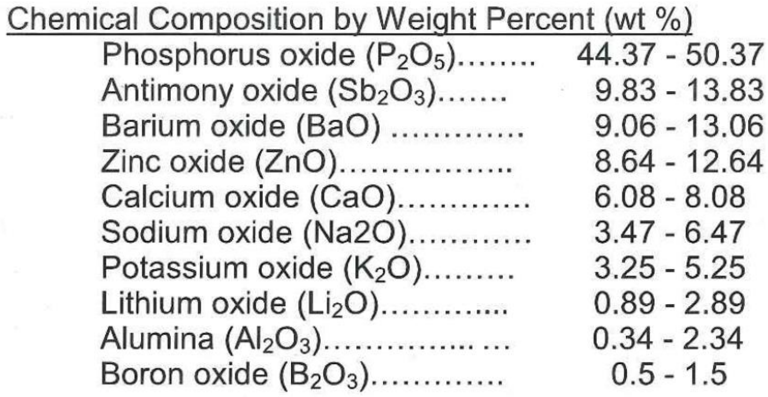
- Selected coating agent: Soda-lime glass and Borosilicate glass
  - Inexpensive, chemically stable & extremely workable
  - Targeted thickness: < 0.5 µm
- Method: sputter thin film coating



Motorized rotation for conformal coatings

Glass film deposition

- Powder coatings: GL 1734
  - Used as a sealing glass
  - Solvent: Terpineol
  - Particle size: 5 nm
- Method: Dip-coating (more economical alternative to sputter thin film coating)



Chemical Composition by Weight Percent (wt %)

Phosphorus oxide (P_2O_5)	44.37 - 50.37
Antimony oxide (Sb_2O_3)	9.83 - 13.83
Barium oxide (BaO)	9.06 - 13.06
Zinc oxide (ZnO)	8.64 - 12.64
Calcium oxide (CaO)	6.08 - 8.08
Sodium oxide (Na2O)	3.47 - 6.47
Potassium oxide (K_2O)	3.25 - 5.25
Lithium oxide (Li_2O)	0.89 - 2.89
Alumina (Al_2O_3)	0.34 - 2.34
Boron oxide (B_2O_3)	0.5 - 1.5

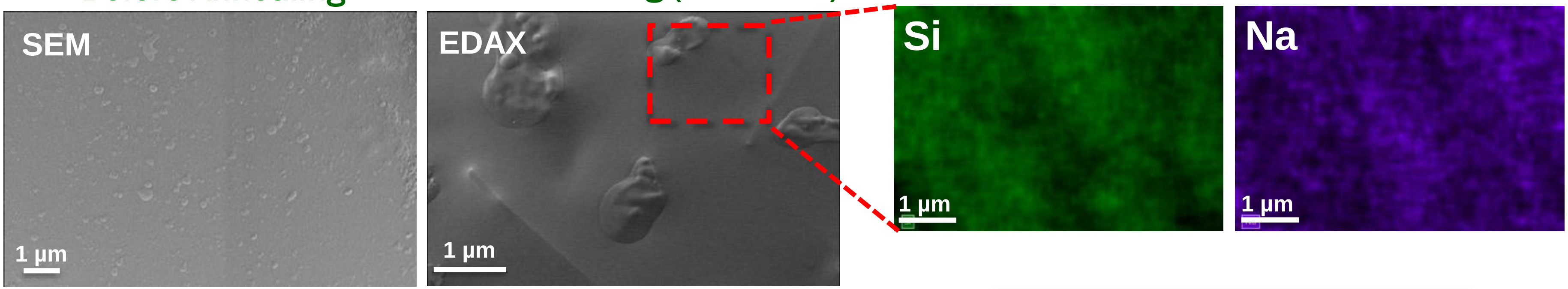
Custom-designed powder (Mo-Sci)

CEIS: Evaluation of Inorganic Coatings

SEM/EDAX show uniform coverage for inorganic glass based coatings

Example 1 – Borosilicate glass coating

Silicon [Si] signal is from microsphere & coating,
Sodium [Na] is from coating

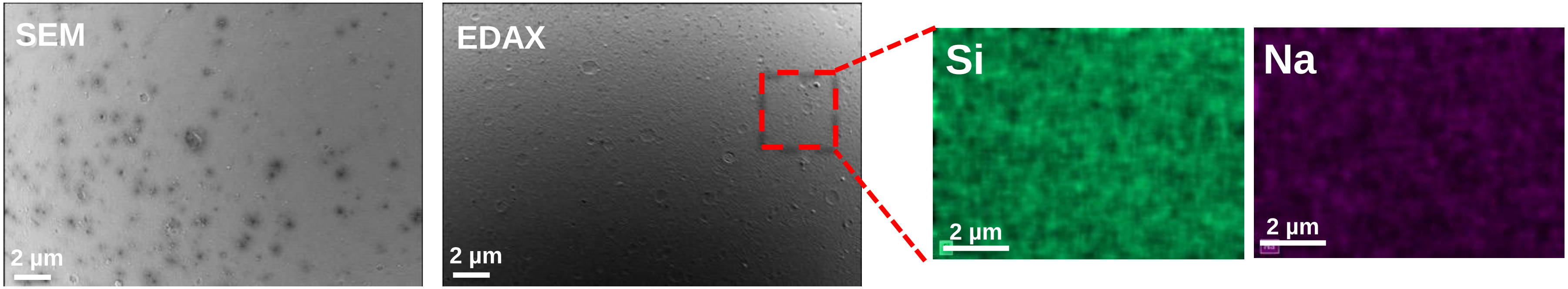


Before Annealing

After Annealing (T=750 ºC)

Strong Na signal → good coating coverage

Example 2 – Soda-lime glass glass coating

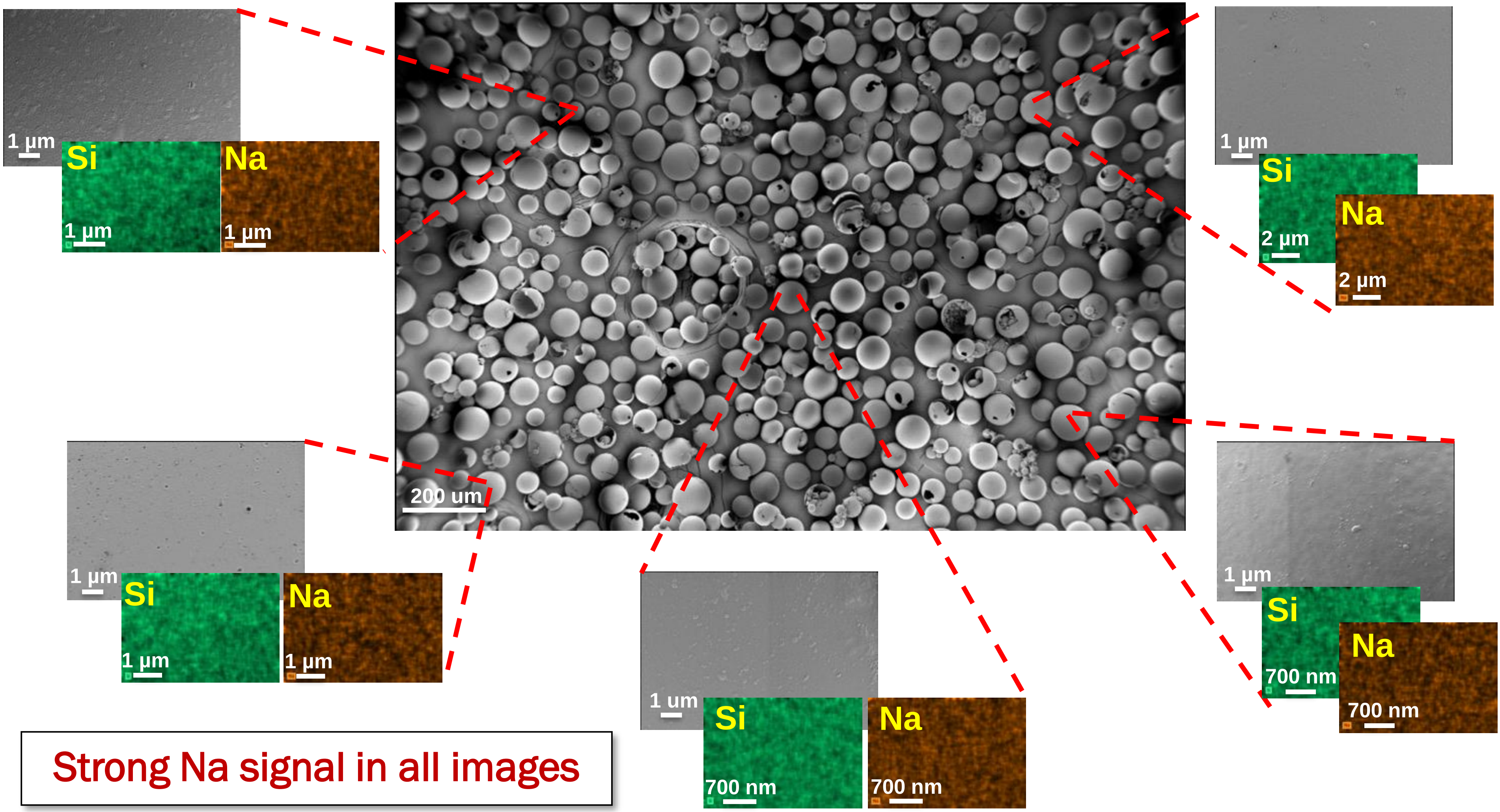


Before Annealing

After Annealing (T=750 ºC)

CEIS: Inorganic Coating

Random sampling of sputtered borosilicate glass coating on microspheres



Strong Na signal in all images

CEIS: Remaining Work

- FY19 (CEIS only funded for FY19)
  - Create conformal coatings with high resistance to gas permeability
  - Create coated spheres with demonstrated internal vacuum
  - Perform preliminary cost analysis
- FY20
  - Define internal pressure to achieve desired step-wise thermal performance (R6/in., R10/in. and R14/in.)
  - Develop 6 x 6 in. prototype CEIS-based insulation that can achieve >R6/in.
- FY21
  - Improved 6 x 6 in. prototype CEIS insulation that can achieve R14/in.
  - Pursue scale-up and commercialization strategy

Preliminary R/inch calculations

$P_{int.}$ (mbar)	k_{air} (W/m·K)	Overall R/in.
10.0	~0.0197	6.8
1.0	~0.0061	12.4
0.1	~0.0008	19.2
0.01	~0.0001	20.8

Assumptions:

- Hollow spheres of 70 μm average diameter
- Binder – polyurethane (0.024 W/mK)
- 64% void fraction of randomly packed spheres

Stakeholder Engagement

- Both PVIS and CEIS are early-stage R&D projects

- Potential industry partners
  - Akzo Nobel: manufacturer of Expancel polymeric spheres
  - MoSci: manufacturer of hollow microspheres
  - Orca Coolers: may consider manufacturing if process is simple

- Start licensing discussions after proving that we can control vacuum level and retain vacuum within the spheres
  - PVIS: US Patent Application Serial Number 62/769,590
  - CEIS: Invention Disclosure 201804138, DOE S-138,805

- Collaborating with ORNL team that is developing novel models that predict effective thermal conductivity in new insulation materials

- Presentation at Buildings XIV Conference in December 2019

Thank You

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REFERENCE SLIDES

Project Budget

Project Budget: FY18: $250K FY19: $500K Total: $750K

Variances: none

Cost to Date: $445K

Additional Funding: none

Budget History					
FY 2018		FY 2019		FY 2020 – TBD (planned)	
DOE	Cost-share	DOE	Cost-share	DOE	Cost-share
$250K	0	$500K	0	TBD	0

PVIS: Project Plan and Schedule

Deliverable/Milestone	FY18				FY19			
	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
Section of polymers and blowing agents, and preliminary extrusion trials								
Selected 3 - 5 thermoplastic polymers w/ either glass transition or melting temperatures lower than the processing temperature and a modulus of elasticity > 100 MPa.	🟦							
Selected 3 - 5 blowing agents that are nonreactive with polymers while the sphere is being blown and stable after the sphere has been blown.	🟦							
Modified system to extrude a polymer entrained w/ dispersed blowing agent particles.		🟦						
Selected a polymer & blowing agent that can be extruded to produce spheres.			🟦	🟦				
Optimization of Thermal Conductivity								
Produced 200 µm spheres					🟦			
Extruded parts in which the inorganic additives and polymer are uniformly blended					🟦	🟦		
Produced 100 - 200 µm spheres with ≥50% void faction					🟦	🟦		
Reduced thermal conductivity of base polymer by ≥5% by blending it w/ additives					🟦	🟦		
Produced 100 µm spheres with ≥60% void faction using polymer w/ additives						🟦	■	
Reduced thermal conductivity of base polymer by ≥10% by blending it w/ additives						🟦	🟦	
Developed method to measure the vacuum within the sphere cavities						🟦	■	
Produced 100 µm spheres with ≥70% void faction using polymer w/ additives							■	🟥
Produced spheres with cavities that are pressurized to ≤100 mbar							■	🟥
Development of Mechanism to Reduce Air Permeability of Base Polymer								
Identified mechanism to reduce the air permeability of PVIS shell to ≤0.3 cm^3/m^2-day						■	■	
Identified mechanism to reduce the air permeability of PVIS shell to ≤0.07 cm^3/m^2-day							■	■

🟦 Completed ■ Regular 🟥 Go/No Go

CEIS: Project Plan and Schedule

Deliverable/Milestone	**FY18**			
	Q1	**Q2**	**Q3**	**Q4**
Material Screening				
Selected base materials, coating agents and method(s), and post-coating thermal processing methods for evacuation and shell densification.	🟦			
Preliminary (year 1) cost estimates of bulk materials and thermal processing, and evaluation of cost-competitiveness with vacuum insulation panels ($0.25/ft^2/R). The eventual target is similar to the projected cost of MAI, which is $0.05-0.12/ft^2/R based on production volume.		🟦	■	
Coated Particle Development and Characterization				
Demonstrated uniform thickness and defect-free (no open pores or voids) coverage of coatings based on micro-structural analysis pre- and post-coating and after thermal processing of prototype hollow spheres. The goal is to create dense coatings of ≤ 2 μm thickness on 50-100 μm spheres.	🟦	🟦		
Hollow spheres developed with dense and conformally-coated shells that exhibit high resistance to gas permeability.		🟦	■	■
Develop and Test Evacuated Particles				
Coated and hollow spheres with demonstrated internal vacuum (10 mbar or lower				🟥

🟦 **Completed** ■ **Regular** 🟥 **Go/No Go**