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Fuel Cycle Research and Development

Functionalized Ultra-Porous Ceramic Nanofiber Membranes and Encapsulation Glass Waste Forms for Nuclear Fuels Recycle

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Modified Open Fuel Cycle (MOC) Peer Review
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Basis of the concept and how it relates to the FCRD MOC goals

- **Combined fuel/waste management idea**

- A simplified process for re-using used LWR fuel that involves:
  - stripping the cladding,
  - crushing/reacting the fuel to be able to remove select components,
  - then re-fabricating into fuel with the addition of fresh fuel.

- Crushing the fuel and performing a simplified heating/hot gas extraction process:
  - separate out the volatile fission products (eg., Cs, Sr, Rb) and poisons (eg., Xe)
  - recycle of the fuel through mixing with fresh fuel and re-sintering

- Utilize modeling to determine:
  - limitations to the number of recycles possible,
  - feasibility of long-term recycling into advanced reactors

- Result: An **INTEGRATED PROGRAM** of modeling, separations, & waste forms for optimized fuel recycle

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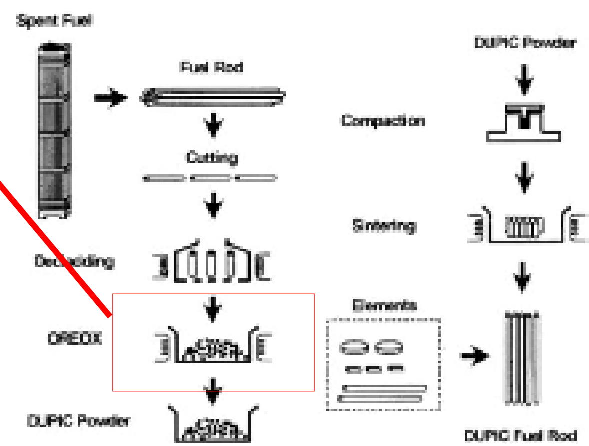
Applicable cycles: DUPIC-like Process, Dry Chlorination

Easy Insertion of Nanofiber Separations Technology into MOC processes

Removal of Fission Products and Poisons for Fuel Recycle:

- crushing the fuel
- performing a simplified heating process and/or hot gas extraction process (≈ 600 -1500°C)
- separate out the volatile fission products (eg., Cs, Sr, Rb) and poisons (eg., Xe)
- recycle of the fuel through mixing with fresh fuel and re-sintering

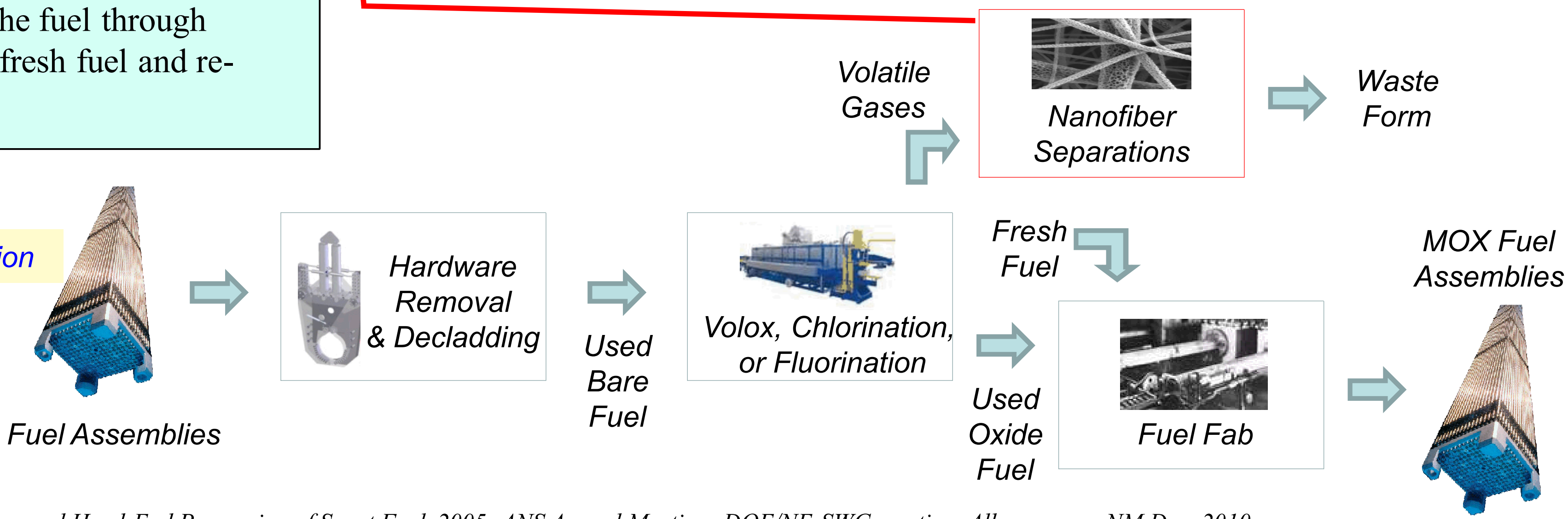
Kang, et.al., Metal.Mater. 2000, 6(6), 583



DUPIC-like Fuel Fabrication Process:

Model process system for insertion of nanofiber membrane & capture products during heating

Dry Chlorination



De Cul, et al., Advanced Head-End Processing of Spent Fuel, 2005; ANS Annual Meeting; DOE/NE-SWG meeting, Albuquerque, NM Dec. 2010

Program Objectives Yr1: Integrated Program to Success

Modeling: Based on what remains in the used fuel oxides, determine how feasible it will be to make a recycled fuel for LWRs (including mixing with fresh fuel) – will use ORIGEN & MCNP

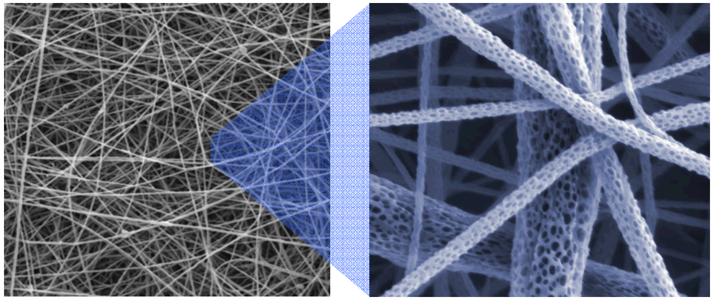
What elements will be released by Volox or Dry Chlorination?

What poisons will remain in the fuel to be recycled?

How many recycles are possible?

Separations: Getter Material

Ultra-Porous Ceramic Nanofiber Membranes for tunable high selectivity gas separations



Primary pore: inter-fiber

Secondary pore: intra-fiber

Waste Forms: Flexible Compositional Matrices

Easy Incorporation of Separations Materials & Captured Gases

One-step processing, no purification or further separations needed

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The Likelihood of Implementing the Proposed Concept

✧ *Proposed Separations and Waste Forms Excellent for One-step Process*

The proposed technologies utilize (1) membrane based microporous ceramic fiber structure, functioning as a sorbent filter, and (2) low temperature encapsulant Waste Forms. Both are currently under production at SNL.

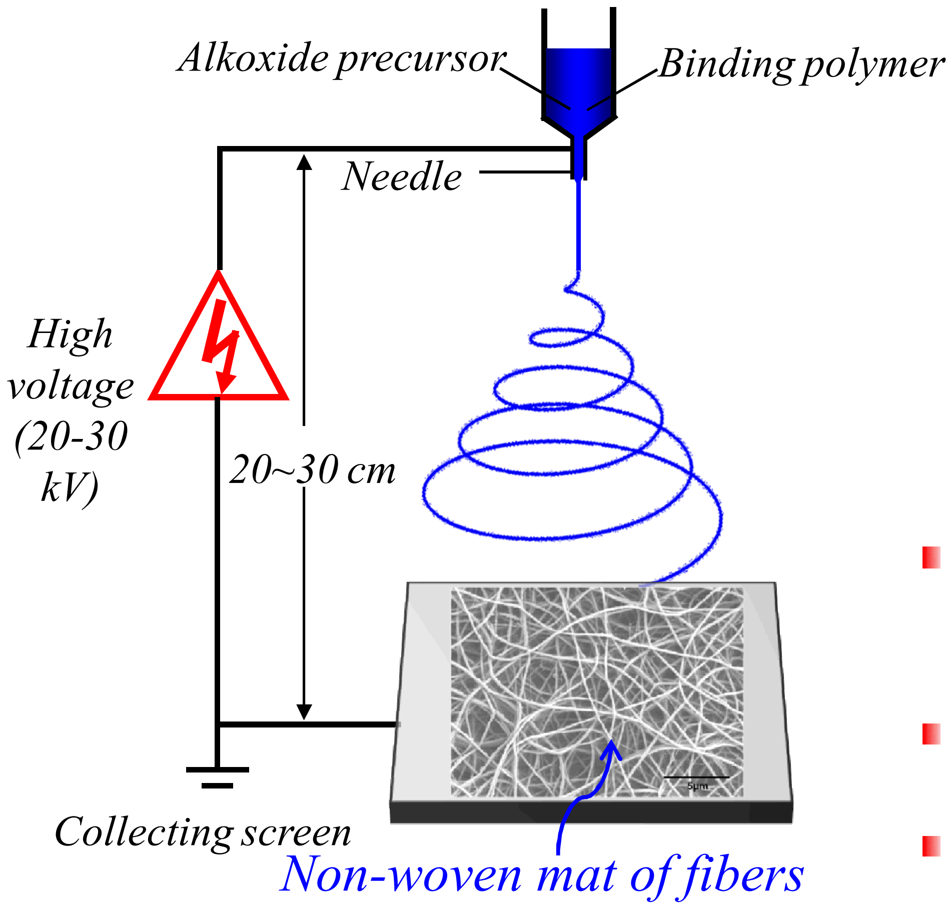
Nanofiber Membranes:

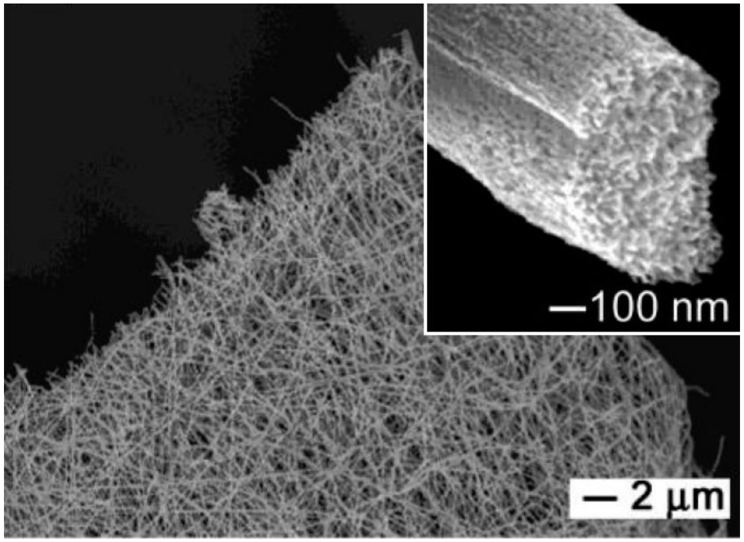
- **High flux** (accessibility to high open surface area)
- **Easy Insertion in off-gas streams** (membrane)
- **Compatible with innovative separation technologies**
- **Chemical, mechanical, radioactive durability**
- **High capacity** (high waste loading)
- **Selectivity** (catch trace amount of residue)

✧ *Currently, technology Readiness Level 4*

- Commercialized manufacturing technology of nanofibers available
- Commercial and patented technology for functionalization of porous metal oxides (eg., zeolites) for gas separations (Nenoff, et.al., US Patent *6,494,326*)
- Waste Forms proven in laboratory setting with similar materials
- Success in project will lead to TRL#5 (validation in relevant environments)

Ceramic Nanofiber Membranes: Electrospinning + Sol-gel



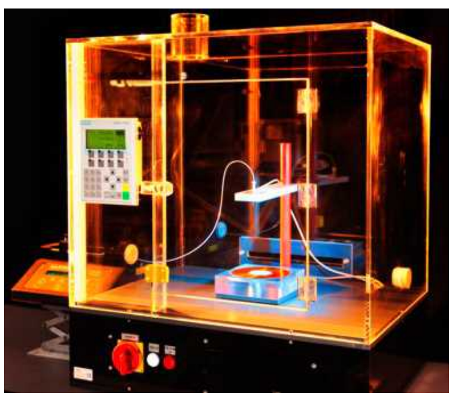


- Coaxial electrospinning:
  a) sol containing alkoxide precursor
  b) matrix polymer
- Phase separation leads to polymer nanoscale domains within metal oxide.
- Polymer is removed and ultra-porous ceramic fiber is produced.

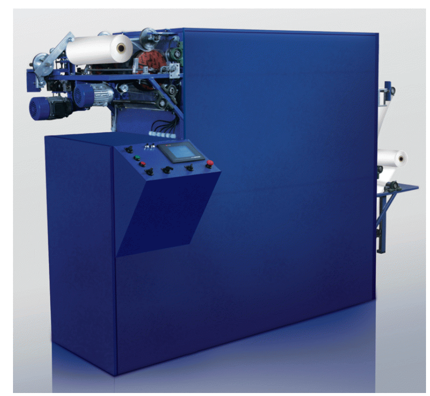
✧ Challenge: tune the *Secondary pores* for **size** selectivity of gases

Advantages of ultra-porous Nanofiber Membranes

- High porosity → high surface area → high flux
- Fibril membrane sorbent readily incorporate into adv. fuel cycles
- Readily dispersed into solution, no aggregation, no pellet needed
- Readily separated from aqueous phase after sorption
- Materials flexibility and engineering capability
- Cost effective and scaling-up ready (commercial products)



~$20,000



€45,000
≈ $60,000 USD

Research → Industry

Strategies for Fission Gases and Poisons Immobilization

- Polymer and solvent composition will be varied extensively to control the morphology of electrospun ceramic nanofibers and to design tailored pore size.

- Three Methodologies of Tuning Nanofibers to Specific Gas Sorption:

  1. Design and incorporate high selectivity and high affinity via surface functionalization on porous structures. (Chemisorption)

  2. Composite Nanofibers (Physisorption and Chemisorption); zeolite nanocrystals introduces with alkoxide and binding polymer for zeolite coating on nanopores' surface

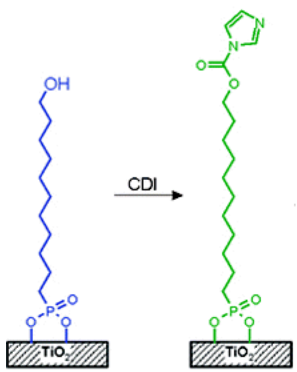
  3. High flux membrane as support for Zeolites and Metal Organic Framework (MOFs).

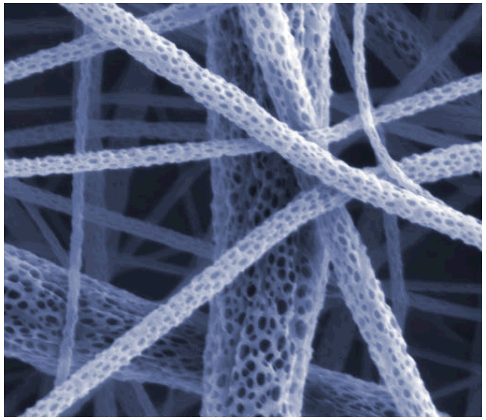
- Alternative ultra-porous ceramic nanofiber membranes (borosilicate, aluminosilicates, etc) compatible with current baseline waste forms (eg., low temperature glass, grout and silicogeopolymers).

Methodologies of Tuning Nanofibers
1. Surface Functionalization for High Affinity and Specificity

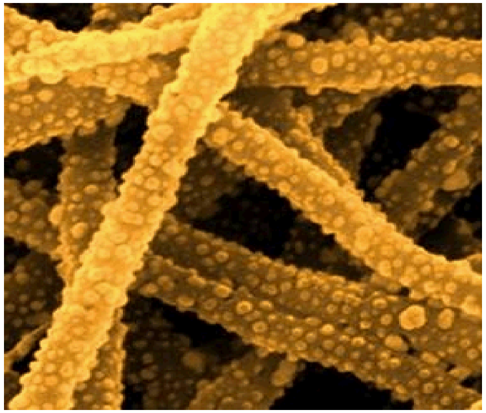
Functionalized porous surface for high affinity and specificity capturing of off-gas products.

- Covalent Functionalization
  - Phosphonation[1]
    e.g. Phosphonic acid with TiO_2 surface result in covalent Ti-O-P bonds in large pH range, stable in hydrolysis.
  - Amidation[2]
    Plasma-enhanced CVD for reactive amine
  - Carboxylation[3]



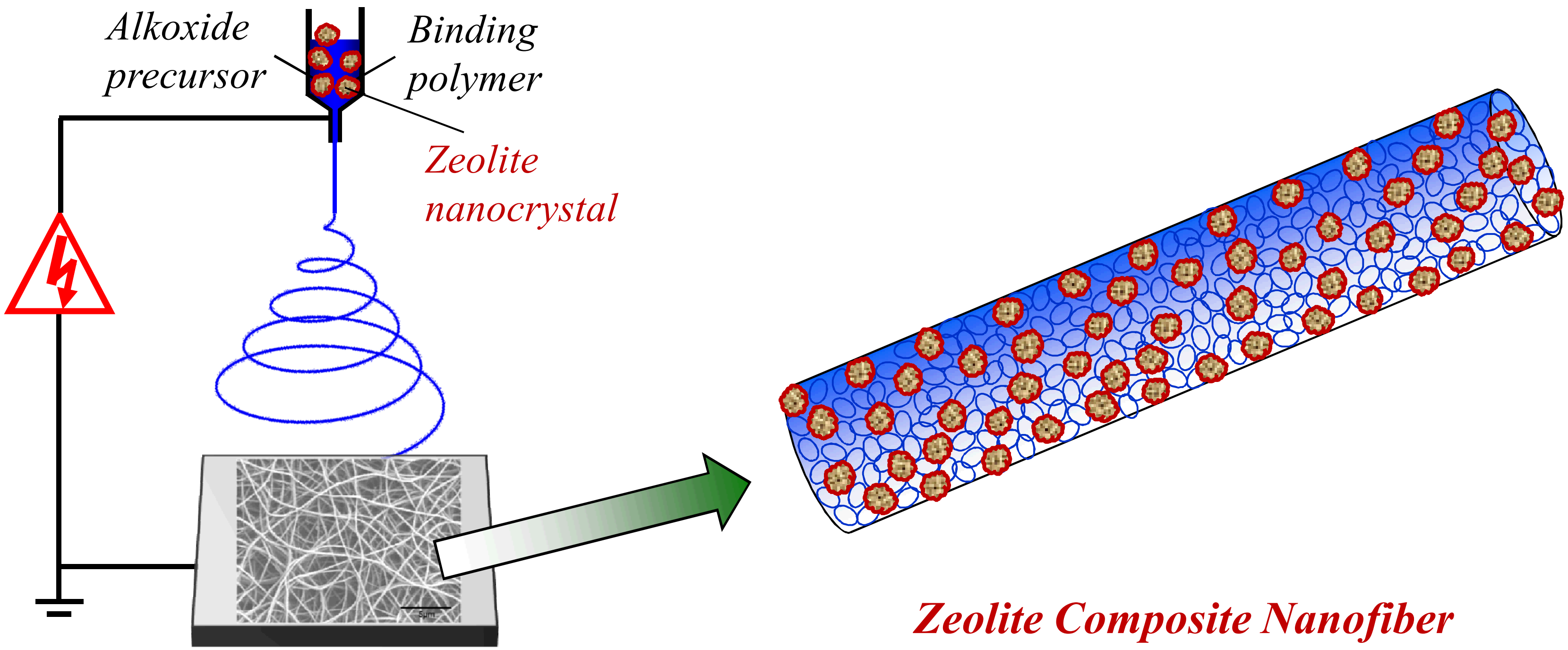


- Transition metal in-situ synthesis
  - Photocatalysis reduction of metal salt[4]
    e.g. Au, Ag, …



[1] Adden et al, *Langmuir* (2006), 22, 8197; [2] Mukherjee et al, *Appl.Mat.Inter*. (2010), 2, 397;
[3] Gomathi et al, *J. Mat.Chem* (2009), 19, 988; [4] Li et al, *Chem.Phys.Lett* (2004), 394, 387

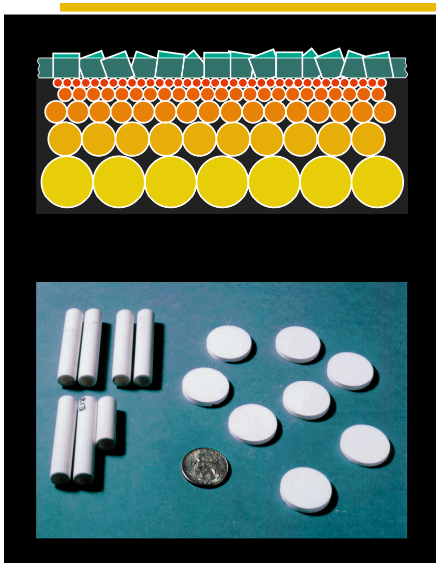
Methodologies of Tuning Nanofibers
2. Composite Nanofibers



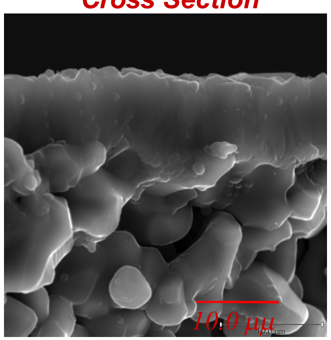
- Nanopores provide high flux transportability of gas molecules to zeolites
- Uniform insertion/distribution of zeolite nanocrystals among interconnected nanopores
- Will examine if entrapment of gas is irreversible under extreme temp, pressure, acid pH;
- How will entrapment affect incorporation into final waste form?

Methodologies of Tuning Nanofibers

3a. High Flux Support for Zeolites both on bulk surface and coating internal pores

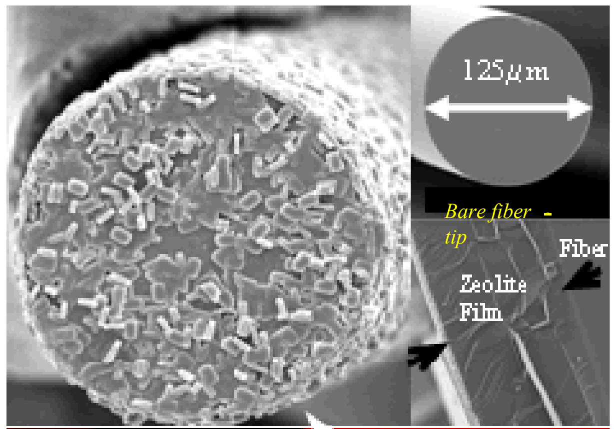


MFI Zeolite/Al_2O_3 Membrane Cross Section



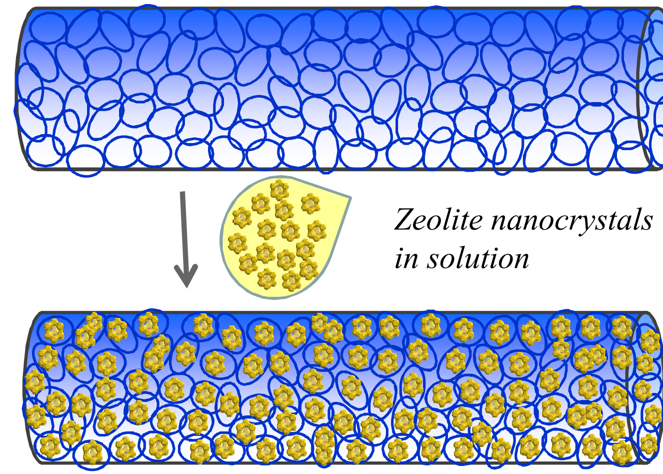
Nenoff et. al., Chem. Rev., 2007; Micro.Meso.Mater. 2003, 66, 181

(1) Bulk Surface Zeolite Modification Of Fibers



Chem.Mater, 18 (2006) 4

(2) Internal Pore Surface Modification Of Nanofiber

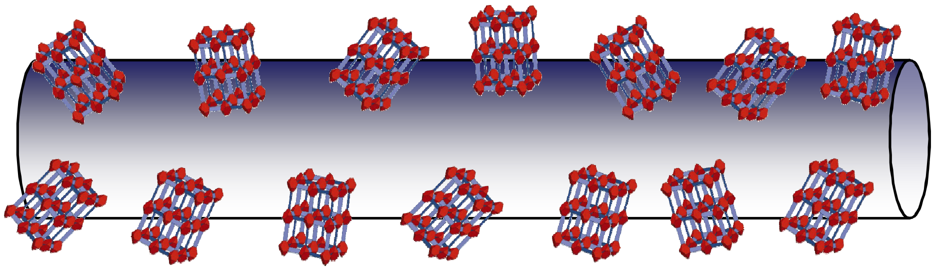


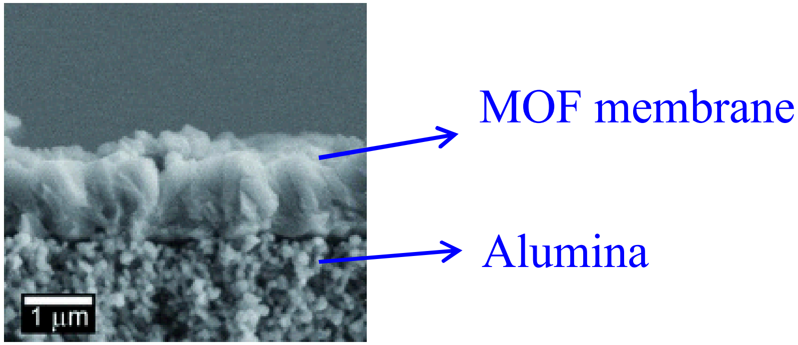
SNL developed Zeolite Membranes on Alumina or Silica supports, plus literature preps on nanoparticle growth on nanofibers = leveraged ability to modify surface (bulk) and internal pores of ceramic nanofiber membranes for fission product gases and poisons

Methodologies of Tuning Nanofibers
3b. High flux support for MOFs

Propose: *ultra-porous nanofiber as continuous support for MOFs,* ***growth*** *or* ***deposition****, for high-flux separation or immobilization*

- Levearge from Zeolite membrane SNL skills, equipment, knowledge
- Metal Organic Frameworks (MOFs) are novel porous crystalline materials with large surface area and preferential surface adsorption capability.
- Ideal if MOFs particles can be spread out on *high-flux* microporous supports
- MOFs have already been Leverage grown on porous ceramic surfaces





Li et al, *Angew.Chem.Int.Ed* (2010), 49, 548

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Alternative Ceramic Nanofibers

- Additional Material Tuning can be achieved by modification of nanofiber composition
- With combination of electrospinning and sol-gel technology, vast populations of ceramic nanofibers can be made: TiO_2, SiO_2, Al_2O_3, V_2O_5, ZrO_2, $MgTiO_3$, CeO_2, SnO_2, $BaTiO_3$, etc, or mixed oxides.
- Particularly, borosilicate glass can be made into nanofiber, which can directly serve as the final waste form.

Challenges

- ✧ Fabricate stable, robust, ultra-porous ceramic nanofiber structures through effective phase separation control.
- ✧ Surface functionalization for high specificity and affinity.
- ✧ Tailor porous fiber structure as support for molecular sieves (MOFs, zeolites…) distribution.

Li et al, *J.Am.Ceram.Soc*. (2006), 89, 1861; Tanriverdi et al, *Mat.Sci-Poland.* (2007), 25, 957

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Scientific Benefits to Ceramic Nanofiber Technology

- High flux
- High surface area
- Non-powder
- High waste loading
- Aqueous streams
- Off-gas streams
- High Selectivity
- Chemical durability
- Radioactive stability
- Flexible material choice
- Final or part of final waste form

- Cost savings (capital, production, disposal, etc)

  Electrospinning organic fiber production has been commercialized; economic mass production; no hazard products generation.
- Solves difficult waste management problem

  High surface area, high flux, high permeability, no aggregation, no pellet needed, easy separation, low pH aqueous streams, as waste form or part of waste form.
- Likelihood of success (implementation)

  Commercial viability proved; significant potential for use in large-scale industrial production.
- Performance benefit (lower release for influential radionuclides, Pu, Np, I, Cl, Tc, etc)

  Excellent specificity and affinity to capture off-gas products through physichemsorption, or as molecular sieves support.
- Flexibility (multiple stream/fuel cycle applications)

  Excellent fitting in both UREX+ and Electrochemical fuel cycles for multiple streams, open, modified open, closed fuel cycles.
- Compatibility with innovative separations approach

  Stability in extreme conditions, high flux, high selectivity, flexible material choice, allows for good compatibility.

Waste Form Incorporation of Loaded Ceramic Nanofiber Membrane

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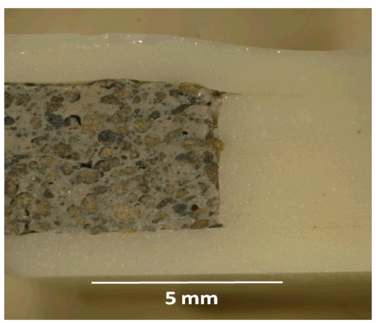
EXAMPLES Include:

Homogenous Glass Waste Form
Contains: 50 wt% AgI/50 wt% BiZnB
500˚C for 3 hr
(Garino, et. al., Ceramic Transactions, **2010**, 224, in press)



Core-Shell Waste Form:
Glass shell (BiZnSi)
AgI-MOR/Ag/Glass core 80/20/5
(Garino, et. al., JACerS, 2010, submitted)

Room Temperature Silicogeopolymer Waste Form containing AgI-Zeolite particles
(Nenoff, etal., GNEP-WAST-PMO-MI-DV-2008-000149)

High Success Probability by Leveraging DOE/NE-SWG Iodine program successes

1-step Separations & Waste Form
- No secondary waste
- Phase compatible
- Temperature compatible

Research Team: Qualifications, Experience, Capabilities

Team Members:

• Tina Nenoff, SNL, DMTS, 23 years experience in synthesis/characterization of porous materials and membranes, 125 papers/book chapters, 8 patents awarded, and a member of the 1996 R&D100 Award in CSTs for Cs separations.

Current: PI on two DOE/NE efforts including for selective iodine (I_2) gas sorption with zeolites and MOFs, plus I_2 storage in glasses, ceramics and oxides.

Past: Lead PI on DOE/ITP and H_2 programs in zeolite membranes for light gas and Hydrocarbon separations.

Past: Lead PI on $4.9M, 4 year CRADA (SNL, BP, Ozok Systems, NM Tech Univ), zeolite membranes for xylene isomer separations; $2.5M, 3yr CRADA (SNL, Goodyear Chemicals, TEMEC Inc.) zeolite membranes for hydrocarbon separations.

• Benjamin Cipiti, SNL, PMTS, 6 years experience in fuel cycle research and development, with experience in reprocessing plant modeling.

Currently direct funding projects from DOE/NE-SWG, NEAMS, and MPACT

Past SNL/LDRD programs in modeling of advanced fuel cycles, recycling, waste reduction and optimization using ORIGEN and MCNP

• Haiqing Liu, SNL, LTE, 10 years of experience working with electrospun nanofibers and nanofiber composites for DOE/BES programs at SNL and LANL

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Budget and Milestones

Budget: $300K/year; if successful, subsequent years at $500K/year

Schedule: Key R&D Goals and Project Milestones

Goal/Milestone	Completion Date
Modeling Fuel Cycle	
Preliminary Feasibility Study	09/15/2011
Separations: Nanofibers Synthesis	
Synthesis of SiO_2 & TiO_2 nanofibers	07/15/2011
Functionalize nanofibers w/MOFs and amines	09/15/2011
Separations: Nanofibers Sorption Capability Studies	
Structural/Gas Sorption Nanofibers	9/15/2011
Structural/Gas Sorption Nanofibers/MOF or amine	10/30/2011
Waste Form Development with Nanofibers	
Heat Treatment and Encapsulation	12/15/2011
Durability Studies (eg., PCT)	12/15/2011

Budget and Milestones (out years)

Continuation of Project, in FY12-13
Budget: Projected at $500K/year

Expanded Effort Focus on:

- Modeling - prediction of number of possible recycles
- Variations of nanofibers composition for sorption optimization
- Mixed Gas Streams separations and sorption studies

Advanced Separations:
insertion of nanofibers into fuel plenum for in-situ sequestration

Advanced Waste Forms:
HIPping Studies of loaded nanofibers (ANSTO; INL)
Target future CRADA program between
SNL / Univ. Cincinnati / {industrial partner: eg., AREVA}/{fuel lab: eg., INL}

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Tie to Program and Other Campaigns

Reduced Separations to a One-Step Process with a

Universal Getter and Sequestration Material

Direct Ties to:

Development of DUPIC-like Process (Fuels)
Dry Chlorination Process (Separations)
MPACT (increased proliferation resistance)

Expanded Program: Joint Fuels and SWG Campaigns

- fuels campaign can be used to determine how the recycled fuels
- can be re-formed and what level of new fuel addition will be required

Ultimate Outcome:

- reduce the cost complexity of reprocessing
- implementation in existing nuclear plants
- contribute to secure and economic implementation of advanced fuel cycles in the US

Benefits if Project Yr1 Successful

Goal:
Eliminate dissolution and reduce separations into a one-step process

Economics:
plant with a small footprint
small number of waste streams
Commercialize Process with a Separations/Waste Form and Modified Open Fuel Cycle (MOC) Application

Currently, technology is at TRL #4;
Yr1 of Project will bring it to TRL#5, outer years to TRL#6

One-step separations and sequestration of the released gases and fission products provides a simplified, universal waste form
vast majority of the fuel to be recycled back into the fuel cycle

Select Publications and Patents from Team Members

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Tina Nenoff:

- ”Radioactive Iodine Capture in Silver-Loaded Zeolites Through Nanoscale Silver Iodide Formation” *JACS*, **2010**, *132*(26), 8897.
- ”Development of Waste Forms for Radioactive Iodine”, *Ceramic Transactions*, **2010**, 224, in press.
- “… Zeolite Membranes for High Selectivity and High Flux for Hydrogen” *Langmuir*, **2009**, 25 (9), 4848.
- “Chemistry of Hydrogen Separation Membranes”, *Chem. Rev*., **2007**, 107, 4078.

- A New method for synthesizing defect-free thin film composite zeolite/sol-gel membranes, US Patent 6,494,326, December 17, 2002.
- Cesium Silicotitanates for Ion Exchange and Waste Storage, US Patent 6,482,380, November 19, 2002.
- Niobate-based octahedral molecular sieves, US Patent 7,122,164, October 17, 2006 .
- Gas Impermeable Glaze for Sealing a Porous Ceramic Surface, US Patent 6,716,275, April 6, 2004

Benjamin Cipiti:

- “Separations and Safeguards Performance Model” SAND2009-4896, August 2009
- “An Assessment of Spent Fuel Reprocessing for Actinide Destruction and Resource Sustainability” SAND2008-5980, September 2008.

Haiqing Liu:

- “…Nanofibers by Electrospinning”, *Int.J.Electro.Nanofibers*, 1 (1): 51-62 (2007).
- “…Nanofibers as Subwavelength Optical Waveguides Incorporating Quantum Dots”, *Small*, 2 (4): 495-499 (2006)
- “…Transport in PANI-$BaTiO_3$ Nanofibers”, *Nano Lett*, 6 (5): 896-900 (2006).
- “…Nanofiber Field Effect Transistor”, *App.Phys.Lett*. 87 (25): 253106
- "Polymeric Nanowire Chemical Sensor", *Nano Lett*, 4 (4): 671-675

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