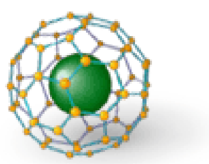
Commercialization of Alumoxane Nanoparticles

A Journey from Ceramics and Catalysts to Bone Replacement and Fuel Cells

RICE



Andrew R. Barron

OXANE
Nanostructured Innovations

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Andrew R. Barron

BSc (1983) - Imperial College, Chemistry (Geology/Materials)
PhD (1986) - Imperial College, Chemistry
Post-doc (1986-87) - University of Texas at Austin

Assistant Professor (1987-91) - Harvard University, Chemistry/MRL
Associate Professor (1991-1995) - Harvard University, Chemistry/MRL

Full Prof. and Welch Chair (1995-?) - Rice University, Chemistry, MEMS

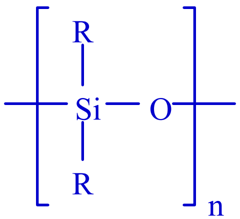
Research since 40! - Catalysis and biology of SWNTs and C_{60}

Founder - Gallia (sold to TriQuint), **Oxane**, NatCore

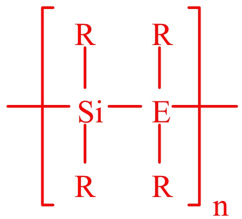
Racing - Club/Pro (US/UK), management of ALMS Team.

Where did it all start?

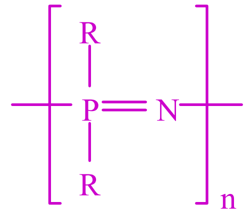
Commercial and academic interest in “inorganic polymers”



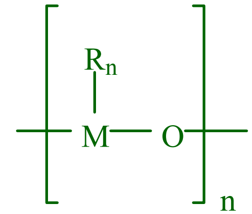
Polysiloxanes



Polysilanes & polycarbosilanes



Polyphosphazenes



Metalloxo polymers

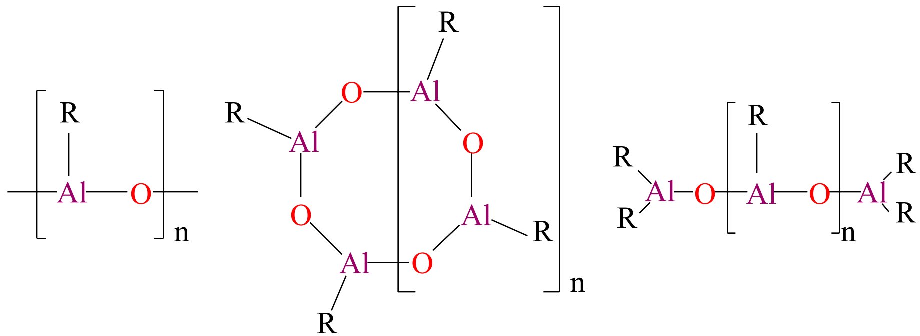
What are Alumoxanes ?

Substituent, X	Application
R	catalyst and co-catalyst
OR, $OSiR_3$, O_2CR	ceramic precursor
Cl	antiperspirant, deodorant

Alternative names: aluminoxanes, alumina gels

Our structure

What is the Structure of an Alumoxane ?



Actual structure based upon a simple mineral

Traditional approach: "bottom-up"

$$AlX_3 \xrightarrow{H_2O,\ acid} [Al(O)_x(OH)_y(X)_z]_n$$

hydrolysis of a small molecule
but...
alumoxanes have a core structure analogous to boehmite
so...
can they be prepared from the mineral?

The Barron approach: "top-down"

$$[Al(O)_x(OH)_y(X)_z]_n \xleftarrow{HX} [Al(O)(OH)]_n$$

Synthesis of Carboxylate Alumoxanes

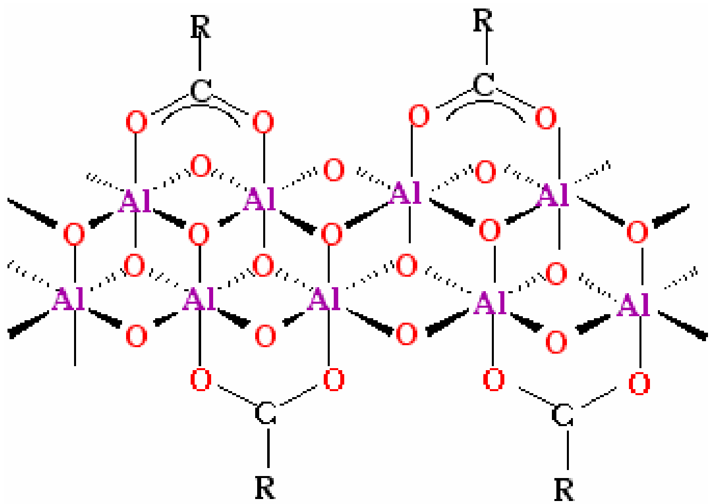
$$[Al(O)(OH)]_n \quad + \quad RCO_2H\ (xs)$$

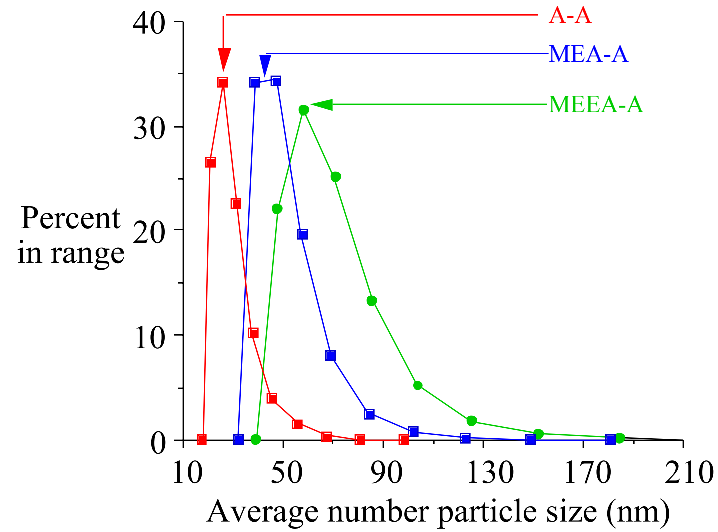
$$\downarrow$$

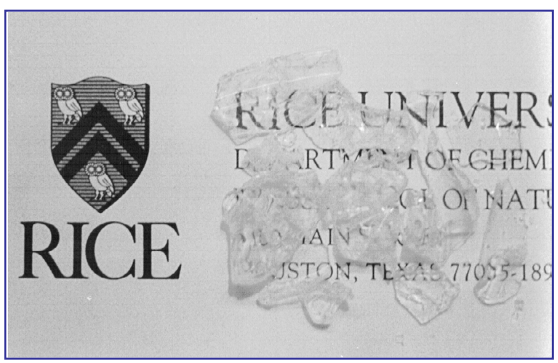
$$[Al(O)_x(OH)_y(O_2CR)_z]_n$$

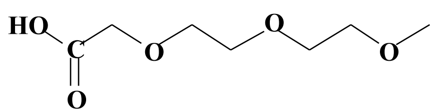
Top/bottom

What are Carboxylate-Alumoxanes?

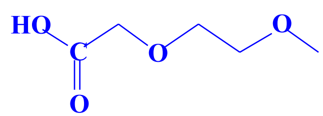




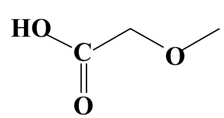




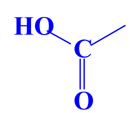
methoxyethoxyethoxyacetic acid (MEEA-H)



methoxyethoxyacetic acid (MEA-H)



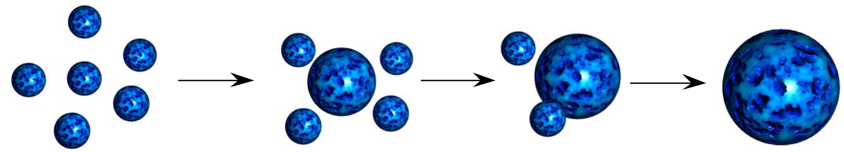
methoxyacetic acid (MA-H)



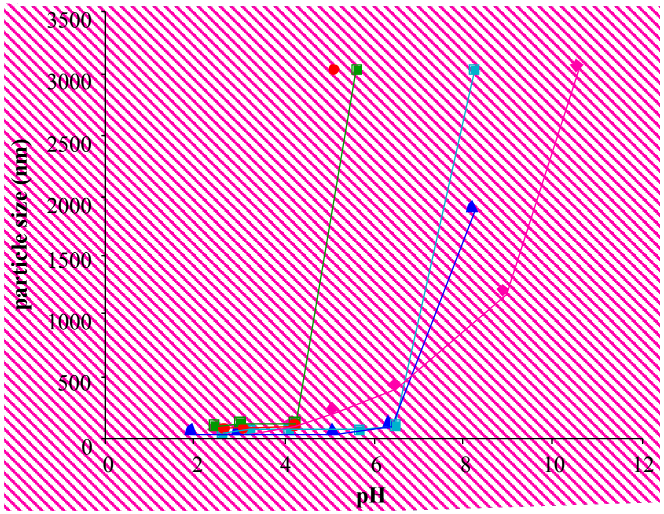
acetic acid (A-H)

pH

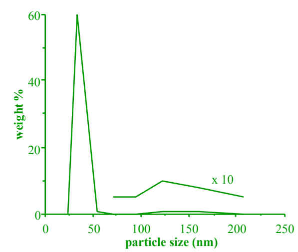
How does the particle size change with pH?

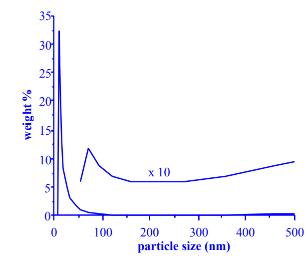


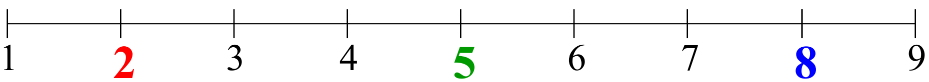
Seeded particle growth - several small alumoxane particles agglomerate to form a larger particle in a step-wise fashion

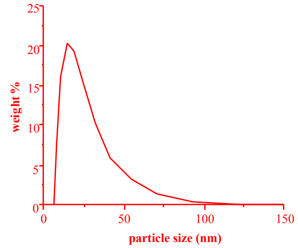


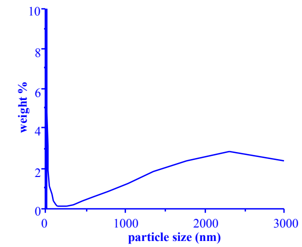
A-A (■), MA-A (■), MEA-A (●), MEEA-A (◆), and L-A (▲)











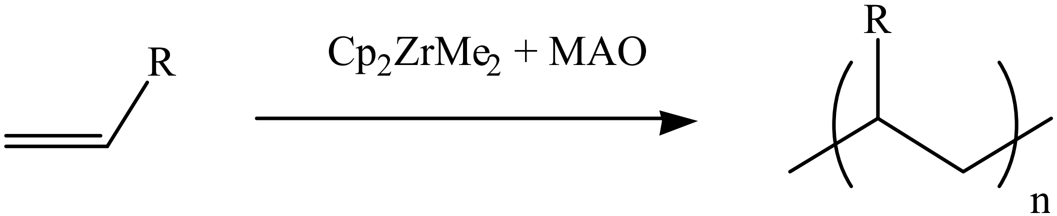
Oops

Alumoxanes are Nanoparticles **not** Polymers

Problem: Funding from ONR "Polymer Division"!

No polymer… no funding!

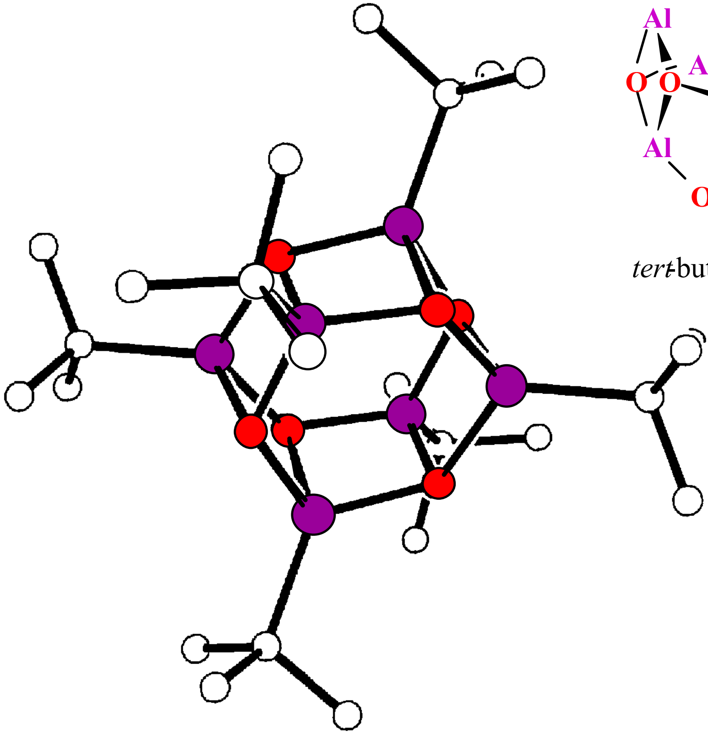
Substituent, X	Application
R	catalyst and co-catalyst
OR, $OSiR_3$, O_2CR	ceramic precursor
Cl	antiperspirant, deodorant

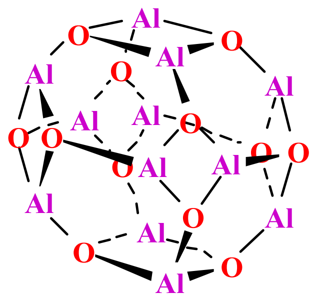


Our proposal

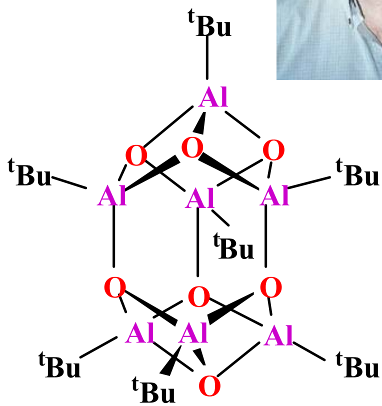
What are the structures found for Catalyst Alumoxanes?

- Al-O cage structures
- Aluminum 4-coordinate, oxygen 3-coordinate
- Electron precise - not apparent as Lewis acids
- No alkyl exchange
- n = 6, 7, 8, 9, 12





tert-butyl groups omitted for clarity



Compound	^{27}Al	^{17}O
MAO	140-155 (1750)	55 (800)
TBAO	110-120 (>5000)	55-75 (500)

Wrong!

A Structure of MAO
Proposed in 1993 - Denied in 1993

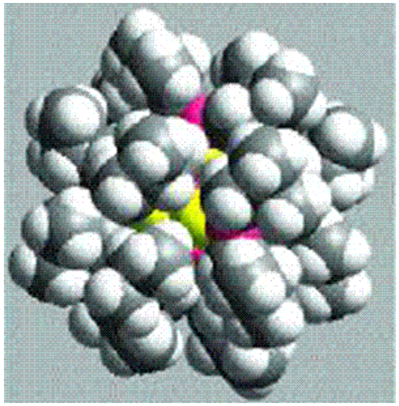
- We proposed simple cage structure
- Demonstrated activity
- Published results in 1993

"No that is not the structure (of MAO) - we know what the real structure is, but we are not able to discuss it" - *Exxon Researcher at the ACS National Meeting*

Exxon subsequently filed a patent claiming "nanoparticle" alumoxanes with sizes based upon the our published structures!

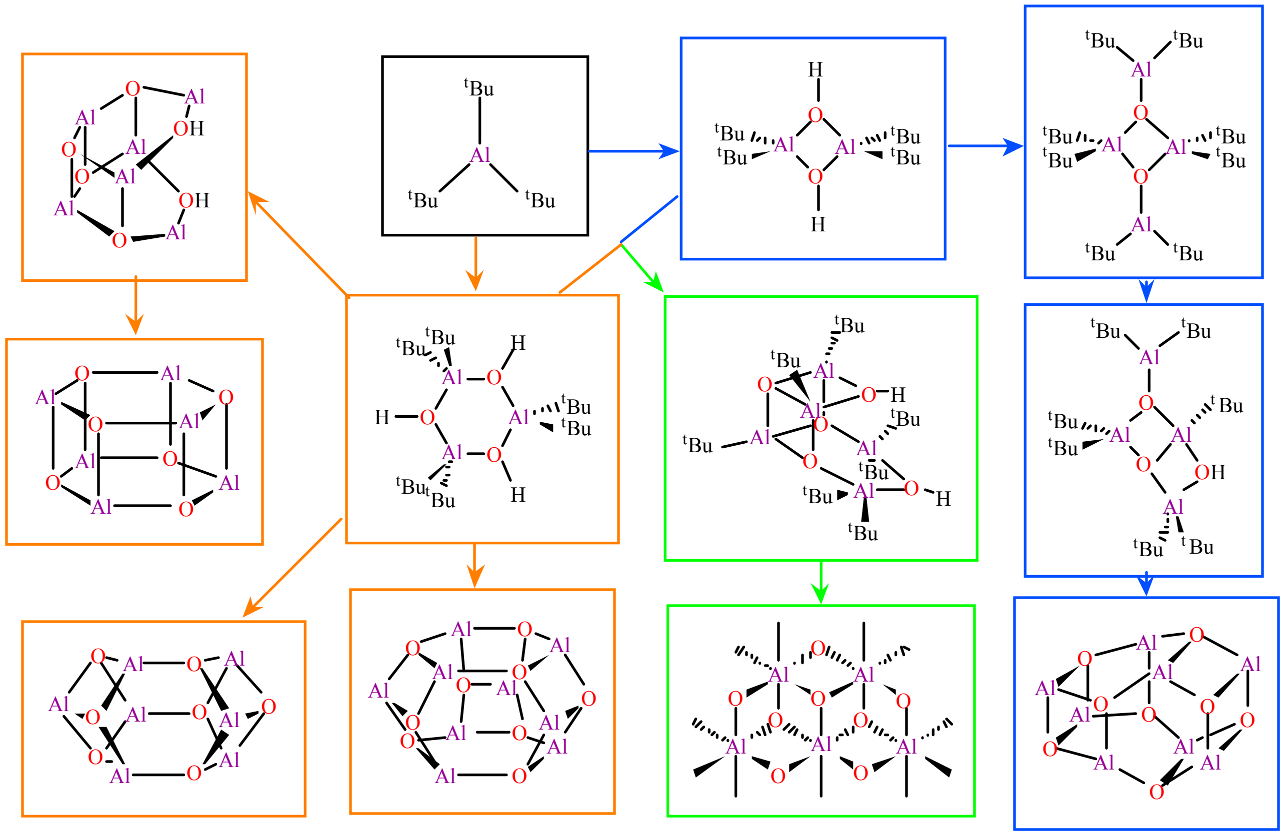
Support for our proposal

- Further chemistry of caged compounds (Roesky)
- No reactivity of ring structures (Power)
- DFT calculations (Ziegler)
- Isolation of commercial catalyst (Goodall)



gel

Relationship Between Various Structures and the "Undesirable" Gel



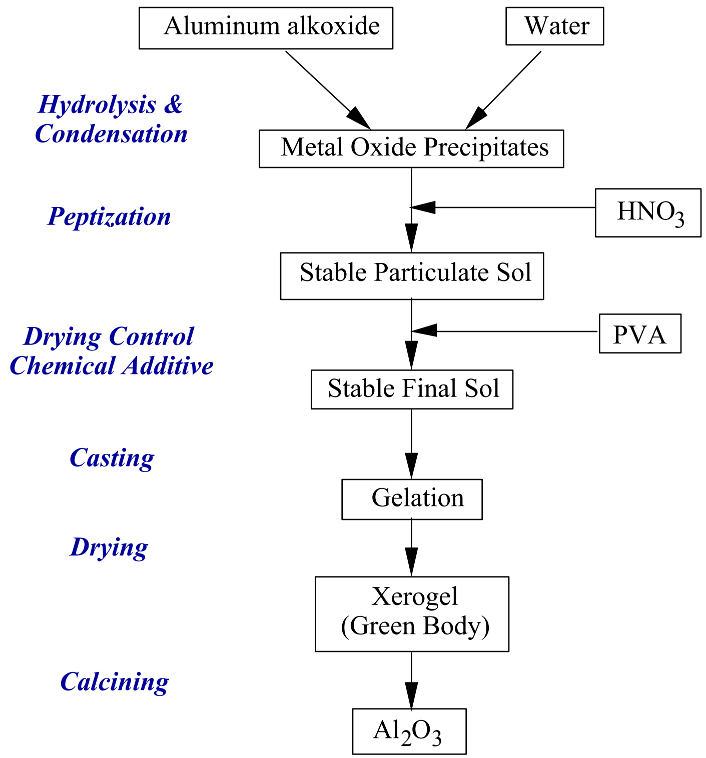
Relationship between gel and non-alkyl alumoxanes prompted return to carboxylate alumoxanes

problems

Problems with Alumina Ceramic Processes

The environmental impact of alumina-based ceramics are negligible.

Unfortunately, the same cannot be said about their preparation.



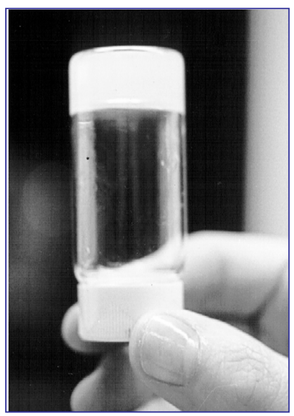
clean

RICE

Environmentally benign synthesis of alumoxanes

dirt vinegar water ⟶ alumoxane nanoparticle

$$[Al(O)(OH)]_n + RCO_2H\ (xs) \xrightarrow{H_2O} [Al(O)_x(OH)_y(O_2CR)_z]_n$$



. Synthesis on a large scale

. Cheap starting materials - \$ 0.50/lb

. Inifinite range of carboxylic acids

. Stable - months without change

. Processable

. Versatile - "infinite" chemical composition (Al)

. Non (low) toxicity - gluconic acid (bio-compatible)

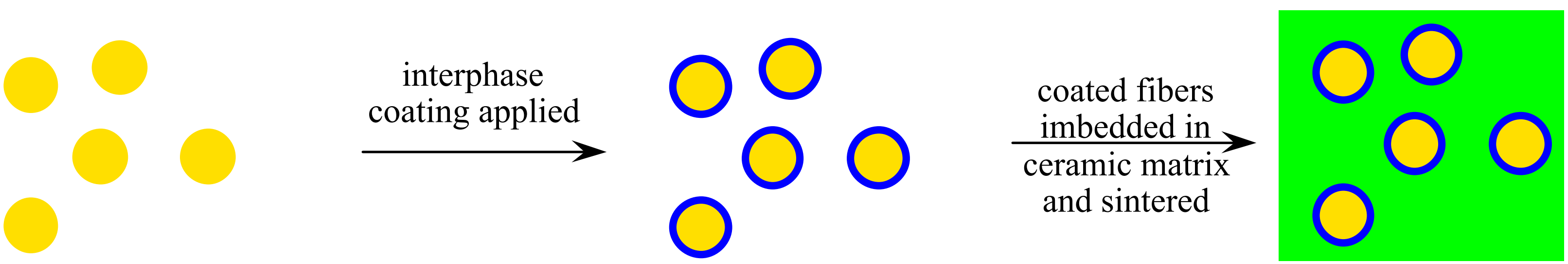
. Environmentally benign synthesis and processing

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

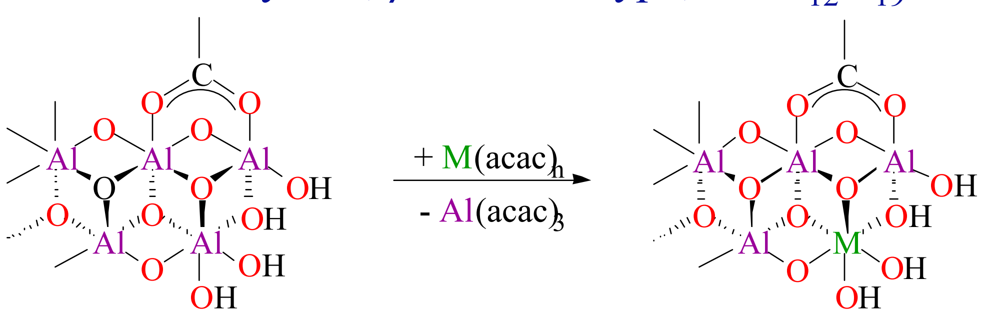
aluminate

Fabrication of Fiber Reinforced Ceramic Matrix Composites (FRCMCs)

. FRCMCs - reduce or eliminate catastrophic brittle failure
. Fiber-matrix interface - sufficiently weak to allow debonding
. Choices of fiber and matrix - limited
. SiC, carbon or sapphire fibers - react w. the matrix
. Interlayer - prevent deleterious chemical reactivity



Suitable materials - layered, β-alumina type, $CaAl_{12}O_{19}$ and $LaAl_{18}O_{18}$



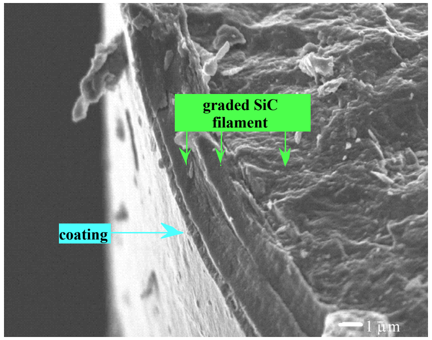
composite

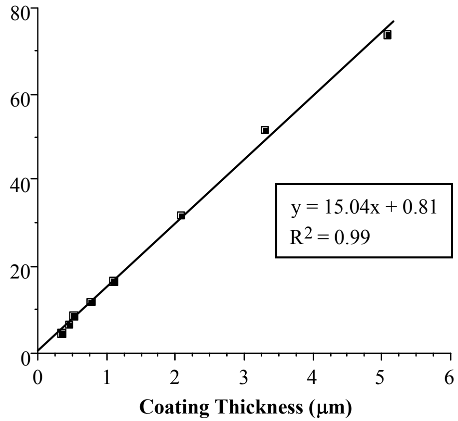
Alumoxane-derived Ceramic Interphase Layer

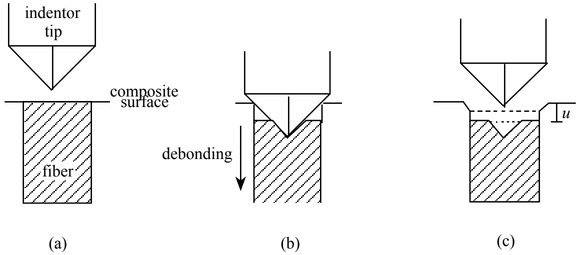
dip coating from aqueous solution; rapid drying; single dip/fire sequence

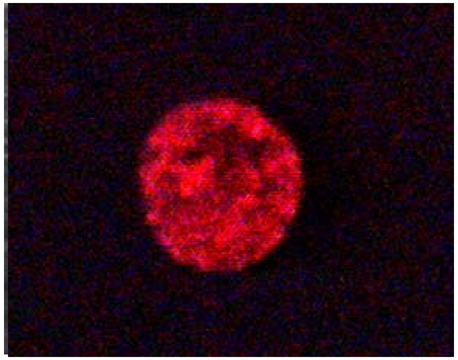
FESEM image of a $CaAl_{12}O_{19}$ (hibonite) coating on Textron SCS-6 graded SiC fiber

The coating is uniform and cohesion is good





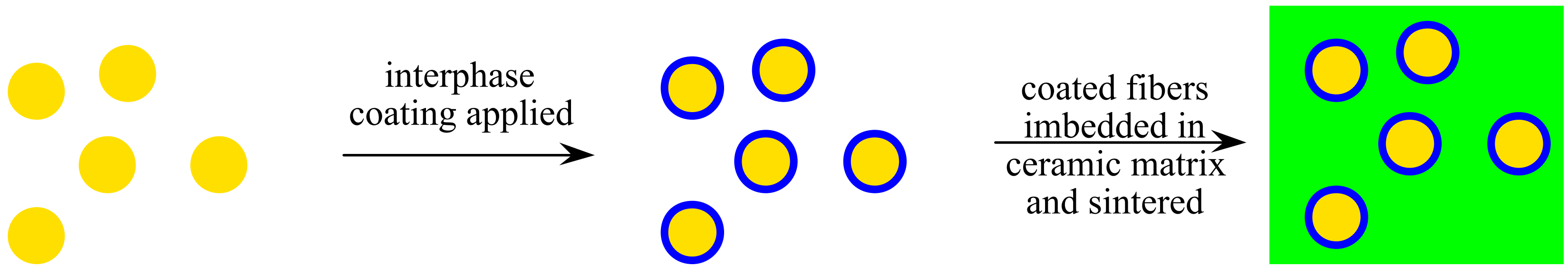




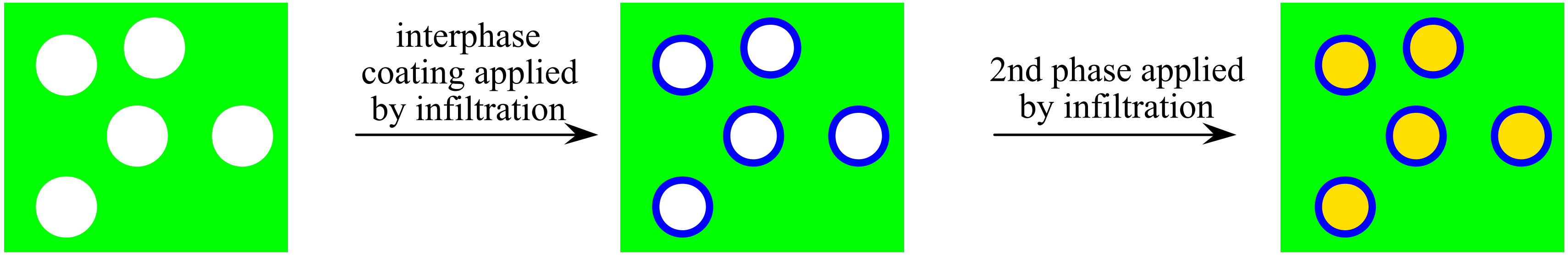
Alumoxane derived coatings show superior coverage as compared to sol-gel methods

alternative

Alternative Fabrication of FRCMC

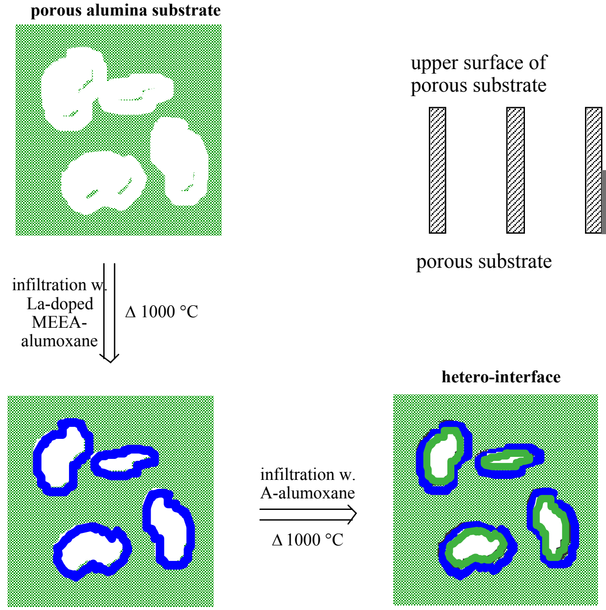


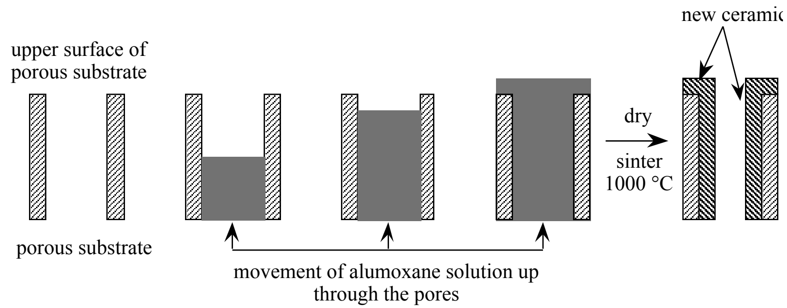
Limited range of ceramic fiber materials

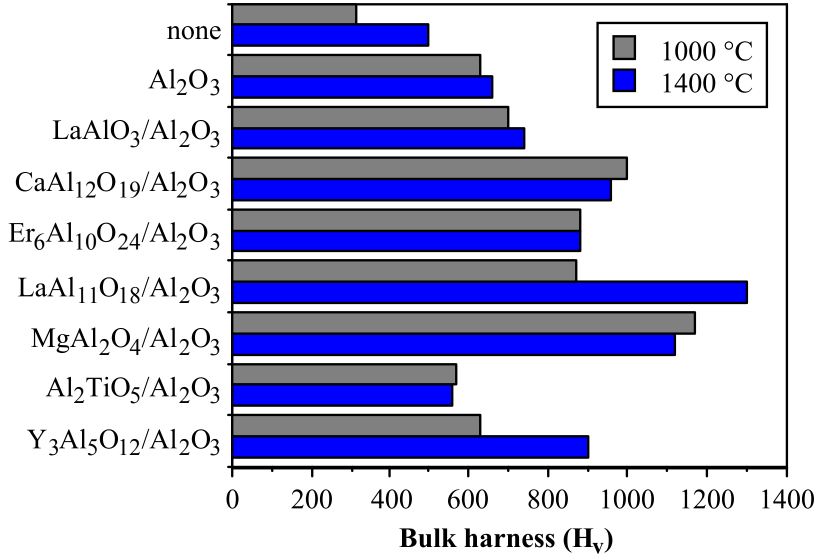


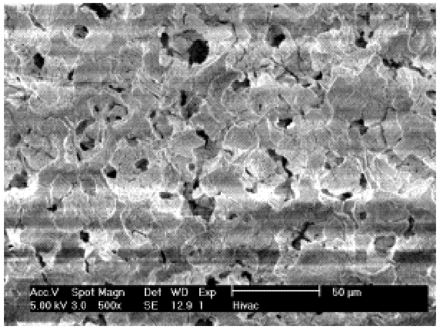
infiltrate

Infiltration Synthesis of a Ceramic-Ceramic Composite

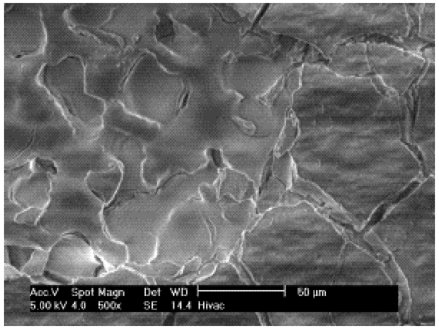








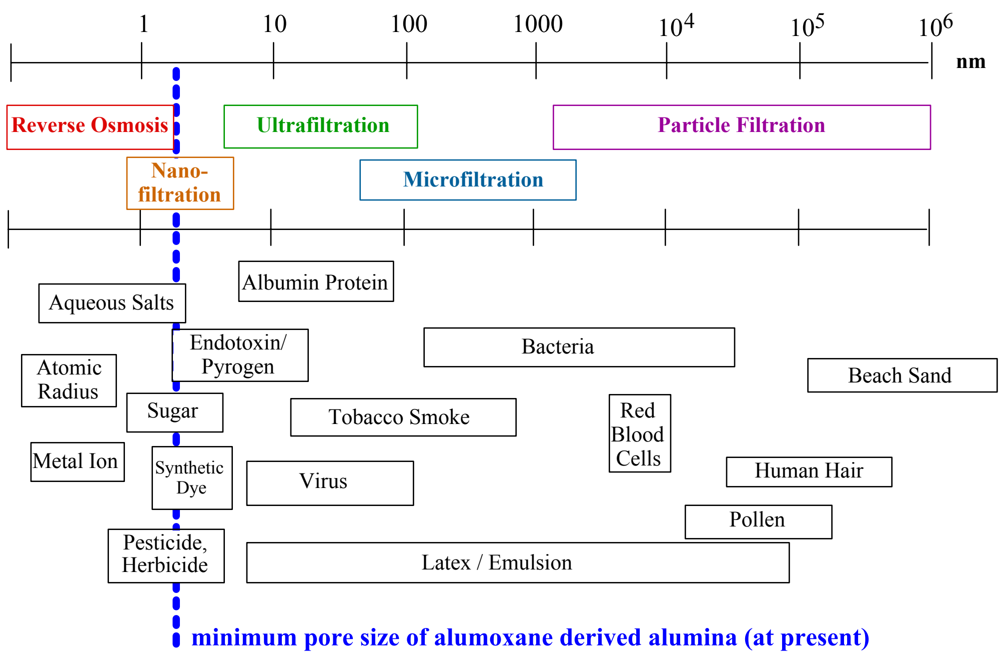
YAG ceramic (untreated)



Infiltrated by 12%wt A-A, fired to 1000 °C

filter

Why is Pore Size Important?

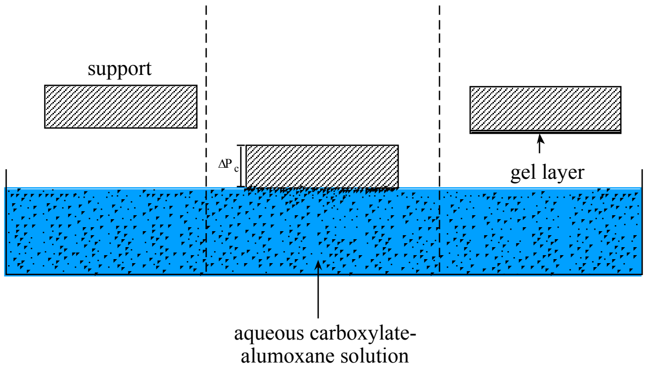


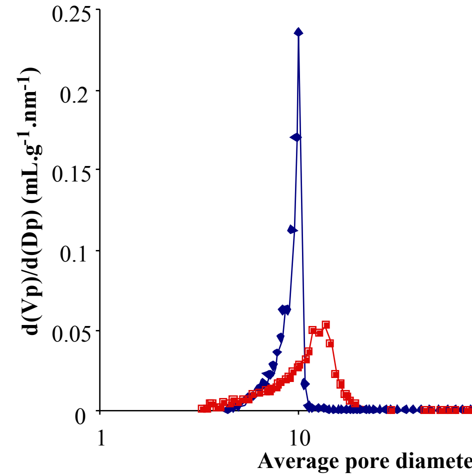
Industry	Application
Food and Beverage	wine stabilization and purification, concentration of skim milk
Petroleum	oil/water separation
Semiconductor	production of ultrapure water and purification of process fluids
Medical	injection water
Automotive	recovery of electrodeposition paints
Industrial Waste	concentration of oily waste

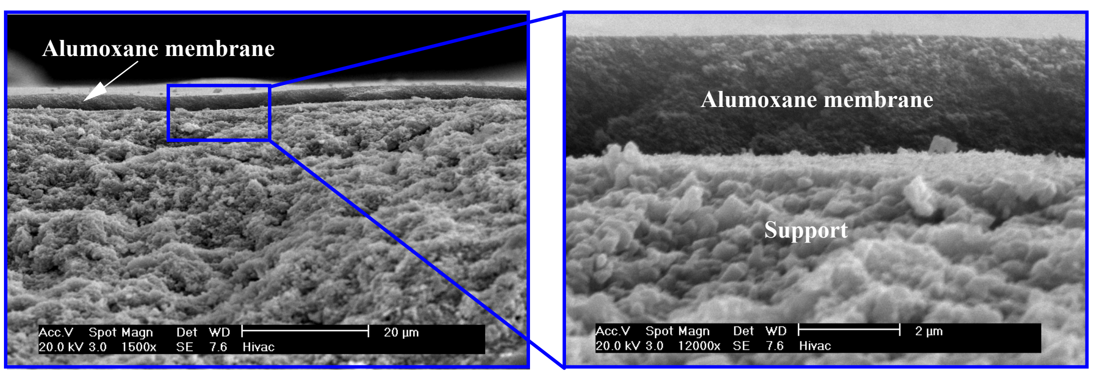
	Powder sintering	Sol-gel	metal-oxane approach
Process conditions	n/a	organic or strong acid	water
Energy consumption	high	low	low
VOC	yes	no	no
Ceramic yield	n/a	low	high
stability	n/a	hours	months to years

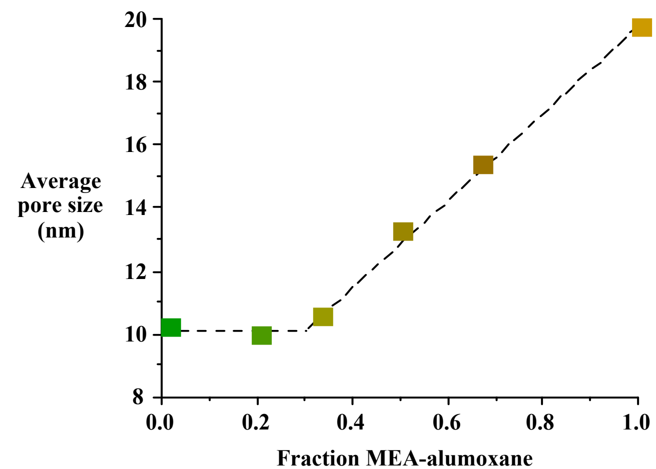
Make filter

Formation of Asymmetric Filters using Carboxylate-Alumoxanes







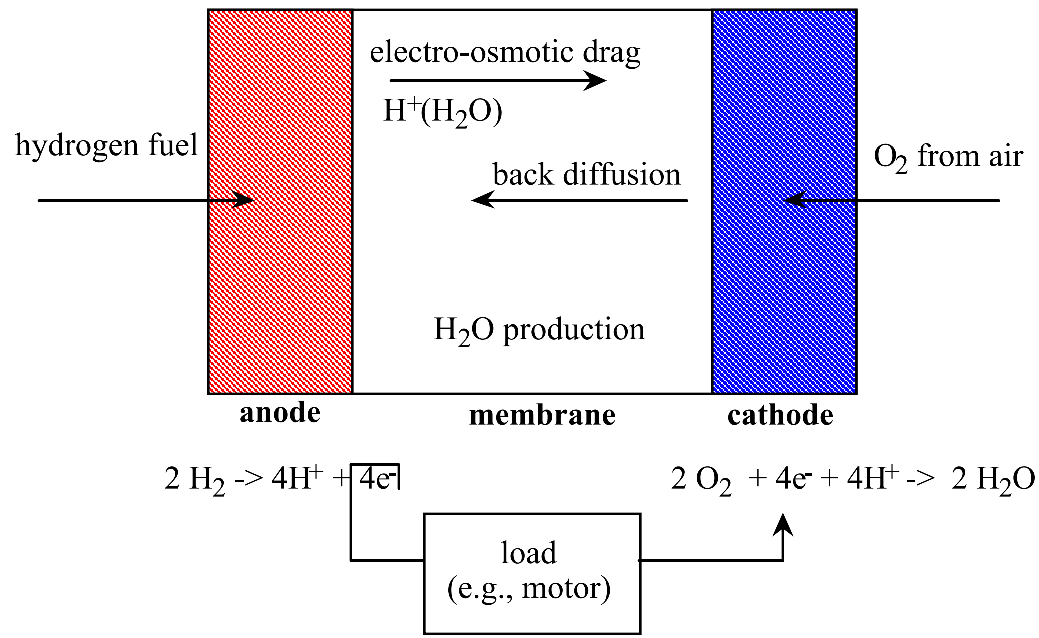


Ferroxane

Membranes for Proton Exchange Fuel Cells

Applications:
- electric vehicles
- stationary power
- emergency power

Transport:
- EU - buse program (2001)
- CA ZEV program (2003)
- Practical - 2020 (Federal)

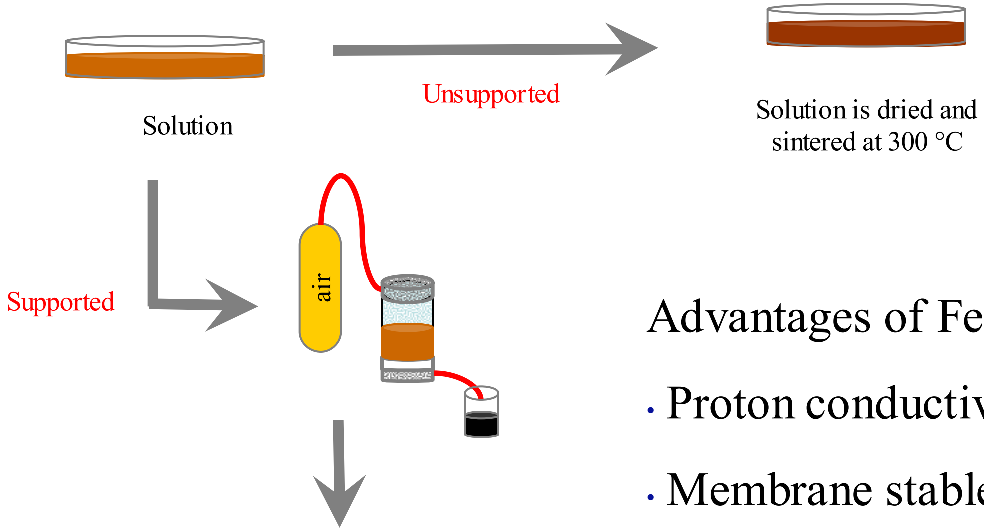


Disadvantages of Nafion-derived membrane:
- High cost
- Limited operating temperature
- High dependence on humidity

ours

Synthesis of Ferroxanes

$$[Fe(O)(OH)]_n + RCO_2H\ (xs) \longrightarrow [Fe(O)_x(OH)_y(O_2CR)_z]_n$$



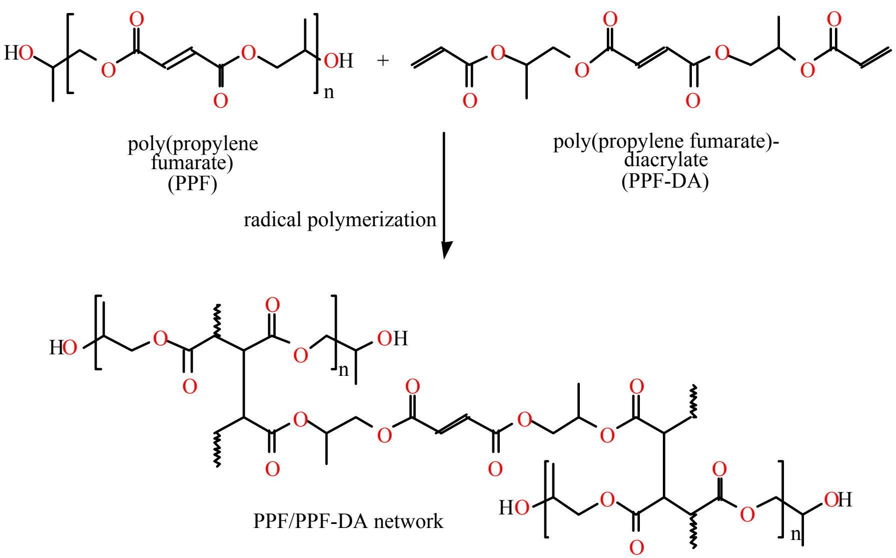
Advantages of Ferroxane-derived membrane:

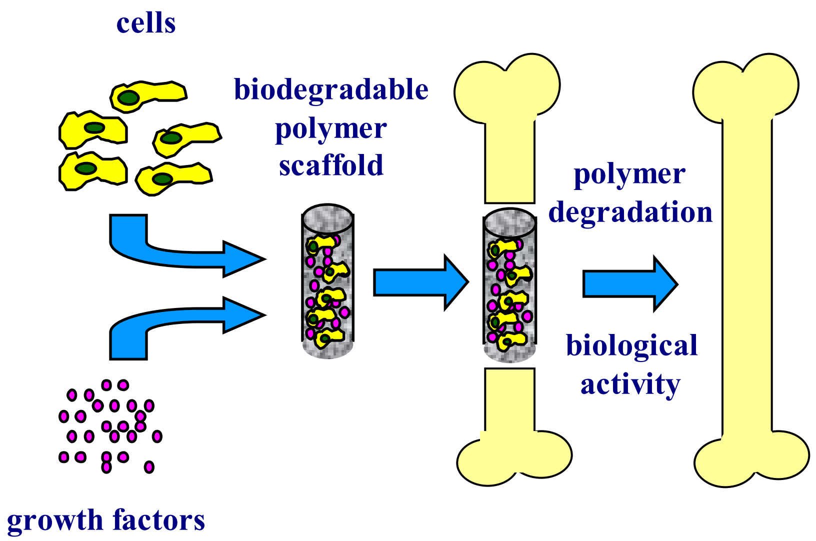
- Proton conductivity indifferent to relative humidity
- Membrane stable at elevated temperatures
- Proton conductivity comparable to Nafion
- Significantly reduced cost of production
- Possibly reduced total installed system cost
- Possible methanol crossover benefit

Bone Tissue Engineering

Develop bone tissue substitutes based on synthetic biodegradable polymers that will:

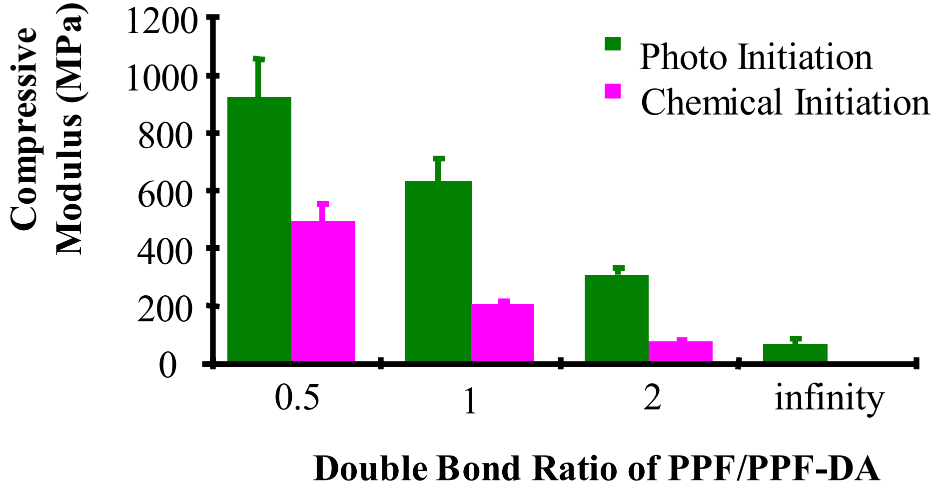
- Provide sufficient mechanical support to the wound site
- Act as a substrate for biological activity
- Eventually degrade and be replaced by new tissue





poly(propylene fumarate)/poly(propylene fumarate)-diacrylate (PPF/PPF-DA).

Mechanical Properties and Requirements



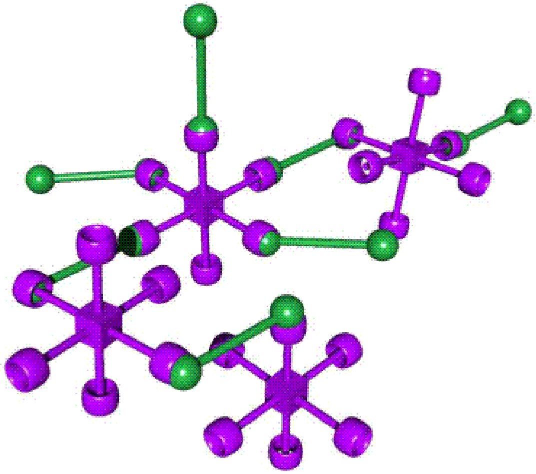
PPF/PPF-DA material properties can be controlled by the double bond ratio and initiator system.

Scaffolds must exhibit mechanical properties similar to those of bone

Material	Compressive Modulus (MPa)	Flexural Modulus (MPa)
Cancellous Bone (Porous)	**100**	**200**
Cortical Bone (Compact)	**17,000**	**17,000**
PPF/PPF-DA	**1,800**	**3,000**

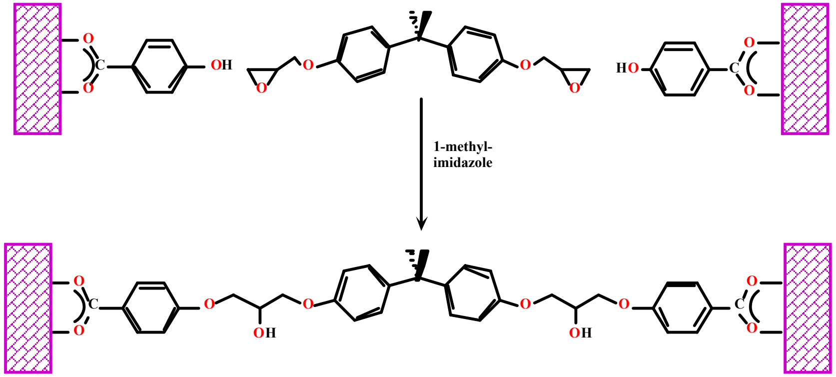
Nanoparticle Composites:
A Potential Route to Achieving "Natural" Strength

- Nanoparticles can mechanically reinforce polymer matrices:
  - Polymer chain immobilization
  - Polymer interface pinning
- Nanoparticle must be biocompatible and readily functionalized



Alumoxane-based resin system

Initial results with epoxides

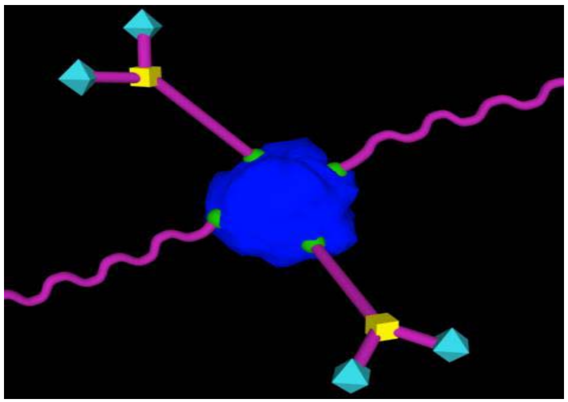


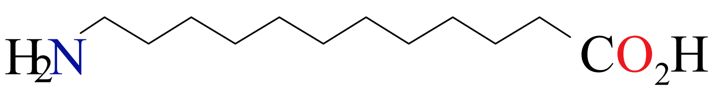
6-fold increase in flexural modulus

Our results

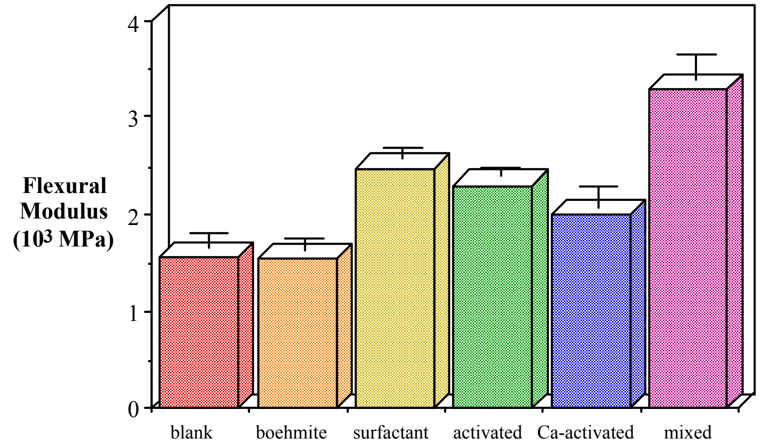
Alternative Approaches

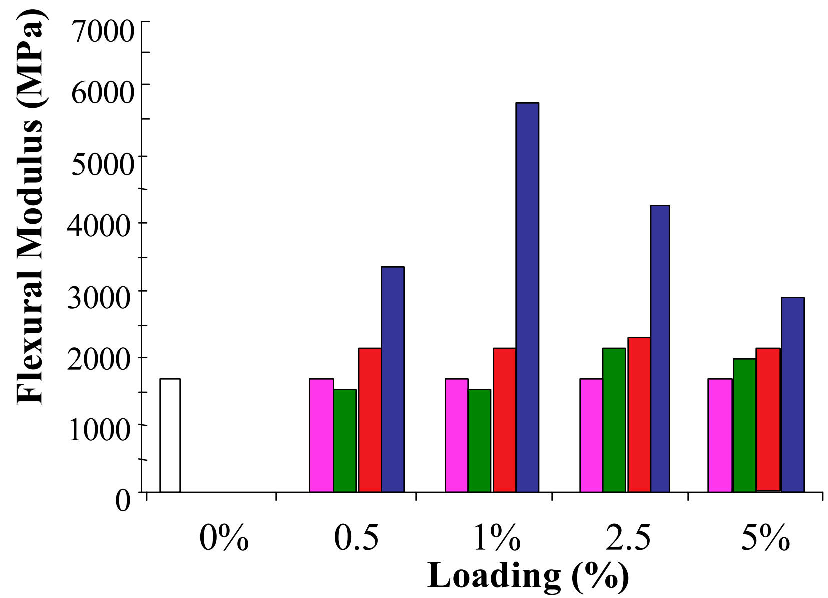
Achieve an activated dispersion of nanoparticles





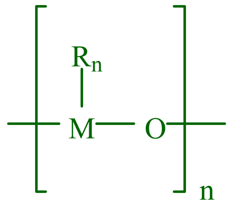
- Resin
- Unmodified boehmite
- Diacryloyl lysine alumoxane
- Stearic acid alumoxane
- Acryloyl undecanoic amino acid alumoxane

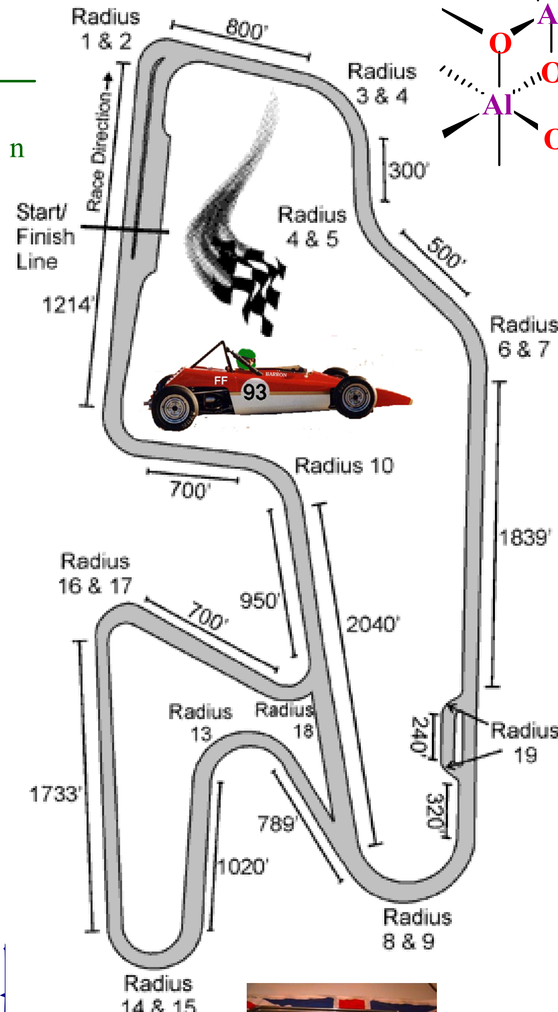


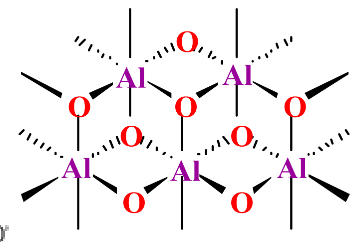


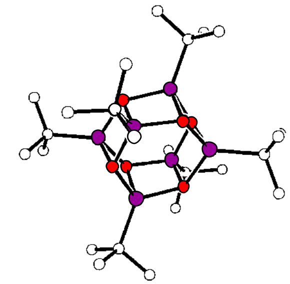
circles

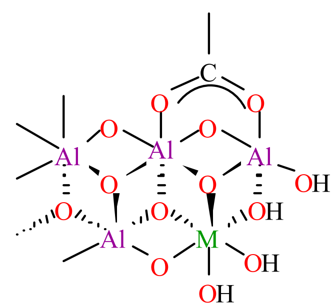
Going Round in Circles!

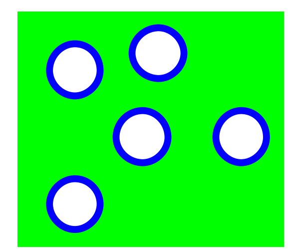


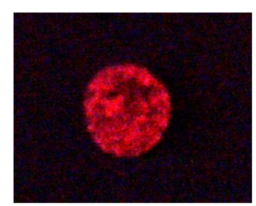


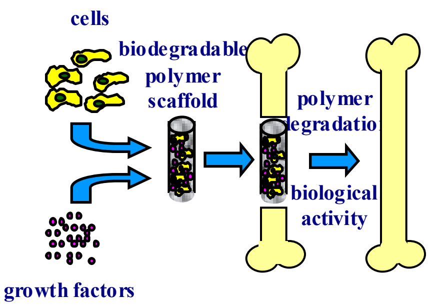


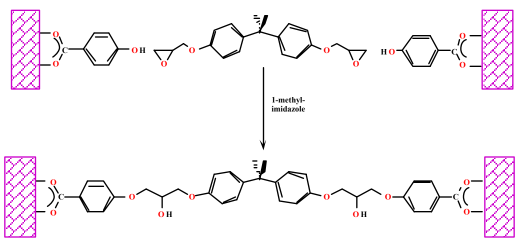


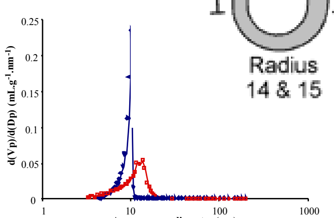










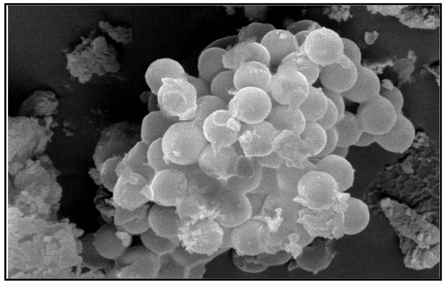


Oxane

Moving Towards Commercialization

OXANE
Nanostructured Innovations

- Energy-focused Rice University nanotechnology spinout, Barron, Wiesner, and Coker
- Two core innovations, alumoxanes and ferroxanes, enable the development of next generation *controllable-density proppants, high surface area adsorbents, fuel cell membranes, coatings and other high-value products*
- Solid international IP position



Who?

Who is on the Oxane Team?

- Chris Coker, President
  - Founder of a SRI/Taproot Ventures-backed communications startup
  - Commercialized technology with NASA-Ames scientists while with Taproot Ventures, sourced and evaluated numerous “small tech” opportunities from institutions such as SRI, Cornell, and UT
  - Associate to the CEO of Enron’s global trading organization, Greg Whalley
  - University of Chicago MBA
- Steve Costantino, Chief Technical and Operating Officer
  - Fourteen years with Cabot Corporation
    - Global Director, Tantalum Research & Development
    - Managing Director, New Business Development
  - Ph.D. in Materials Science, Penn State University
- Ryan Loscutova, Senior Scientist
  - Ph.D. in chemistry from Rice University and former Barron-group member
- Russell Smith, Lab Manager
  - Fomer New Product Development Scientist with Penreco, Mud Lab scientist at Baker Hughes (additives focus), and QA Scientist at Akzo Nobel

Summary

OXANE
Nanostructured Innovations

Never Say Never!

- Presentation of "Alumoxanes" @ the first Rice Alliance
- Research key component of EESI and CBEN
- Several false starts…
- Approach by Chris Coker
- Raised $2.6MM from institutional, corporate, and Angel investors
- Moving towards 2 near term products

CBEN
Center for Biological and Environmental Nanotechnology

ENVIRONMENTAL & ENERGY SYSTEMS INSTITUTE of Rice University

RICE ALLIANCE for TECHNOLOGY and ENTREPRENEURSHIP

Rick

Richard Smalley
(1943 - 2005)