Glass Processing

Advanced Fabrication: Sol-Gel Processing

Part I: February 12, 2015

Processing Steps and Chemistry

Part II: February 17, 2015

Applications, Monoliths and Thin Films

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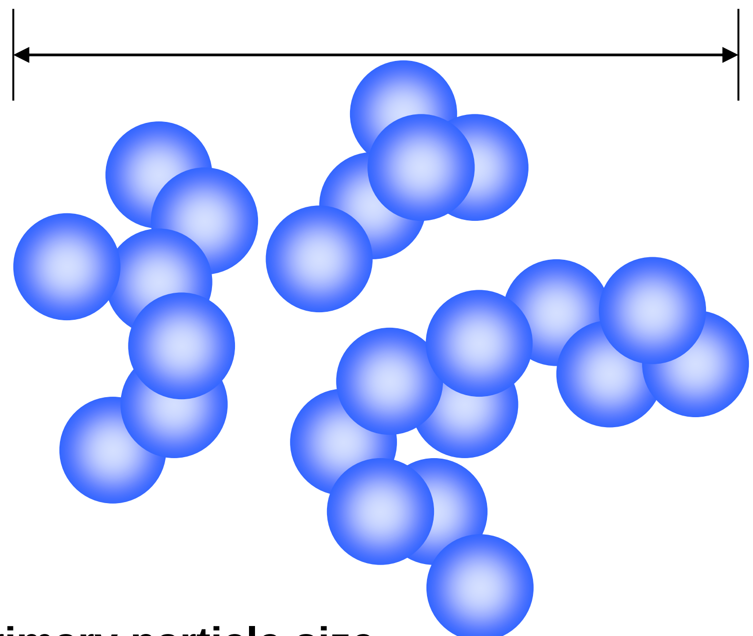
Particulate Silicas

Colloidal Silica

Primary particle size = 50 nm

Fumed Silica

Median Aggregate Size
dependent on Aerosil grade and milling conditions used
(e.g. A 90 aggregate approx. 120 nm - 150 nm)

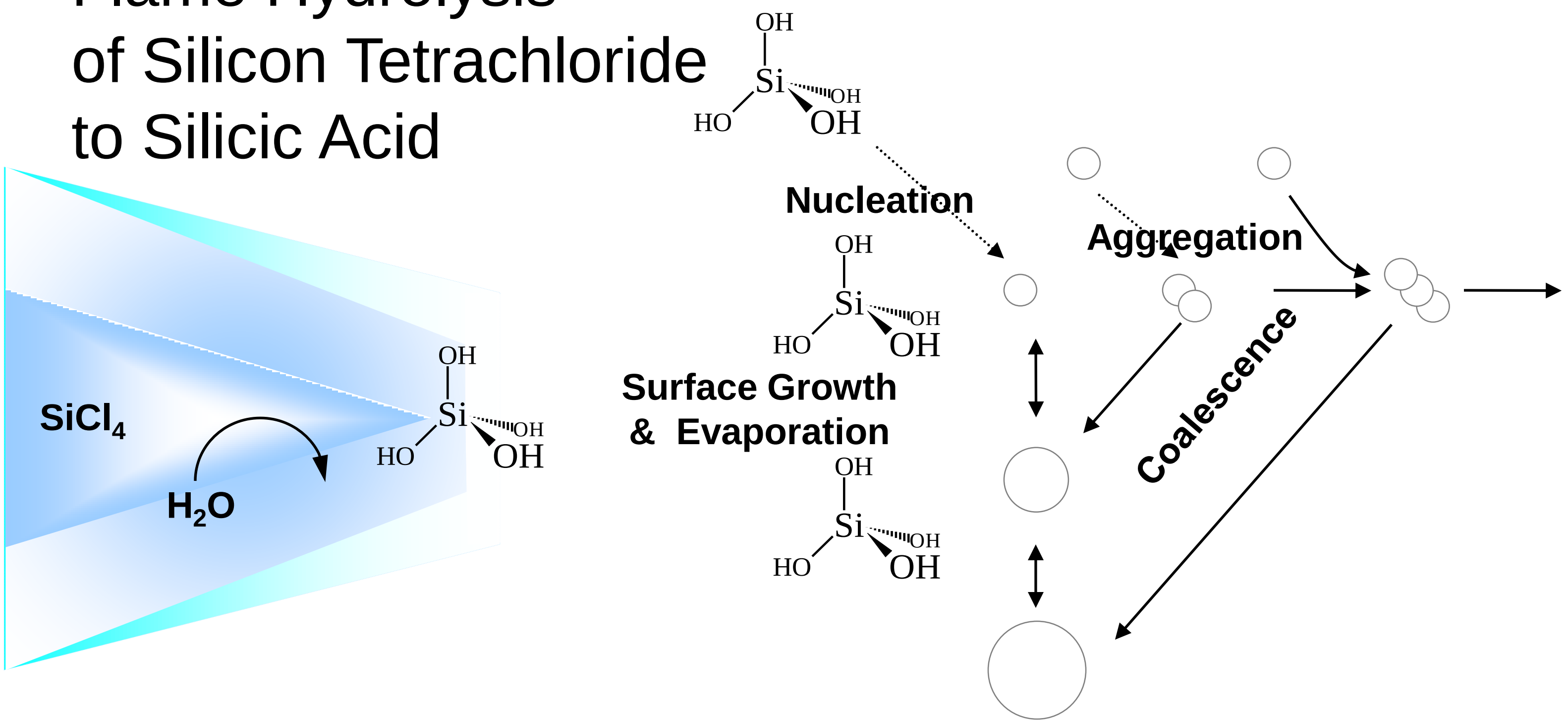


Primary particle size

(Aerosil 90 = 20 nm)

Fundamentals of Particle Formation

Flame Hydrolysis
of Silicon Tetrachloride
to Silicic Acid



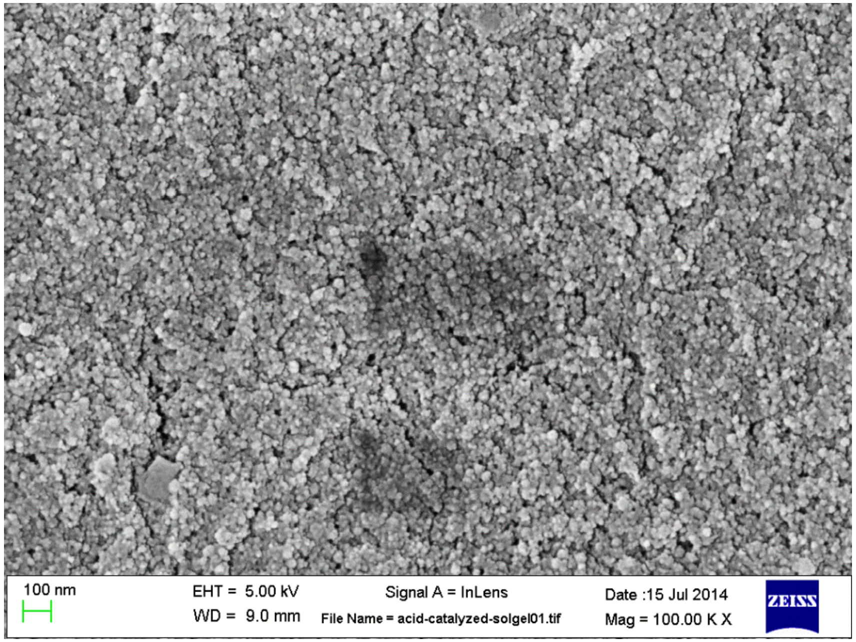
Degussa Aerosil®

Sol-Gel Process: Processing Steps

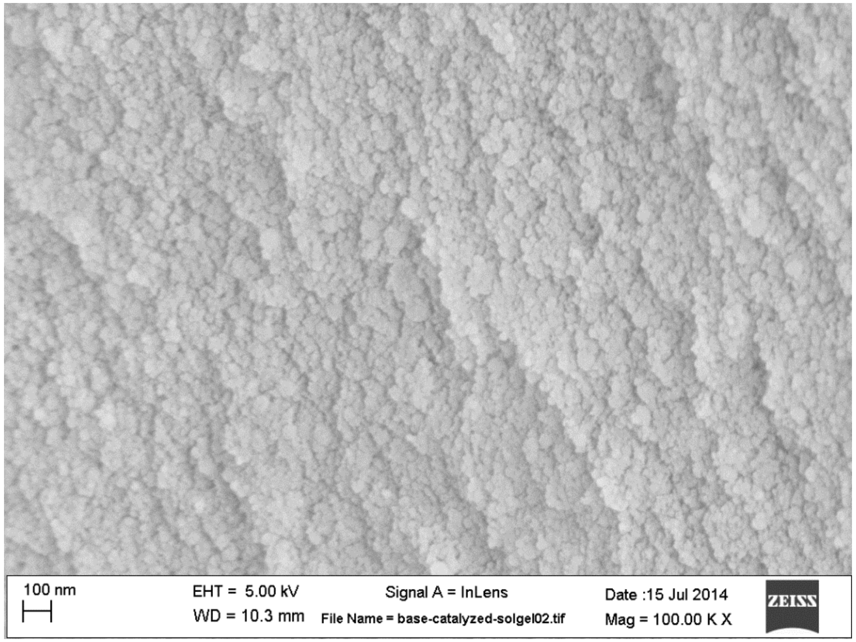
- Formulation
  - Acid-addition
  - Base-addition
  - Dilution
- Reaction
  - Hydrolysis
  - Polymerization
- Gellation – polymerization to "no-flow" condition
- Syneresis- spontaneous expulsion of solvent
- Drying – removal of pore fluid
- Shrinkage
- Consolidation
- Sintering

Scanning Electron Microscope (FESEM) Images of Gels

- Sample prepared by adding nitric acid
- Notice ~30 nm spheres



- Sample prepared by adding ammonium hydroxide
- Not as uniform



Drying

Xerogel

- Natural evaporation
- High capillary stresses
- Shrinkage, as much as 70% reduction in volume
- Problems with cracking

Aerogel

- Supercritical drying/CO_2 exchange
- No shrinkage
- Densities less than 0.1 g/cm^3
- Surface areas > 1,000 m^2/g

Xerogel - Drying leads to shrinkage

Sometimes the reduction in size is close to 70%

The sample on the left (which contains Rhodamine 6B dye) has gelled, synerized, and is beginning to shrink. The shrinkage has been arrested by sealing the container.

If the container is opened and the sample is allowed to shrink and dry, the sample on the right is achieved in about 1 month.

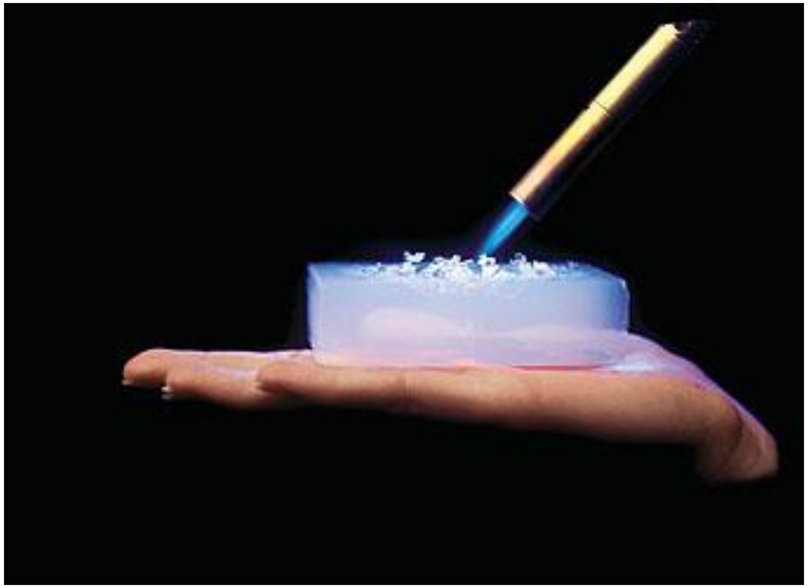
Aerogels – No shrinkage

Aerogels are extremely low density silica gels that can be used for thermal insulation.

Note how the aerogel can protect your hand from the heat of this flame.

Aerogels have many characteristics of silica glass, but they have the density of a cotton ball.

You can see light through them even though they are 85% pores. This is because the pores are smaller than the wavelength of visible light.



(We will come back to aerogels.)

Densification by Sintering

- Mechanisms of Densification
  - Relaxation
  - Dehydration
  - Viscous flow
- Modeled by Viscous Flow Models, e.g. Scherer’s Model, originally used for consolidation of porous preforms for optical waveguides

Determination of Viscosity for Viscous Flow Model

Calculated

$\eta = (\gamma/Kl_o)\,(\rho_s/\rho_o)^{1/3}$

η – viscosity

γ – surface tension

K – sintering parameter

l_o – cylinder length

ρ_s – skeletal density

ρ_o – initial bulk density

Measured in beam-bending

$\dot{d} = (WL^3)/(144I\eta(\rho_r/(3-2\rho_r))$

$\dot{d}$ - deformation rate cm/sec

η – viscosity

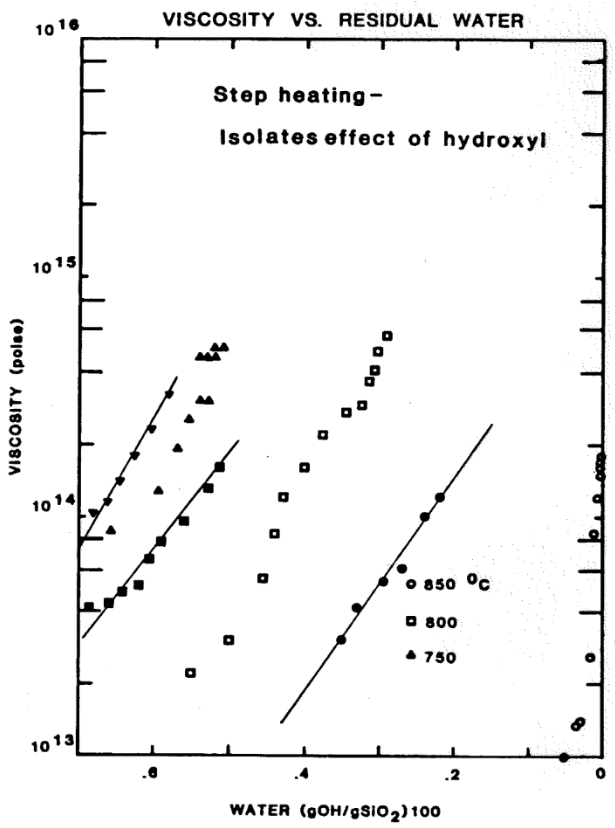
W – central load

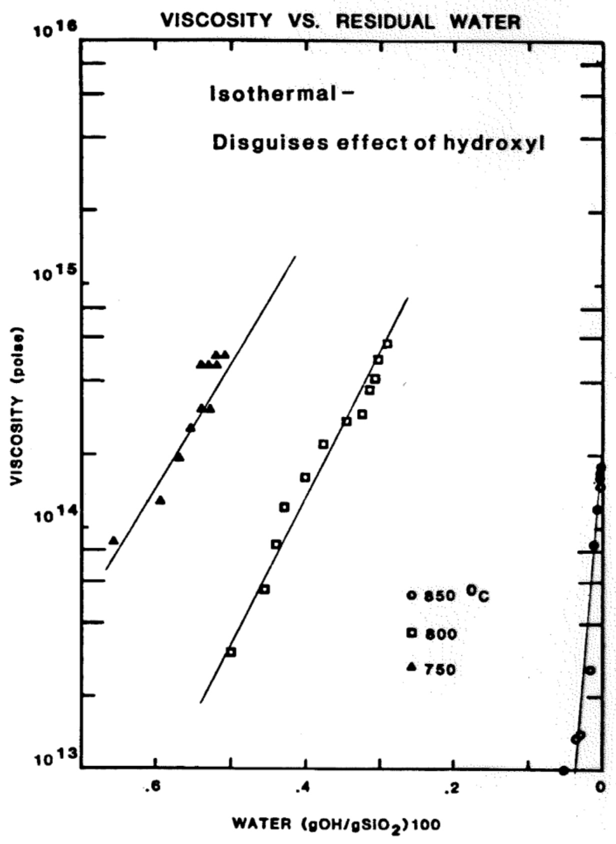
L – distance between supports

I – moment of inertia

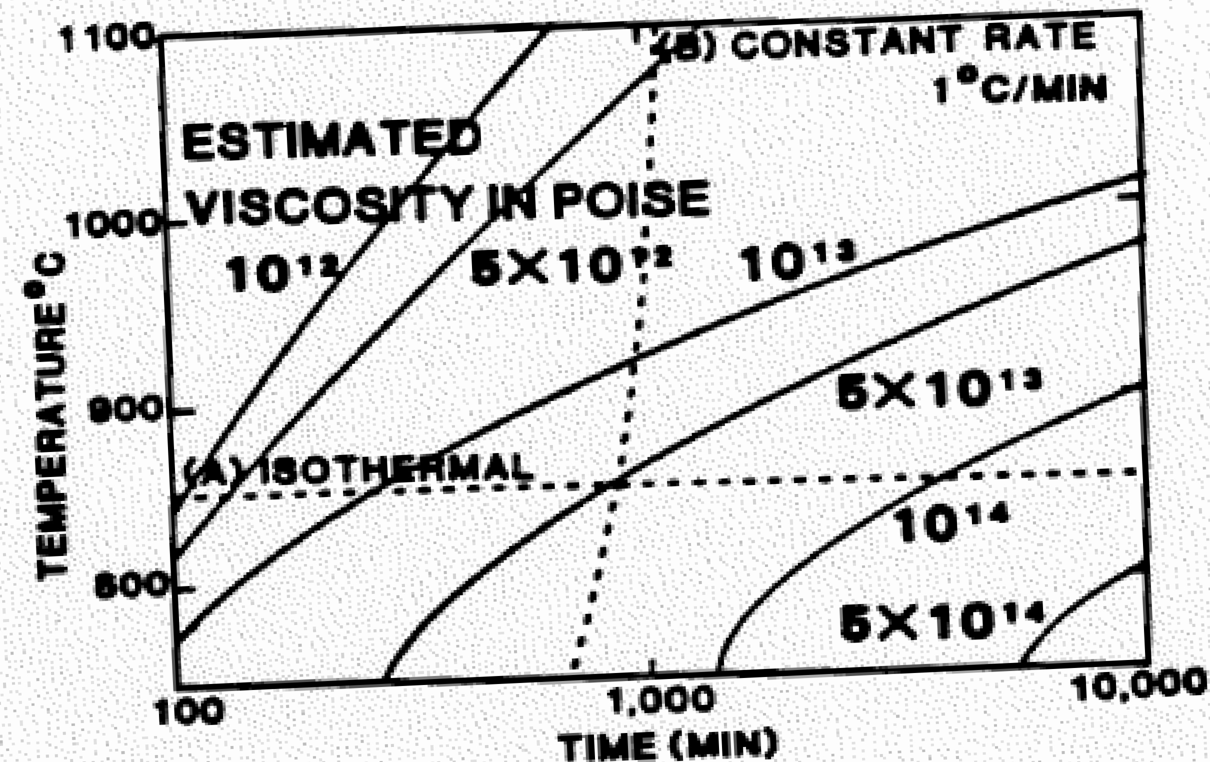
ρ_r – relative density

Separating the Effects of Temperature and Hydroxyl Content





Time and Temperature on the Viscosity Plot

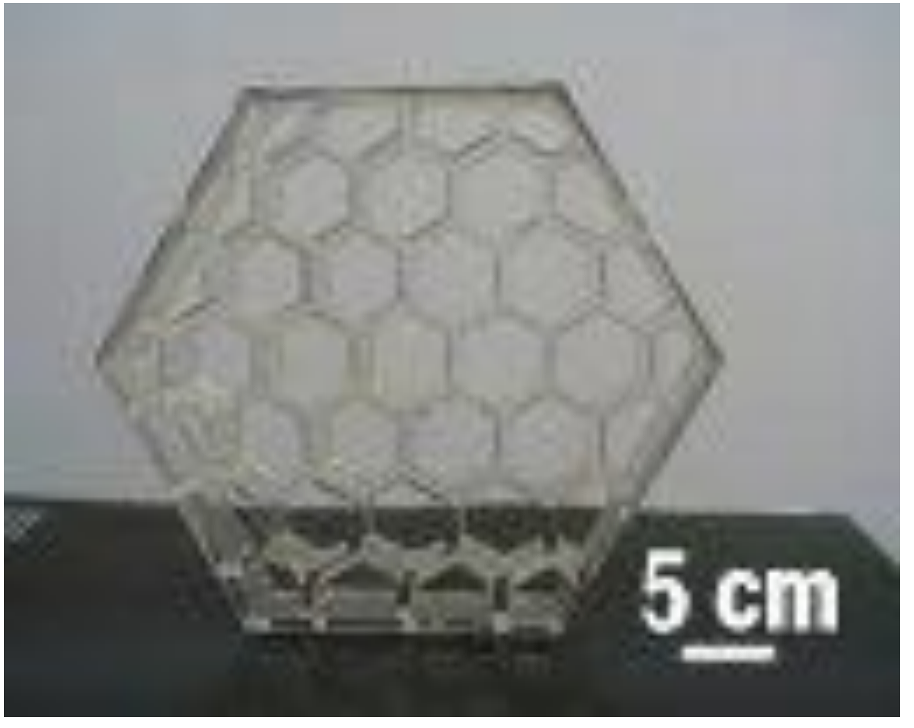


Densification of Pure Silica below 1000˚C

- To sinter requires a balance of dehydration and viscous flow.
- Before dehydration, the viscosity is depressed, which speeds up viscous flow.
- But water trapped in the gel results in bloating.
- A 3-step process takes advantage of relaxation, depressed viscosity, and finally, surface energy to reach full density (physical equivalent of conventional fused silica) by 1000˚C.

L. C. Klein, T. A. Gallo and G. J. Garvey, "Densification of monolithic silica gels below 1000^{o}C", J. Non-Cryst. Solids, **63** (1984) 23-33.

Fully Densified Honeycomb



Equivalent of fused silica from sintered “Shoup Gels”

Sol-Gel Process: Advantages/Unique Features

- Low temperature process
- High purity precursors
- Continuous porosity
- Molecular scale mixing
- Controlled hydrophobicity/ hydrophilicity
- Compatible with polymers
- Coats inside and outside
- Conformal coatings
- Hosts for organic molecules/ biomolecules
- Simple processing equipment (no vacuum)

Examples of Sol-Gel Materials

Form	Bulk	Thin Film	Fiber 	Aerogel	Membrane
Application	Molded Lens/GRIN Canon	Interference Filter (rear-view mirror) MAGNA MAGNA MIRRORS	Refractory (high temp-erature)	Thermal Insulation	Ultrafilter
Composition	Silica or Titania/ Silica	Titania/ Silica	Alumina/ Zirconia/ Silica AZS (3M'sNextel®)	Silica aspen aerogels	Alumina (Hoogoevens)
Attribute of SGP	Purity	Simplicity	Low temperature processing	Hyper-critical evacuation	Porous

History of Aerogels

1930's: Discovery by Kistler, Stanford, suffered set-back when lab blew up

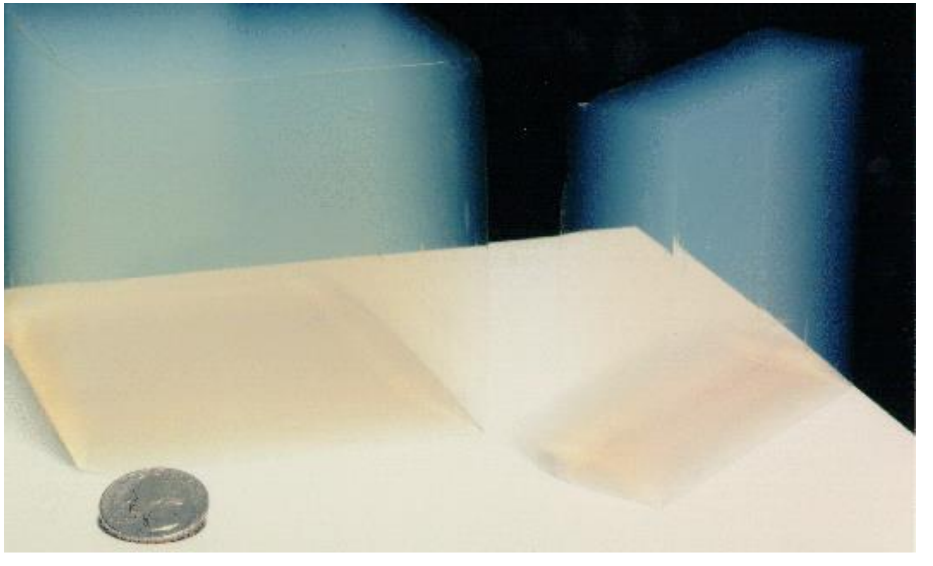
1960's: Teichner, France, rocket propellant storage, quicker production method

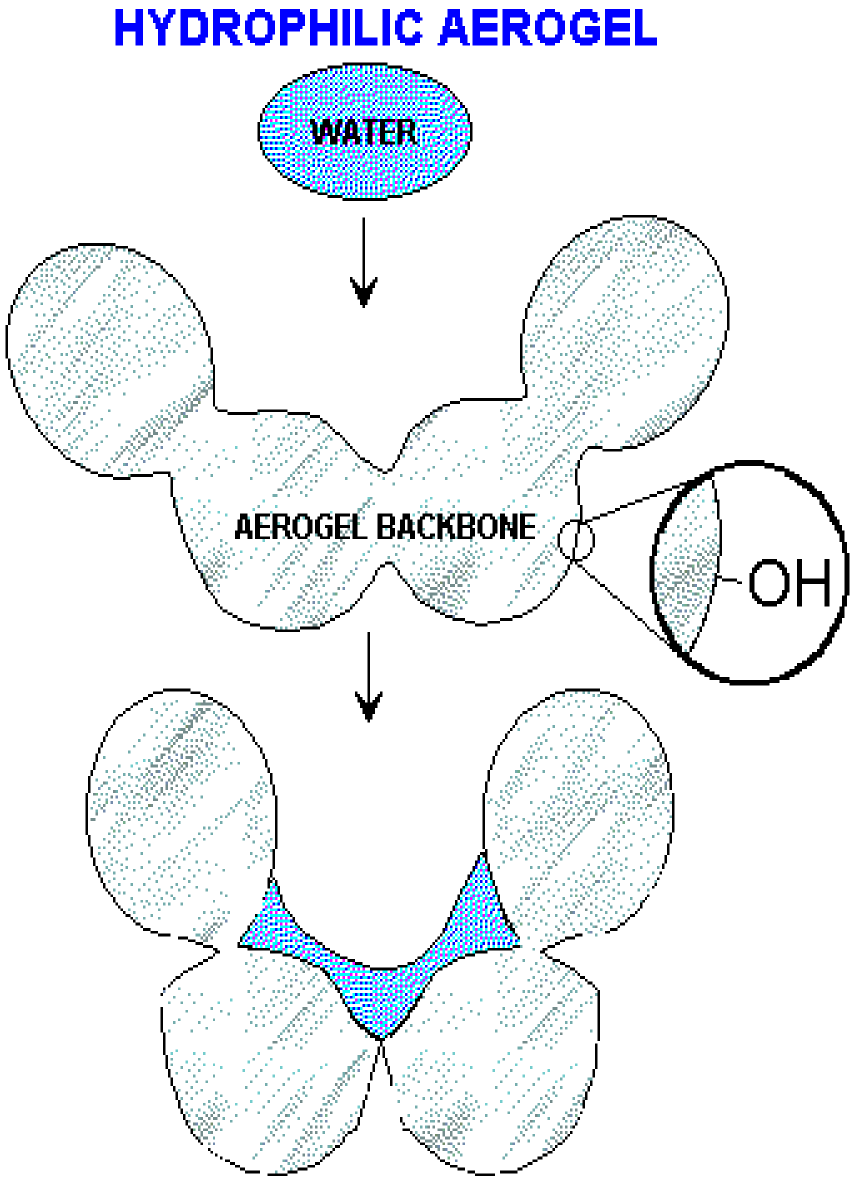
1980's: Henning, Sweden, Cherenkov radiation detectors, first manufacturing facility

1980's: Hunt, LBL--Safer production method, Shuttle missions, Mars Rover

1990's: Brinker, Smith, Sandia NL

eliminate supercritical drying step, "ambigels"

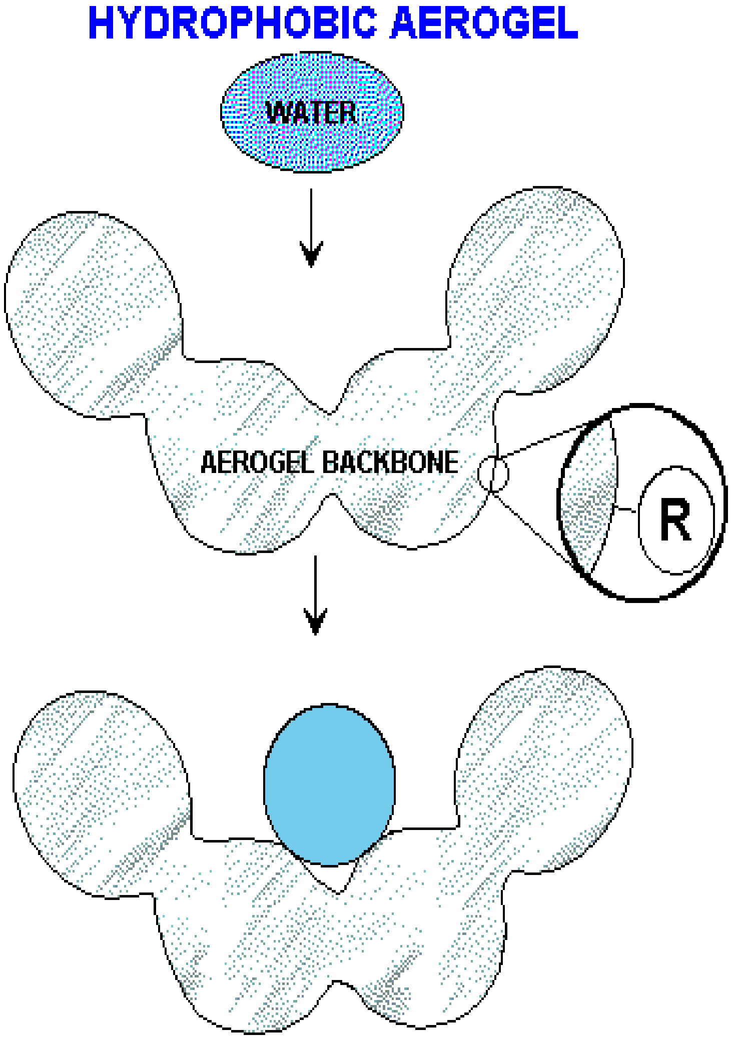




Hydrophilic - affinity for water

Contact angle <90°

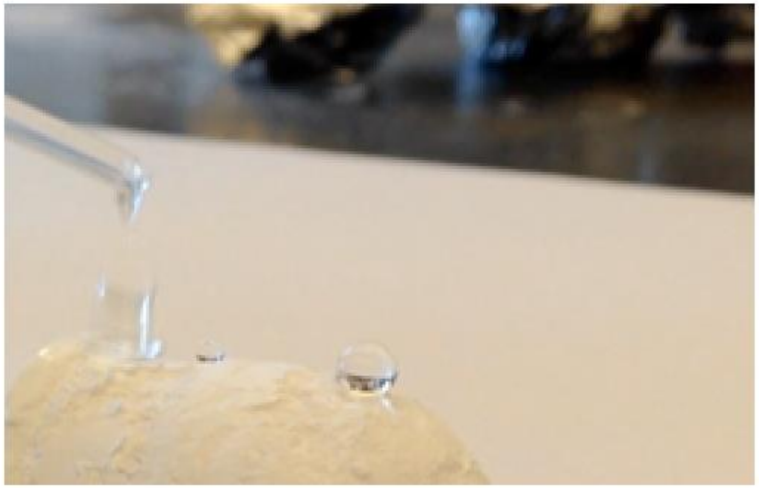
Spreading when angle is 0°



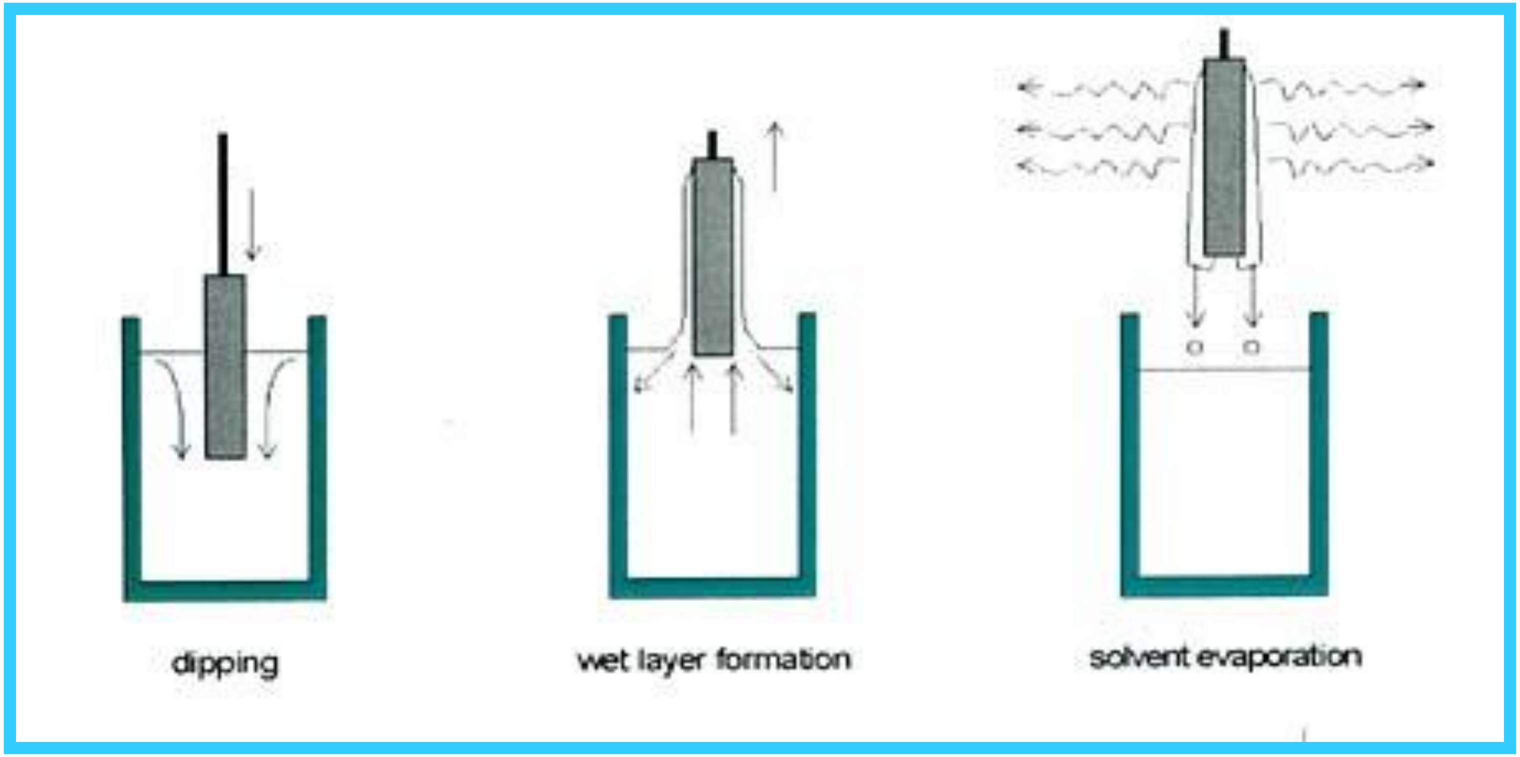
Hydrophobic - water repellent

Contact angle >90°

Bouncing, beading and rolling when angle is 180°



Sol-Gel Process for Coatings: Dipping



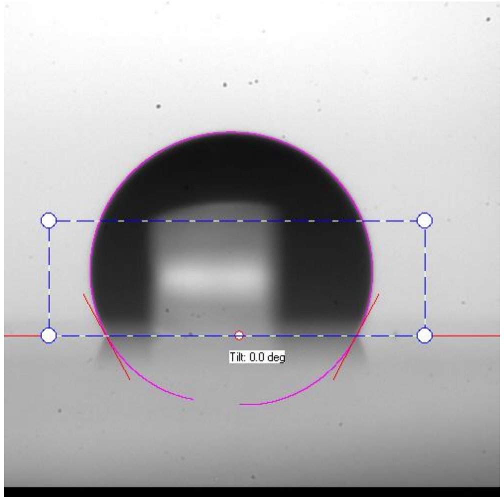
Sol-Gel Coatings for Changing Surface Energy

Water rolling down a hydrophobic coating on glass slide.

A. Jackson, A. Jitianu, and L. C. Klein, "Development of Hermetic Barrier Using Vinyl Triethoxysilane (VTEOS) and Sol-Gel Processing" Material Matters (Sigma-Aldrich) **1** [3], 2006, 11-12.

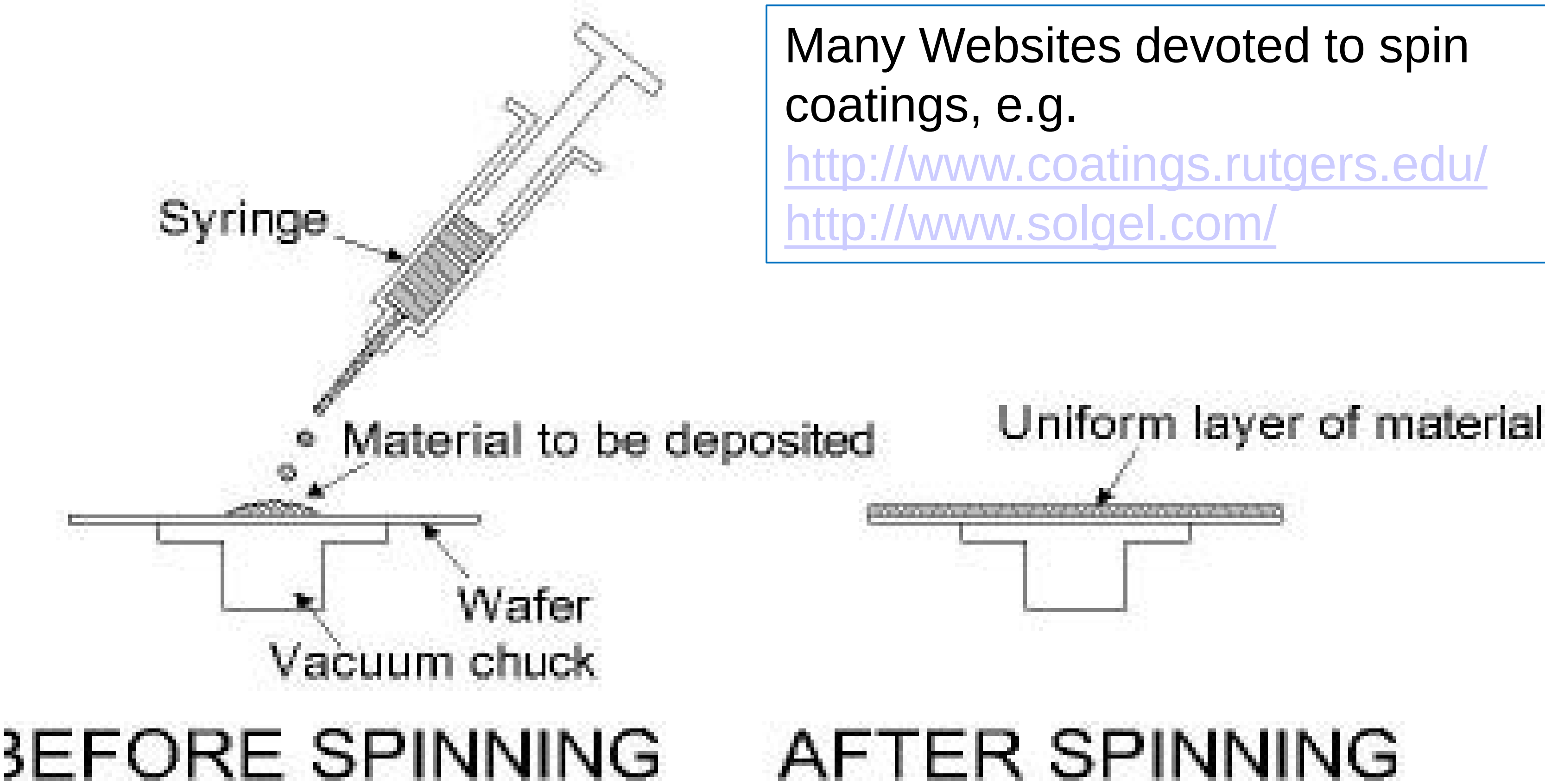
Contact Angle

$\theta = 118^o$



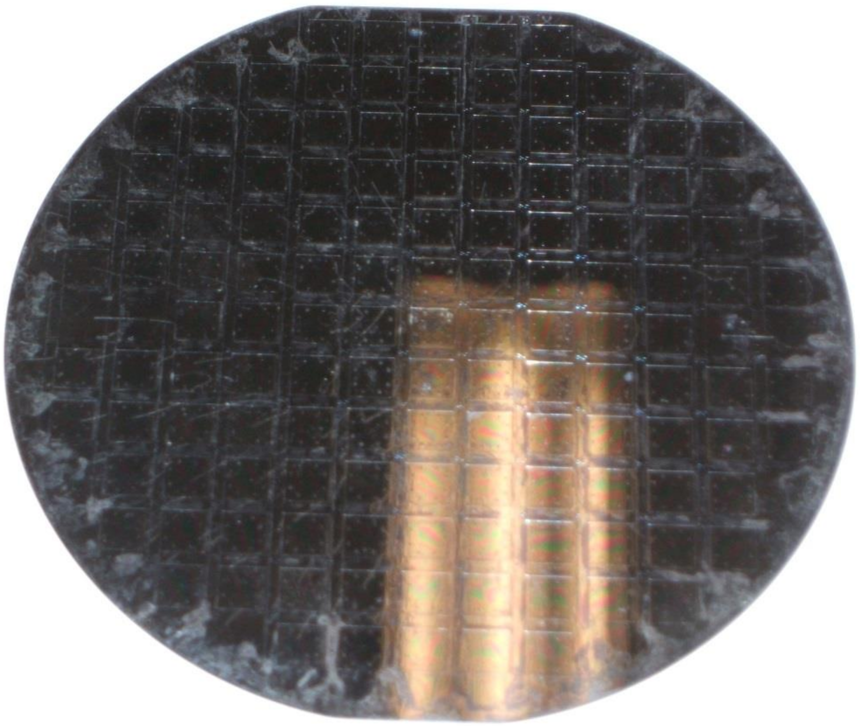
Sol-Gel Process for Coatings: Spinning

Many Websites devoted to spin coatings, e.g.
http://www.coatings.rutgers.edu/
http://www.solgel.com/



Spin Coating with Fringes

A patterned silicon wafer with an electrostatic bonding composition spun on from a sol-gel solution – Generally, there are no fringes because the film is uniform, but a non-uniform samples was photographed here to show the presence of the coating.

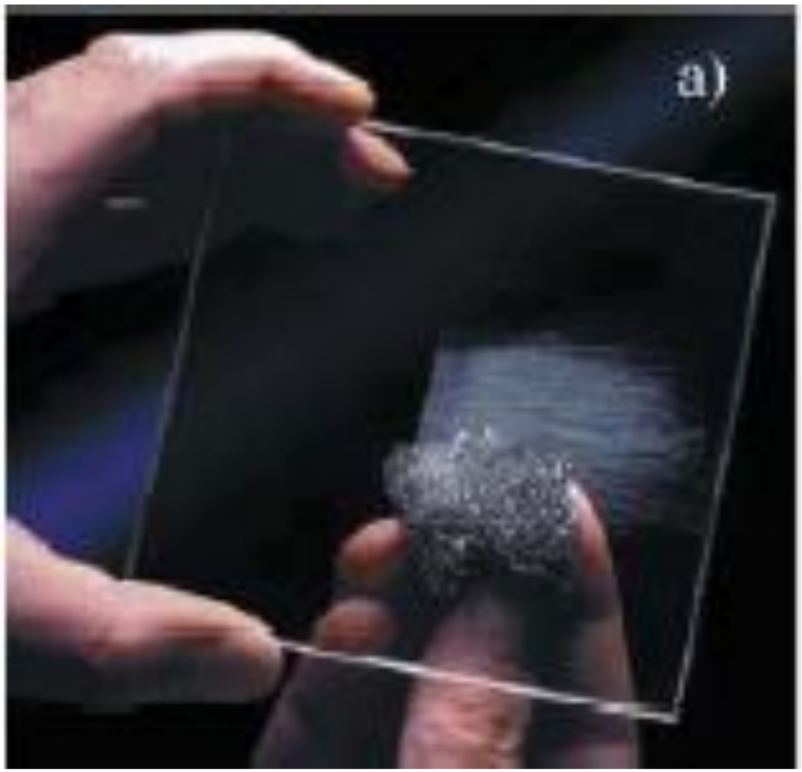


Sol-Gel Coatings for

Optical, Electronic, Magnetic, and Functional Applications

- Photoresist for defining patterns in microcircuit fabrication.
- Dielectric/insulating layers for microcircuit fabrication (SOG)
- Magnetic disk coatings - magnetic particle suspensions, head lubricants.
- Flat screen display coatings - Antireflection coatings, conductive oxide (ITO).
- Television tube phosphor and antireflection coatings
- Self-cleaning, photocatalytic.
- Anti-graffiti, anti-fouling, anti-microbial.
- Electrochromic, photovoltaic, selective absorbers, etc.

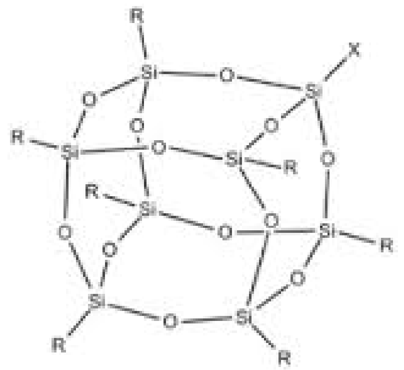
ORMOSILS (organically-modified silicas) are finding commercial applications, for example:



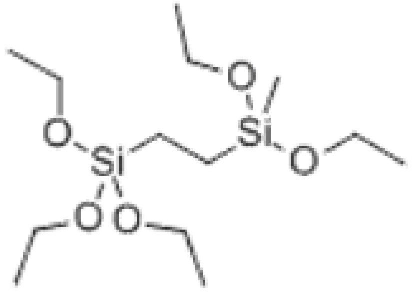
Protective ORMOSIL coatings: Half of glass plate coated with ABRASIL® showing scratch resistance
C. Sanchez, B. Julian, P. Belleville, M. Popall, J. Mat. Chem., 2005, 15, 3559-3592.

Categories of Hybrid Nanocomposites

- Polyoctahydridosilsesquioxanes (POSS) containing cage-like structures R_n'-$Si(OR)_{4-n}$
  - porous



- Silicon oxycarbides, generally formed by thermal decomposition 1(triethoxysilyl)-2-(diethoxymethylsiliyl)ethane (TESDMSE)
  - contain –C-C- bonds



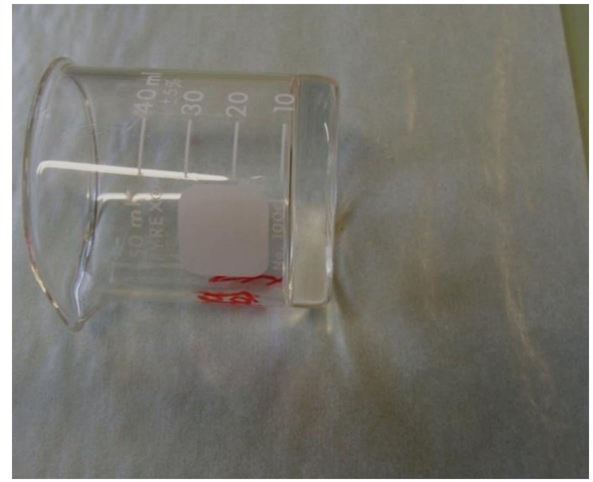
- "Melting Gels"

Melting Gels
(do not really melt, but they show glass transition behavior at or below room temperature)

A special class of organically modified silica sol-gels.

Thermal Behavior:

- rigid at room temperature →



- flows at temperature T_1 →

- consolidates at temperature T_2 ($T_2 > T_1$), when crosslinking is complete
- The process softening → becoming rigid → softening can be repeated many times, until heated to T_2.

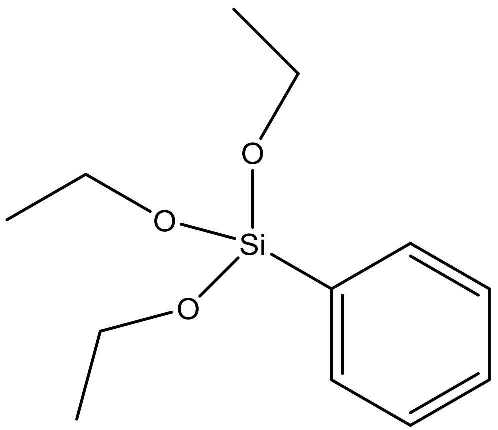
L. C. Klein and A. Jitianu, "Organic-Inorganic Hybrid Melting Gels", J. Sol-Gel Science & Tech., **55**, 2010, 86-93

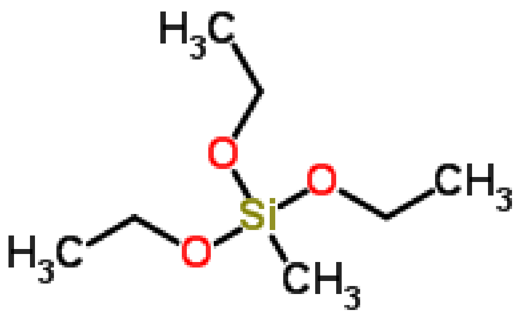
Mixed Substitutions: *Precursors*

To adjust *glass transition*, softening temperature, consolidation temperature, physical properties, etc.

Mono-substituted siloxane

Di-substituted siloxane





Phenyltriethoxysilane (PhTES)
trifunctional

Dimethyldiethoxysilane (DMDES)
di-functional

Hybrid Gels for Patterning and Texturing

- Simpler than focused ion beam (FIB) to mill microlens array on a mold material, which can be later used for replication using a hot embossing process
- Using Microcapillarity in Melting Gel could be much simpler.

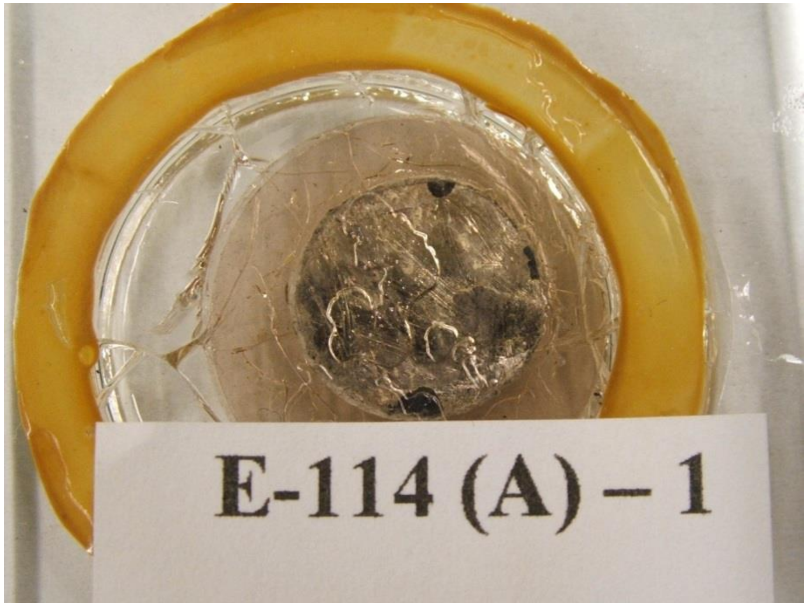
L. C. Klein, B. McClarren and A. Jitianu, “Silica-Containing Hybrid Nanocomposite “Melting Gels”” Thermec 2013 Symposium on Advanced Protective Coatings/Surface Engineering, ed. B. Mishra, M. Ionescu. And T. Chandra, Materials Science Forum, Trans Tech Publishers, Vol. 783-786, 2014, pp. 1432-1437.

Hermeticity

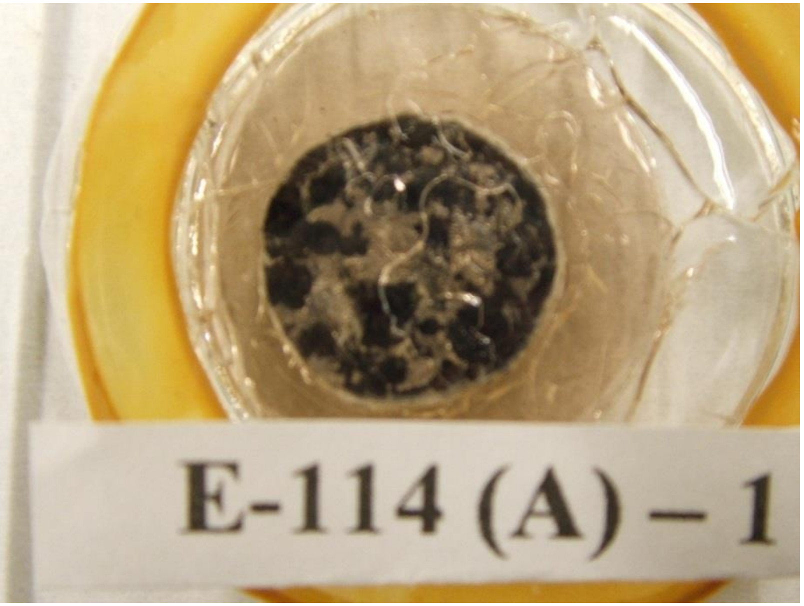
Observe the oxidation of Li metal (shiny disc) protected by poured melting gel (PP ring on glass slide). 70%MTES-30%DMDES stored at 70^{o}C in air.

Decay constant ~.01%/sec^{-1}

A. Jitianu and L. C. Klein, “Encapsulating Battery Components with Melting Gels Ceramic Transactions 250: Advances in Materials Science for Environmental and Energy Technologies III, eds. T. Ohji, J. Matyas, N. J. Manjooran, G. Pickrell, A. Jitianu, American Ceramic Soc., Westerville, OH, 2014, pp. 279-286.

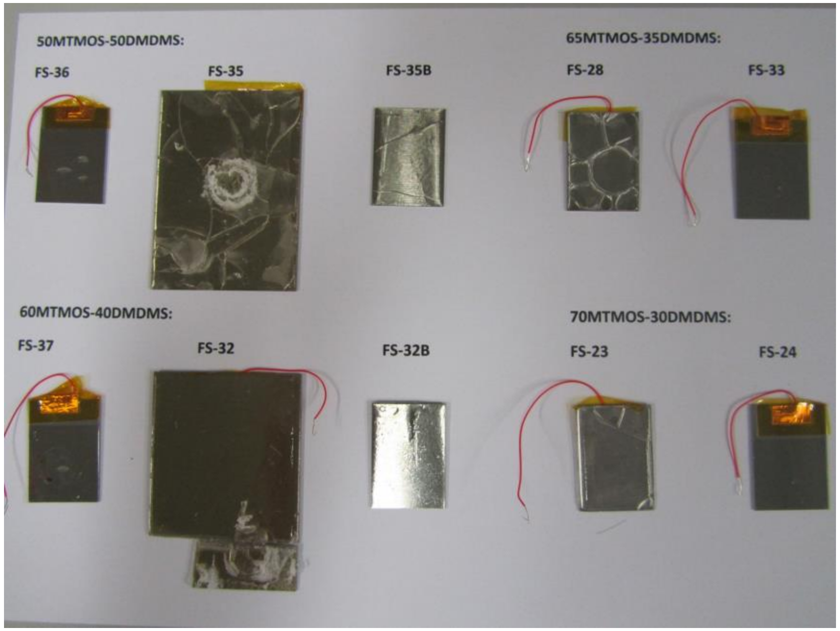


After 24 hours

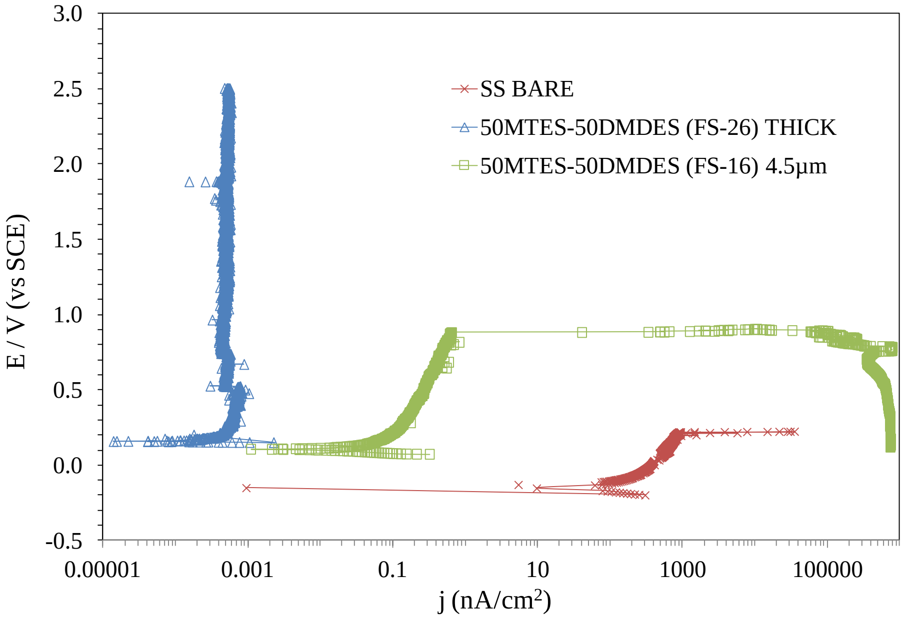


After 504 hours

Anodic Polarization
(First day of immersion in 3.5 wt. % NaCl)



Even a thin coating is able to provide four orders of magnitude lower current density than bare 304 Stainless

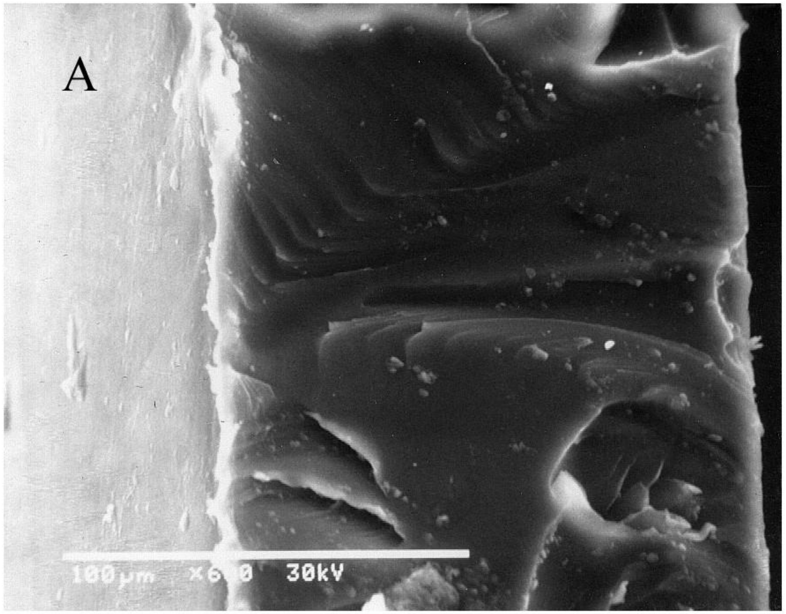


DMR Award #1313544, Materials World Network, SusChEM:

Hybrid Sol-Gel Route to Chromate-free Anticorrosive Coating

Hybrid Membranes for Proton Exchange Membrane (PEMFC)/ Direct Methanol (DMFC) Fuel Cells

SEM micrograph (cross section) of an infiltrated Nafion™ membrane



Results:

- $TiO_2 \cdot SiO_2 \cdot P_2O_5$/Nafion membranes prepared by a precursor-infiltration sol-gel method
- Swelling in methanol was significantly reduced
- Proton conductivity/water retention increased with treatment in phosphoric acid
- Proton conductivity/swelling controlled by the amount of infiltrated oxides
- L. C. Klein, Y. Daiko, M. Aparicio, and F. Damay, "Methods for modifying proton exchange membranes using the sol-gel process", Polymer **46**, 2005, 4504-4509.

Applications for Hybrid Gels

- Substitute for all inorganic glasses
- Low temperature hermetic seal for temperature-sensitive applications
- Hydrophobic coating on metals, glasses and ceramics
- Transparent dielectric coating
- Abrasion resistant coating
- Good adhesive for substrates and electrode materials
- Delivery system for covering selected locations with a syringe (“direct-write”) or pouring
- Medium for texturing and patterning with transfer stamp around glass transition, followed by *consolidation*

Sol-Gel Process: Advantages/Unique Features

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Application	Molded Lens/GRIN (Canon)	Interference Filter (rear-view mirror)	Refractory (high temp-erature)	Thermal Insulation	Ultrafilter
Composition	Silica or Titania/ Silica	Titania/ Silica (Donnelly)	Alumina/ Zirconia/ Silica AZS (3M'sNextel®)	Silica (Aspen)	Alumina (Hoogoevens)
Attribute of SGP	Purity	Simplicity	Low temperature processing	Hyper-critical evacuation	Porous

Sol-Gel Processed *Glasses* Come in Many Shapes and Sizes

Monoliths

Xerogels

Aerogels

Hosts for Dyes

Thin Films

Composites

Hybrids

etc.