# Slurry-Based Environmental Protection Systems

**Beth Armstrong and Glen Kirby**

## Environmental Barrier Coating Workshop
## Nashville, Tennessee

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# Outline

- Overview of coating approach
- Review of surrogate (mullite), doped alumino-silicate, and yttrium silicate coating study results
- Path forward

# Material vs. Process

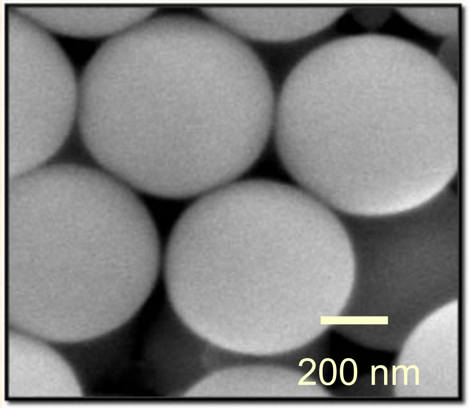
**Coating Performance = f(Material + Processing + Environment)**

| Material | Processing | Environment |
|---|---|---|
| Phase/Structure | Uniform Thickness | Temperature |
| Purity | Porosity/Defects | Atmosphere |
| Reactivity/Diffusivity | Wetting/Adherence | |
| Strength | Flow/Rheology | |
| Surface Tension | State of Stress | |
| Surface Charge | Surface Charge | |

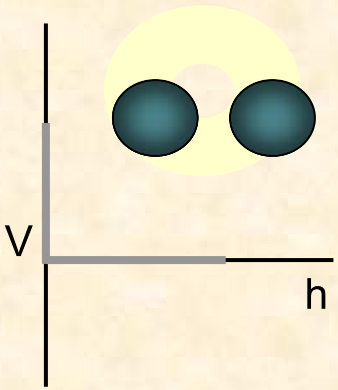
# Tailoring Interactions Between Colloidal Particles

**Colloidal particles --> basic “building blocks”**

- **must control interparticle forces to tailor structure, rheological properties, and drying**

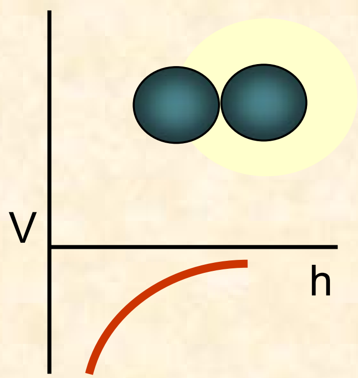



**Hard sphere**



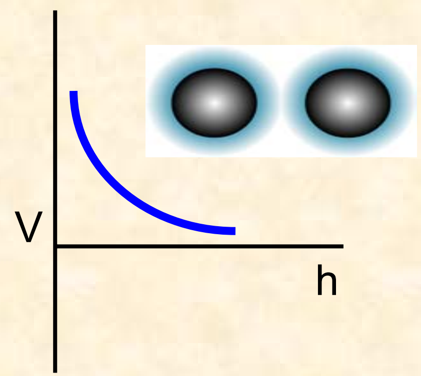

indexed matched
highly screened

**Attractive**



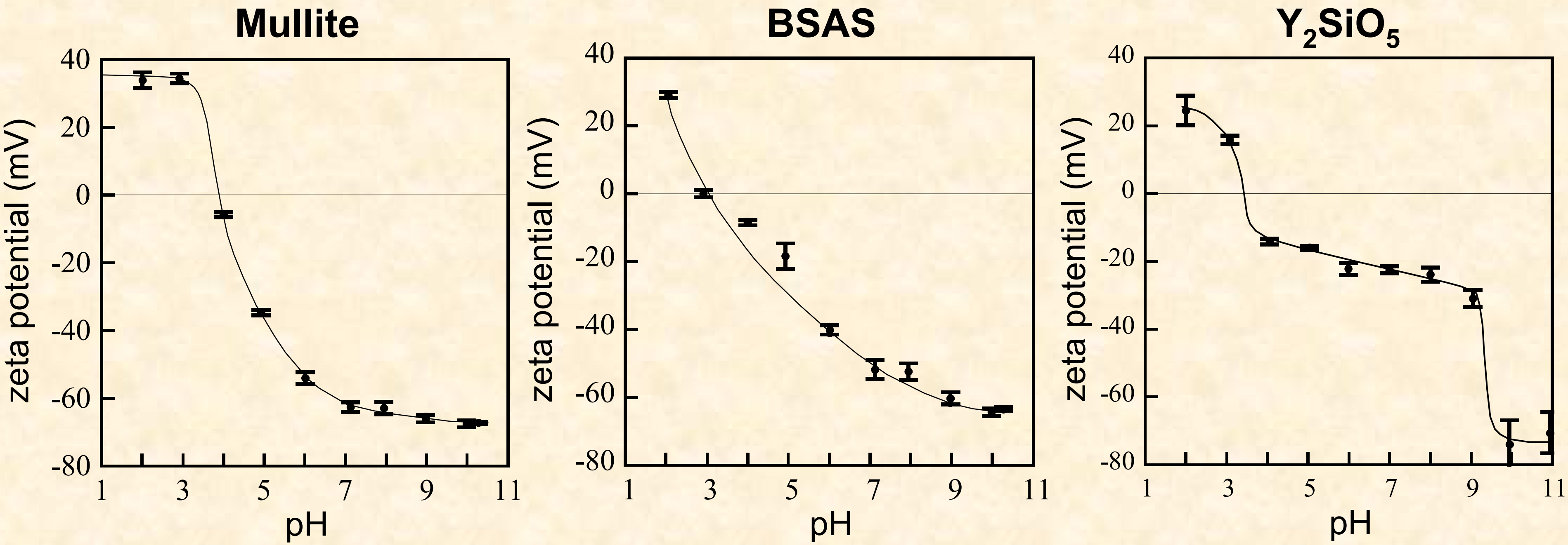

vdw forces
depletion forces

**Soft Sphere**



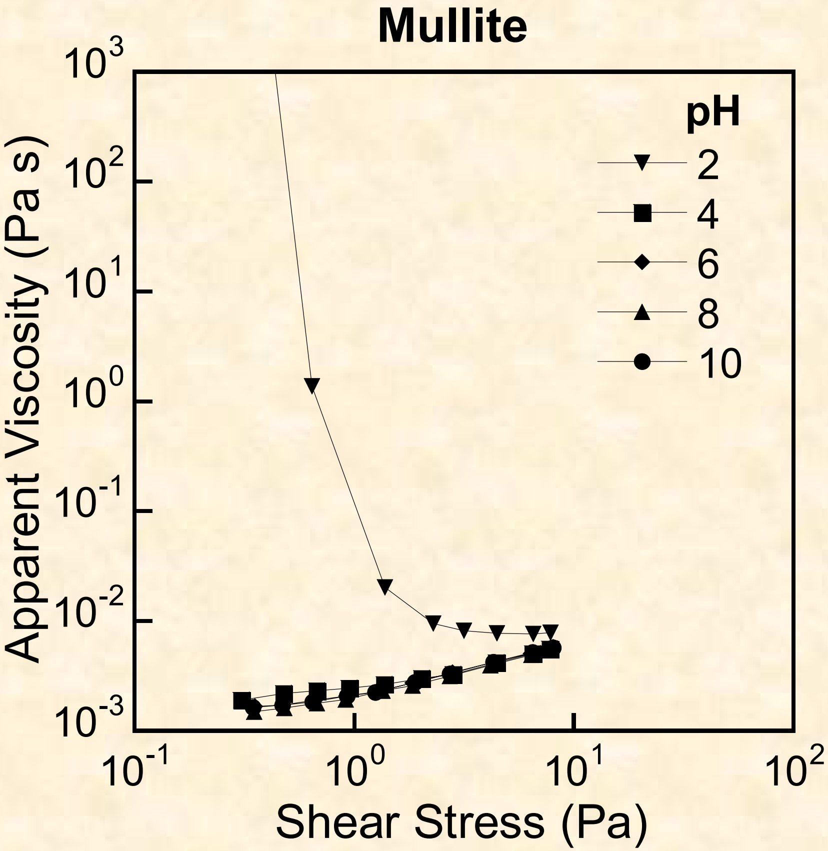

charge-stabilized
steric-stabilized

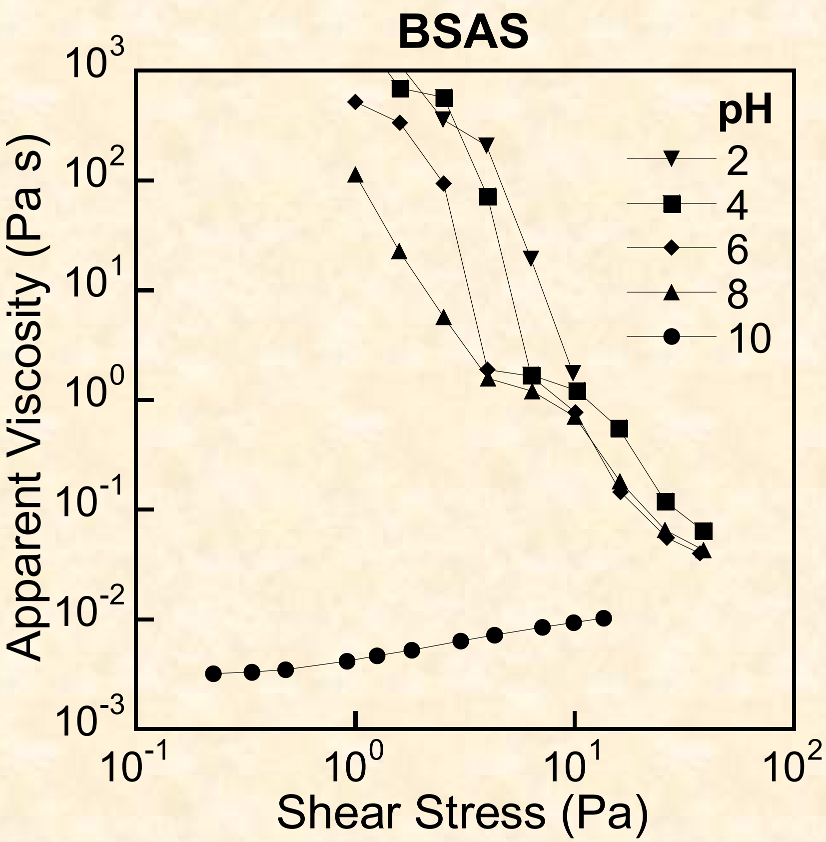
# Zeta Potential of Ceramic Particles in Aqueous Media
## (Dilute Suspensions, $10^{-3}$ vol%)




- **All mimic a $SiO_2$ surface with IEP at pH 3-4**
- **$Y_2SiO_5$ has additional event at pH 9 due to $Y(OH)_3$ formation**

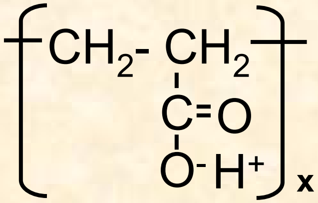
# Charge Stabilization of Ceramic Suspensions
## (25 vol%)



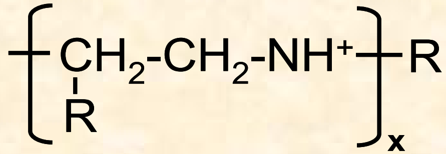
# Polyelectrolyte Dispersants

## Anionic

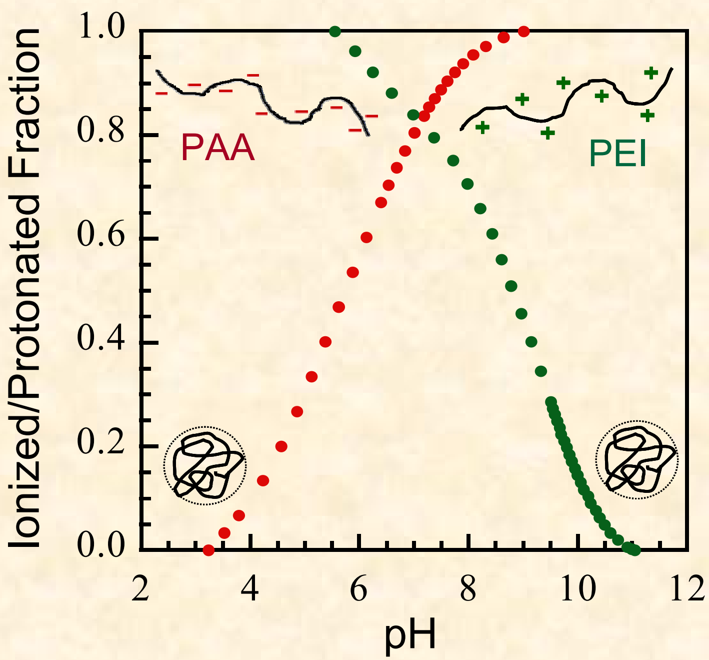


**Poly(acrylic acid) (PAA)**

## Cationic



**Poly(ethylene imine) (PEI)**




## Guidelines for Adsorption

IEP < 6 PEI

IEP 6-8 PAA or PEI

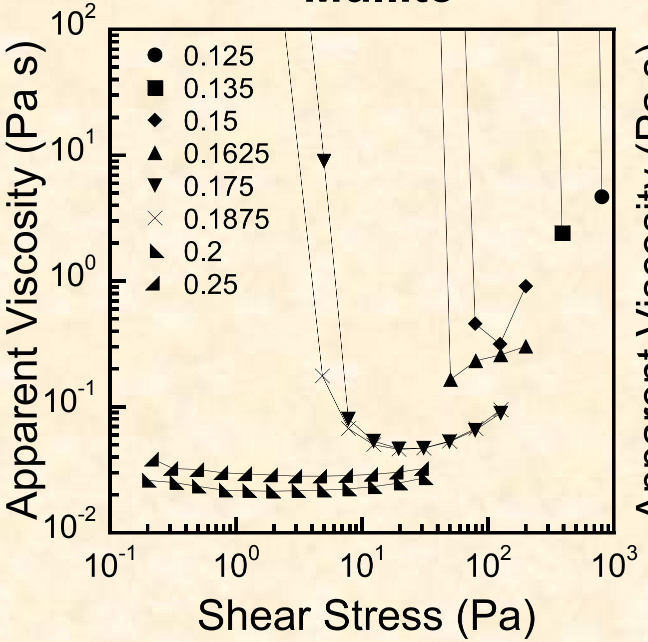
IEP > 8 PAA

| Ceramic Material | IEP | Dispersant |
|---|---|---|
| $SiO_2$ | 3-4 | PEI |
| SiC | 3-4 | PEI |
| $Si_3N_4$ (E10) | 3-4 | PEI |
| BSAS | 3-4 | PEI |
| Mullite | 3-4 | PEI |
| $Y_2SiO_5$ | 3-4 | PEI |
| $Y_2Si_2O_7$ | 5-6 | PEI |
| $Al_2O_3$ | 8-9 | PAA |
| $Y_2O_3$ | 8-9 | PAA |
| MgO | 12-13 | PAA |

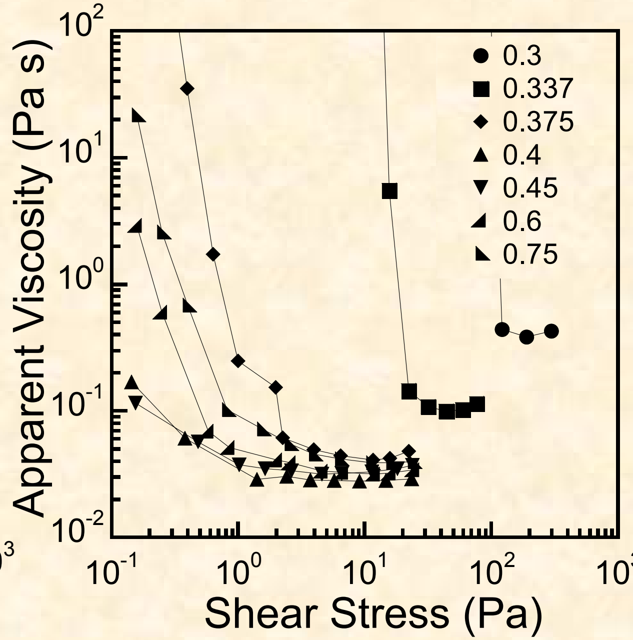
# Polyelectrolyte Stabilization of Ceramic Suspensions

## (45 vol%, pH 7, PEI conc. in mg PEI/m² ceramic)

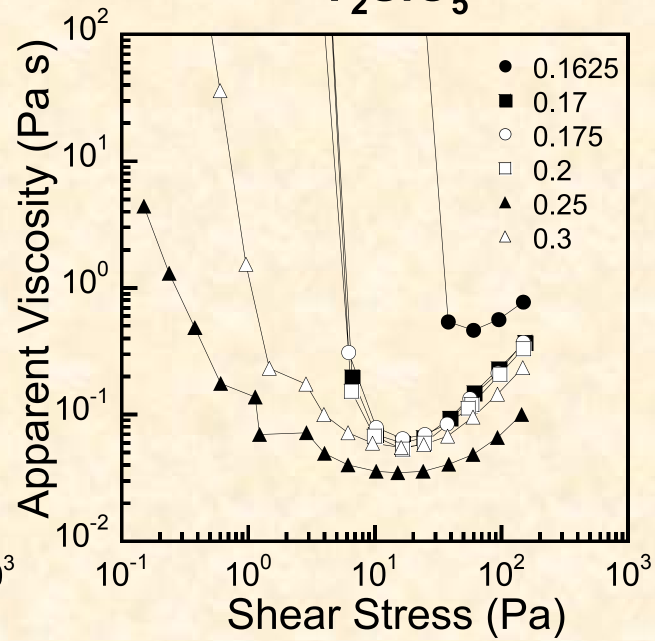
### Mullite




### BSAS

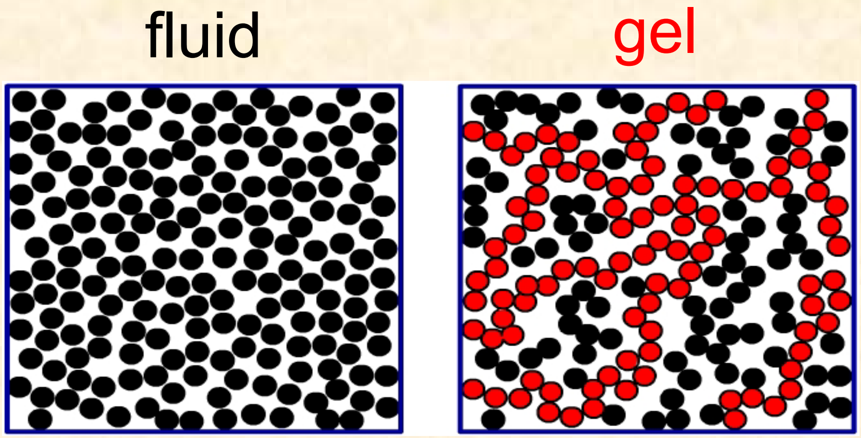



### $Y_2SiO_5$




**$[PEI]_{crit}$= 0.2 mg PEI/m² mullite = 0.4 mg PEI/m² BSAS = 0.25 mg PEI/m² $Y_2SiO_5$**

# Tailoring the Elasticity of Colloidal Gels




Elastic Properties of Colloidal Gels‡

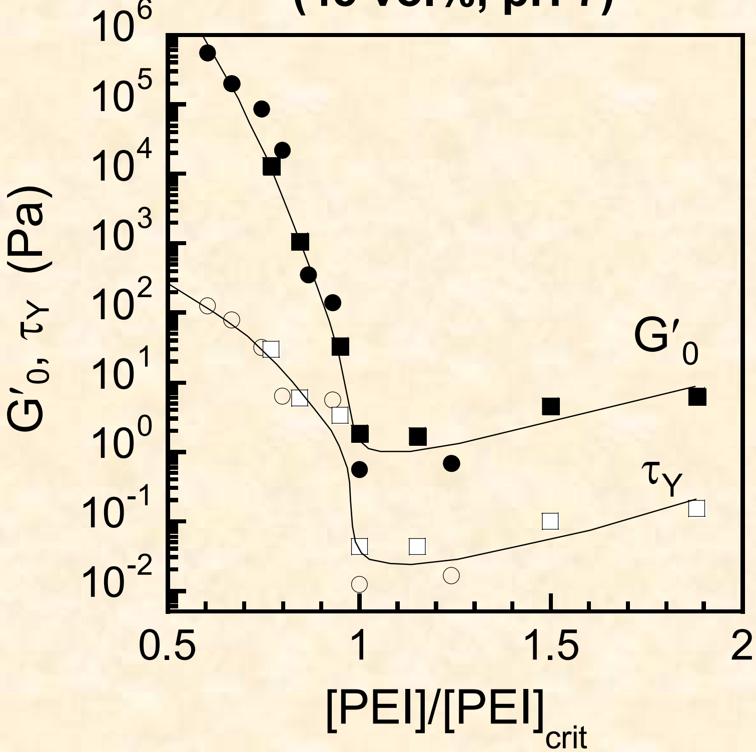
general scaling behavior

$$y = k\left(\frac{\phi}{\phi_{gel}} - 1\right)^{x}$$

| $y$ | $x$ |
|---|---|
| $\tau_{yield}$ | 2.4-2.5 |
| $G'$ | 2.4-2.6 |
| $P_{yield}$ | 2.4-2.6 |
| $\gamma_b$ | -0.7 |

‡ Buscall, R., *et. al.*, *J. Chem. Soc., Faraday Trans. 1*, 1988
Grant, M.C. and Russel, W.B., *Phys. Rev. E.*, 1993
Rueb, C.J. and Zukoski, *J. Rheology*, 1997
Channell, G.M. and Zukoski, C.F, *AIChE J.*, 1997

Mullite (●) & BSAS (■) Suspensions (45 vol%, pH 7)




Elastic properties scale with PEI concentration

# Mullite Dip Coatings on AS800 Silicon Nitride Substrates

## (Mullite Suspensions: 45 vol%, pH 7)

0.15 mg PEI/$m^2$ mullite

0.1625 mg PEI/$m^2$ mullite

0.175 mg PEI/$m^2$ mullite

0.1875 mg PEI/$m^2$ mullite

0.20 mg PEI/$m^2$ mullite

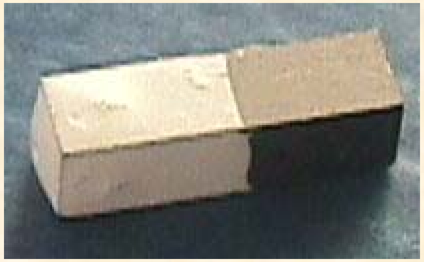
# Mullite Dip Coatings on Silicon Carbide Substrates

## (Mullite Suspensions:  45 vol%, pH 7)

0.15 mg PEI/$m^2$ mullite

0.1625 mg PEI/$m^2$ mullite

0.175 mg PEI/$m^2$ mullite

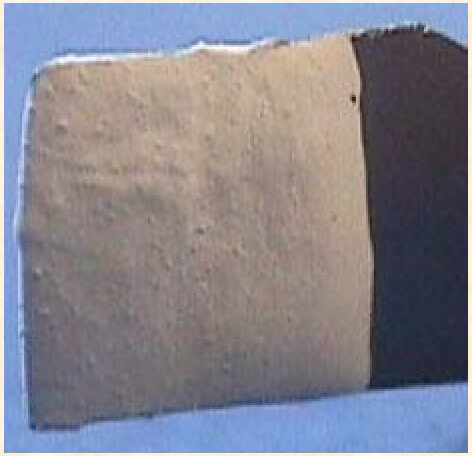


0.1875 mg PEI/$m^2$ mullite

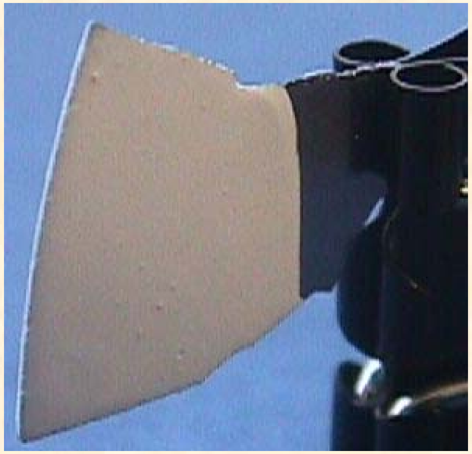
0.20 mg PEI/$m^2$ mullite

# Mullite Dip Coatings on Silicon Wafer Substrates

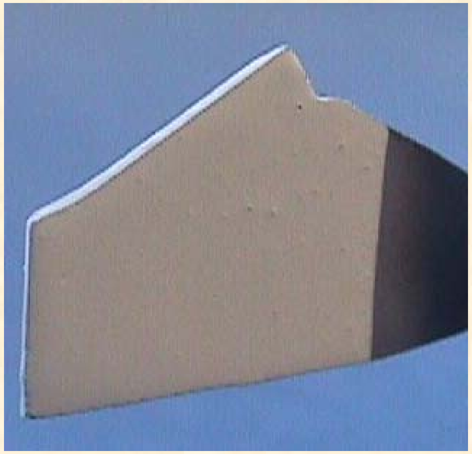
## (Mullite Suspensions: 45 vol%, pH 7)



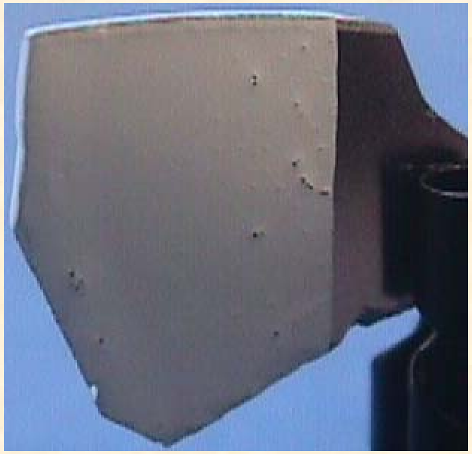
0.15 mg PEI/$m^2$ mullite



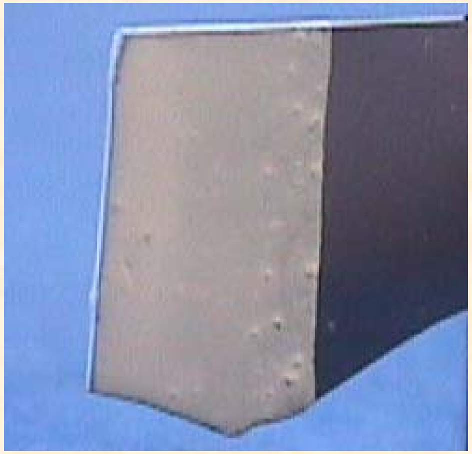
0.1625 mg PEI/$m^2$ mullite



0.175 mg PEI/$m^2$ mullite

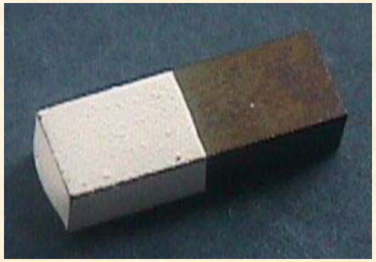


0.1875 mg PEI/$m^2$ mullite

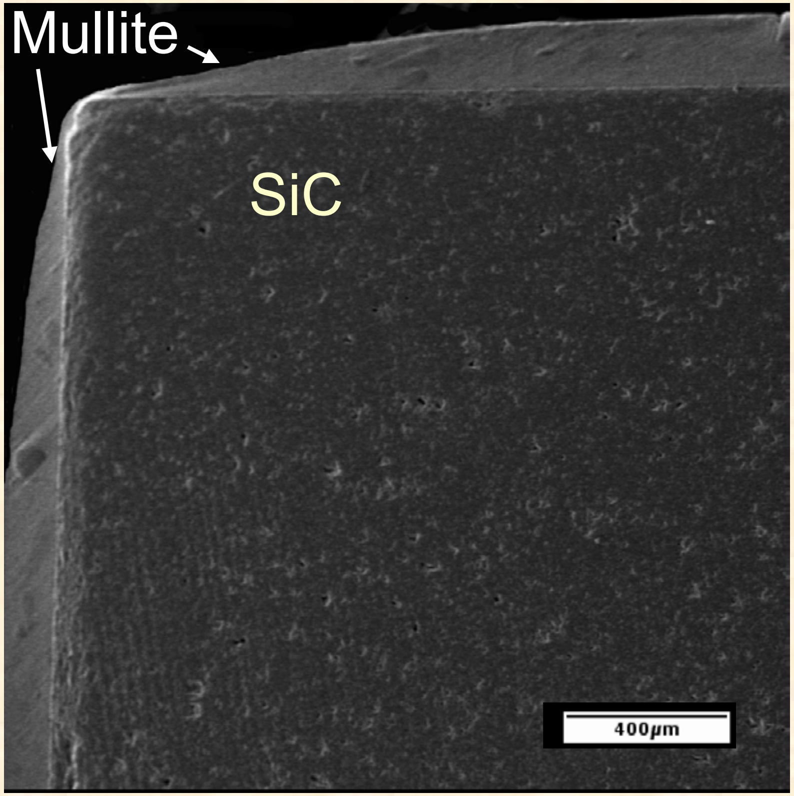


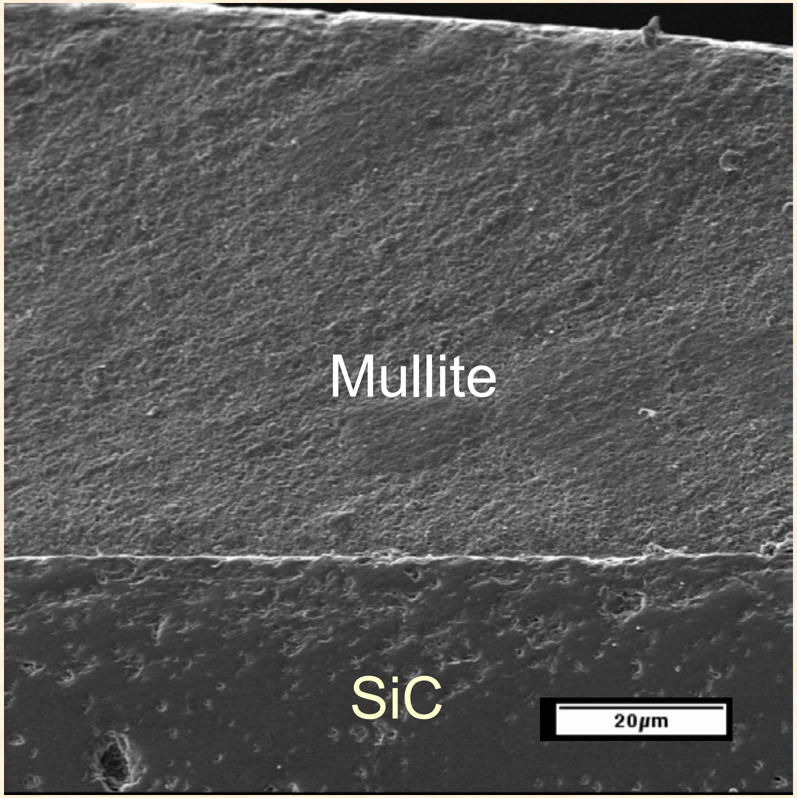
0.20 mg PEI/$m^2$ mullite

# Full Densification Achieved at Reduced Temperatures



Slurry solids loading, 45 vol%
Sintered in air, 1350 $^{o}C$



# Wetting Behavior Controlled Through Use of Additives

**Mullite**

$\phi_{mullite} = 0.25$

| pH | SiC θ | $Si_3N_4$ θ |
|---|---|---|
| 2 | 79.5 | 58.0 |
| 4 | 73.0 | 55.5 |
| 6 | 72.0 | 67.0 |
| 8 | 68.0 | 68.5 |
| 10 | 55.0 | 71.5 |

**BSAS**

$\phi_{BSAS} = 0.25$

| pH | SiC θ | $Si_3N_4$ θ |
|---|---|---|
| 2 | 61.5 | 82.5 |
| 4 | 62.5 | 64.5 |
| 6 | 63.5 | 60.5 |
| 8 | 64.0 | 58.0 |
| 10 | 53.0 | 85.5 |

**Mullite-Latex**

$\phi_{mullite} = 0.25$, pH 10

| $\phi_{latex}$ | SiC θ | $Si_3N_4$ θ |
|---|---|---|
| 0 | 55.0 | 71.5 |
| 0.034 | 49.5 | 50.5 |
| 0.076 | 40.0 | 40.5 |
| 0.201 | 45.5 | 47.5 |

**BSAS-Latex**

$\phi_{BSAS} = 0.25$, pH 10

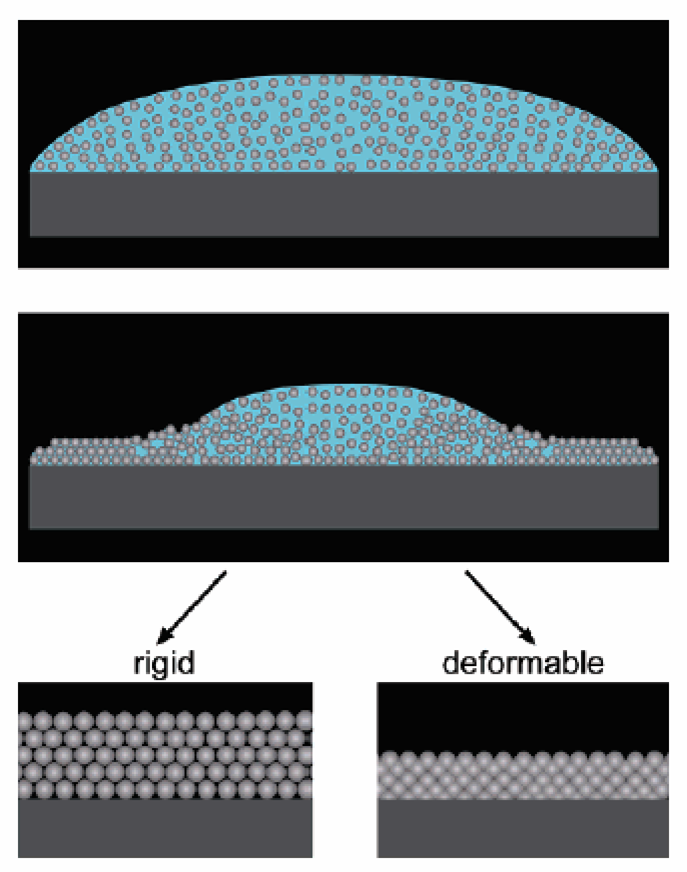
| $\phi_{latex}$ | SiC θ | $Si_3N_4$ θ |
|---|---|---|
| 0 | 53.0 | 85.5 |
| 0.034 | 48.0 | 49.0 |
| 0.076 | 44.5 | 41.5 |
| 0.201 | * | * |

- The contact angle (θ) depends on the surface tension/charge of the substrate and coating material
- The contact angle decreases with use of latex

UT-BATTELLE

# Drying Stresses Reduced with Additives

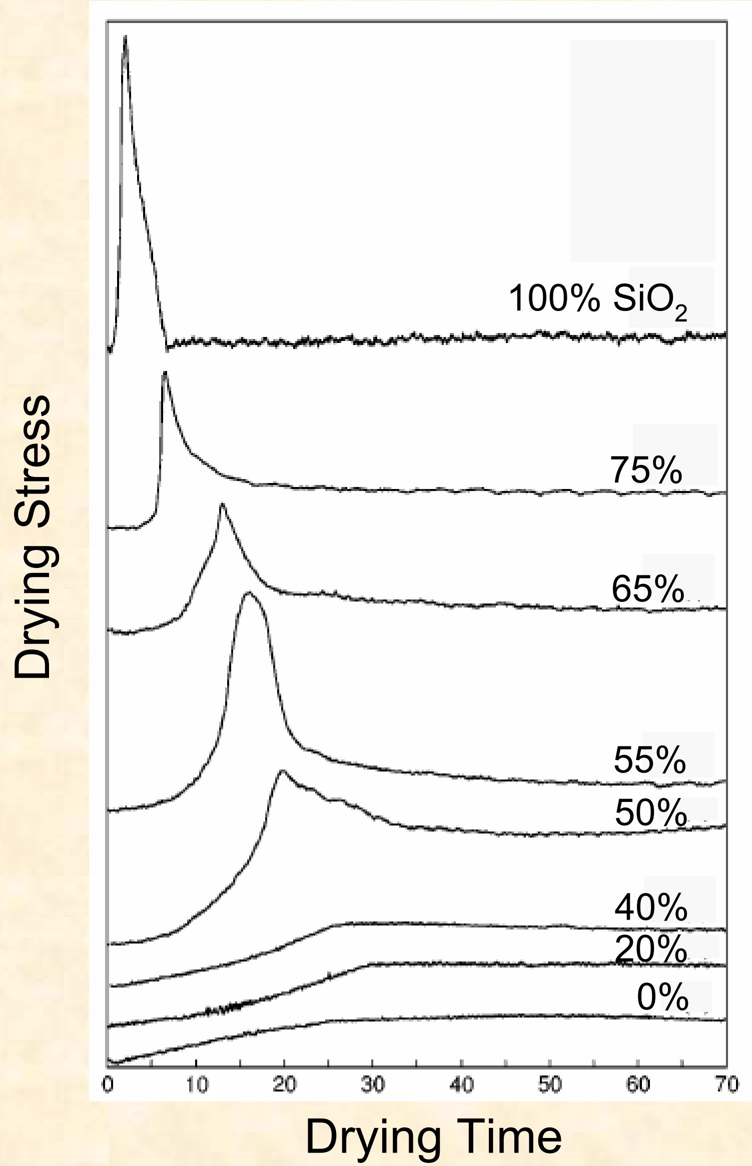
**Ceramic-Latex Binary Suspensions**




Deformable latex particles promote uniform,
Crack-free drying of slurry coatings

C. J. Martinez and J. A. Lewis, *Langmuir*, **18** [12] 2002

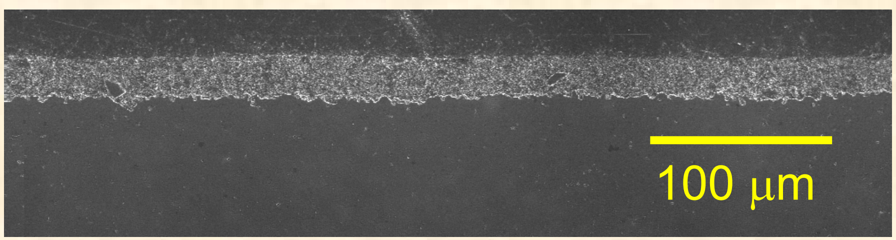
**$SiO_2$-Latex**

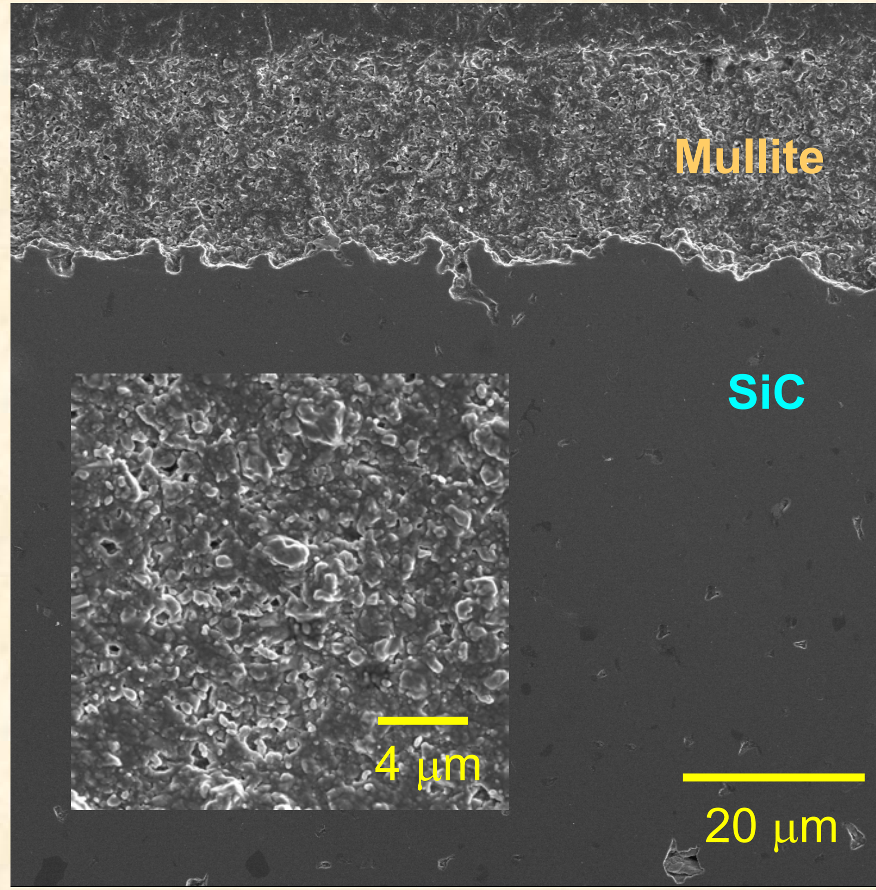


# Formation of Thin, Uniform Mullite Coatings

**Green coating, from 25 vol% mullite suspension w/ latex**


Sintered in air, 1400 $^{o}$C

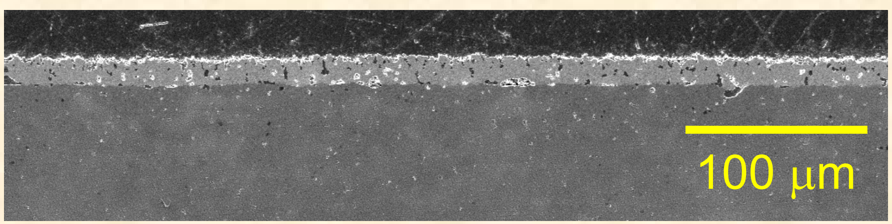


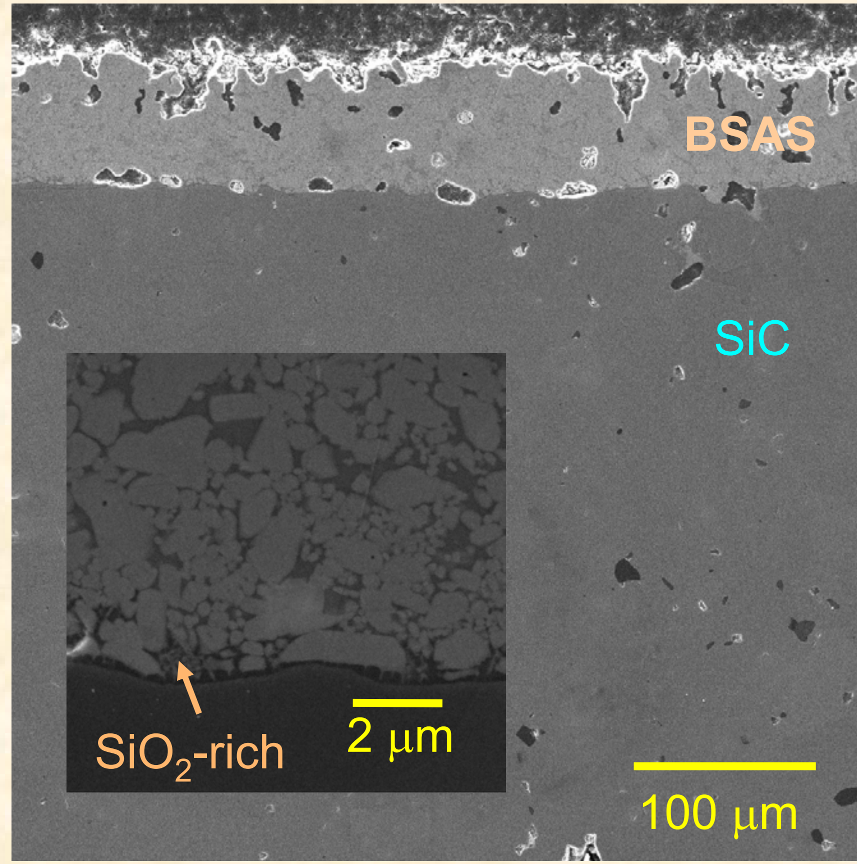



# Formation of Thin, Uniform BSAS Coatings

**Green coating, from 25 vol% BSAS suspension w/ latex**

Sintered in air, 1300 $^{o}$C



# Path Forward

- Develop and test "new" material systems
  - Synthesize and/or acquire materials (rare earth or alkaline earth silicates and aluminosilicates)
  - Test properties in ambient and simulated conditions (CTE, strength, modulus, weight change, microstructure, etc…)
  - Build database and utilize database to identify candidate material systems
  - Slurry coat substrates with key materials and evaluate properties in simulated environments

- Develop understanding of how coating efficacy is changed by interface
  - Thermodynamic modeling
    - study the effect of the environment on the coating
    - study the interface of the coating on the silicon nitride substrate

# Acknowledgements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# Questions?