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Highly Porous Ceramic Foams from Magnesium Oxide Stabilized Pickering Emulsions

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U.S. DEPARTMENT OF ENERGY NNSA National Nuclear Security Administration LDRD LABORATORY DIRECTED RESEARCH & DEVELOPMENT

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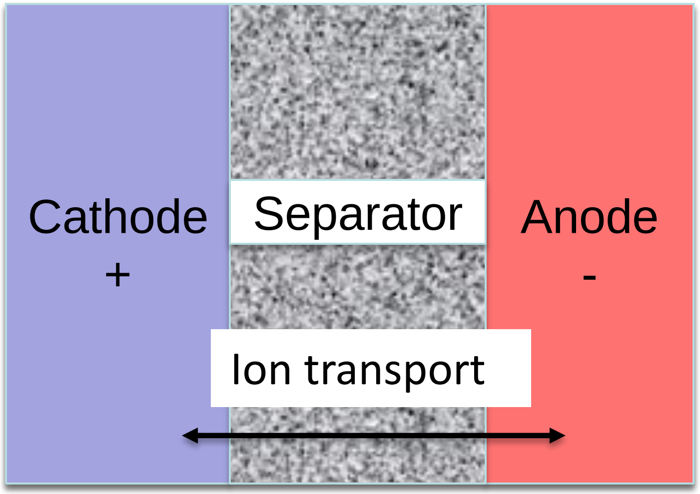
Overview

Goal: Produce *sintered ceramic foam* to electrically isolate the anode & cathode layers in batteries while allowing free ion transport



Current battery separators:

- Polymer separators for Lithium Ion batteries are susceptible to thermal runaway
  - Boeing 787 Dreamliner
- Pressed pellets used for molten salt batteries are expensive to manufacture and need to be thick to be robust enough to handle
- Ceramic foam scaffold backfilled with electrolyte has advantages in either case

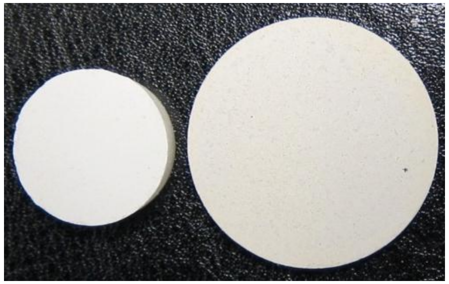
Requirements

Desired scaffold properties

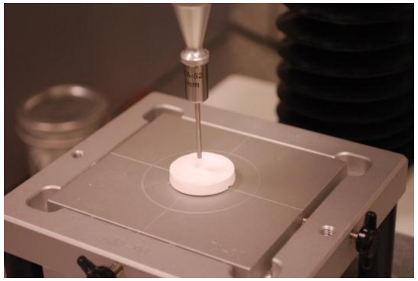
- Porous, but pores small enough to retain electrolyte
- Permeable to ions (connected porosity with low tortuosity)
- Robust enough to withstand manufacturing processes
- Chemically compatible in a wide range of batteries → Magnesium Oxide (MgO)

Processability

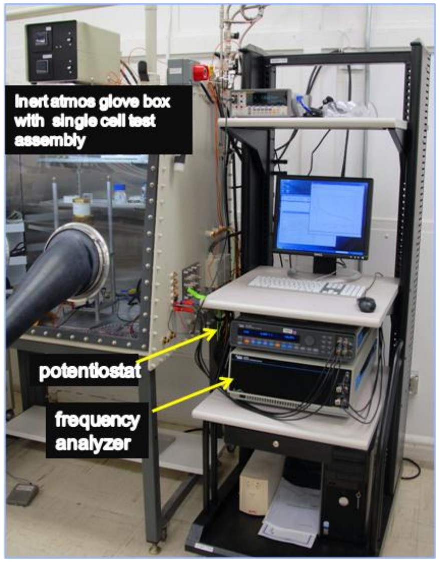
- Can large quantities be processed easily?
- Can robust green ceramic be processed into an appropriate shape?
- Is the sintered foam strong enough?
- Can it be backfilled with electrolyte?
- Does it allow appropriate ionic conductivity?



Separator must be flat and of an appropriate shape



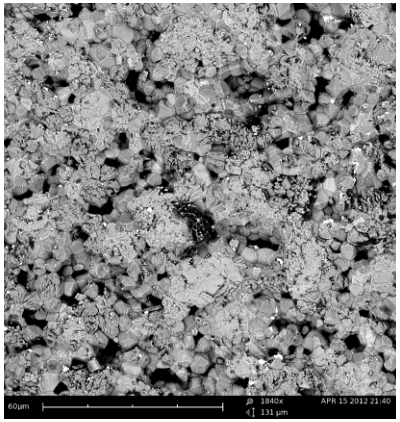
2 mm diameter post driven into sample. Fracture force measured.



The ceramic foams are backfilled with conductive liquid and impedance tested. Molten salt electrolyte requires high temp (>370C) & inert atmosphere glove box.

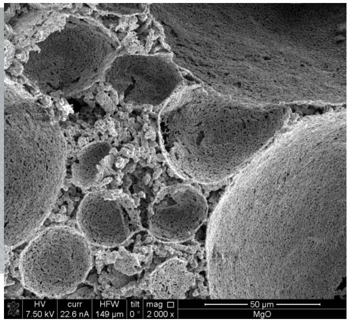
Advanced Ceramics Processes

- Sacrificial template method with tape casting
  - Tape cast ceramic with sacrificial particles that generate pores within the microstructure during sintering
  - Tape cast can be layered to various thickness and punched into variety of shapes



- Foam replication
  - Foam is infiltrated with a ceramic suspension, dried, and sintered, which removes the original foam.
  - Tested MgO/toluene slip and toluene-resistant polyurethane foams.

- Emulsion-based approach
  - Extremely stable MgO Pickering emulsion can be tape cast or molded
  - Nanostructured ceramic allows high porosity and good mechanical strength
  - Focus of this talk



Pickering Emulsion

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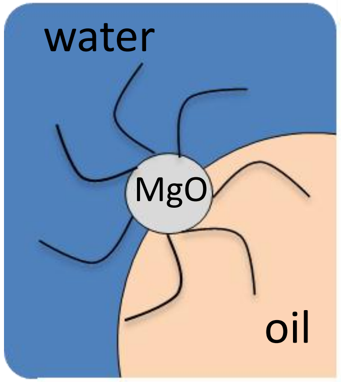
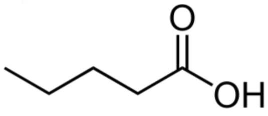
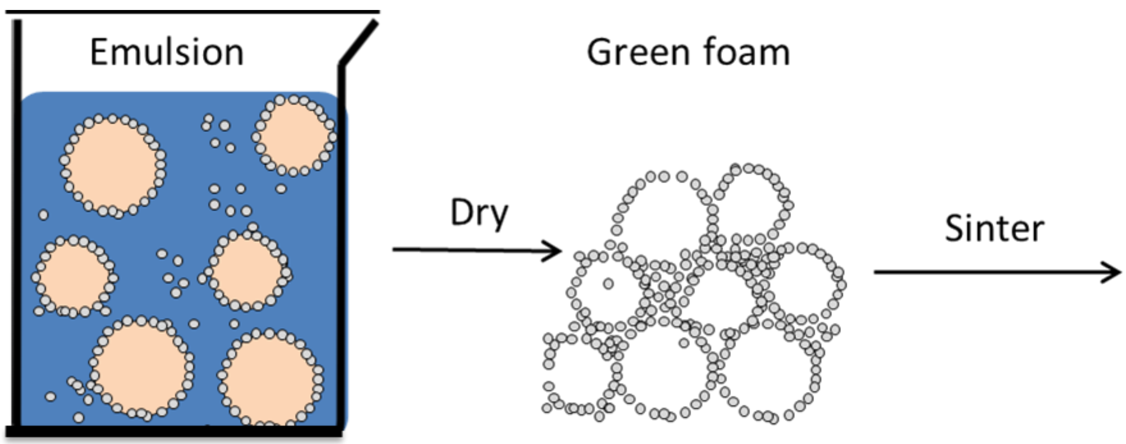
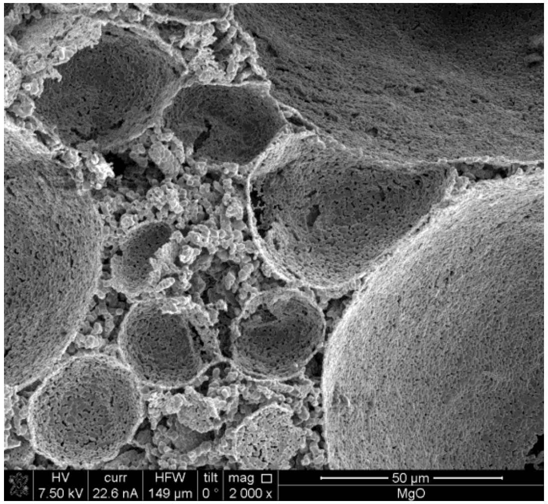
- After Akartuna et al. (2008), ceramics are made from particle-stabilized oil/water emulsions.
- We are focused on MgO ceramics
  - After Hibner et al. J. European Ceramic Soc. 1997 and Gonzenbach et al. Langmuir 2006, we treated MgO particles with carboxylic and dicarboxylic acids to make them neutrally wetting
- Resulting emulsion so stable that the liquids can be dried and leaving a structure of particles behind
- **Ceramic foams with porosity up to 94%**





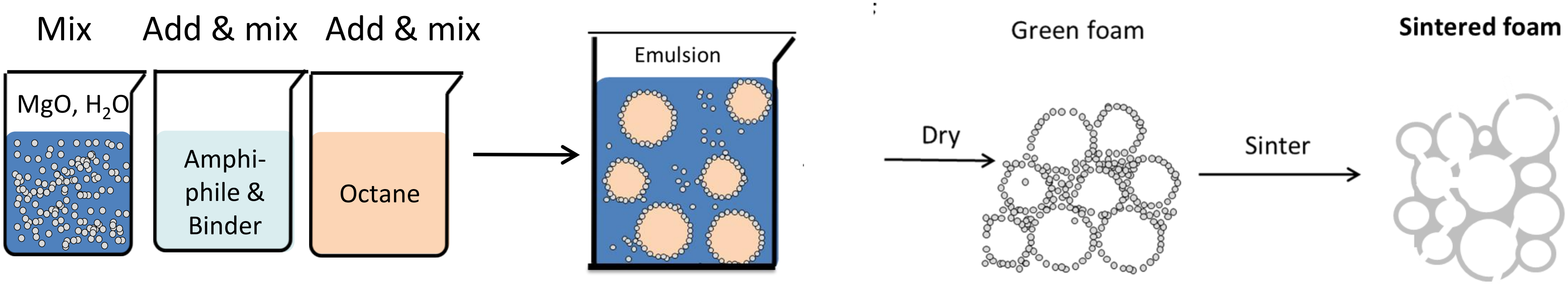
valeric acid





Akartuna et al. Advanced Materials, Langmuir 2008

Large Parameter Space Explored



Process Variables:

- MgO particle size & concentration,
- Milling time
- Amphiphile chain length & concentration
- Binder type & concentration
- Octane amount
- Mixing time & speed

Characterization of emulsions:

- Light scattering (MgO aggregate size)
- Thermal gravimetric analysis (TGA) for brucite amount
- Microscopy for droplet size
- Cryogenic scanning electron microscopy (SEM) for emulsion microstructure

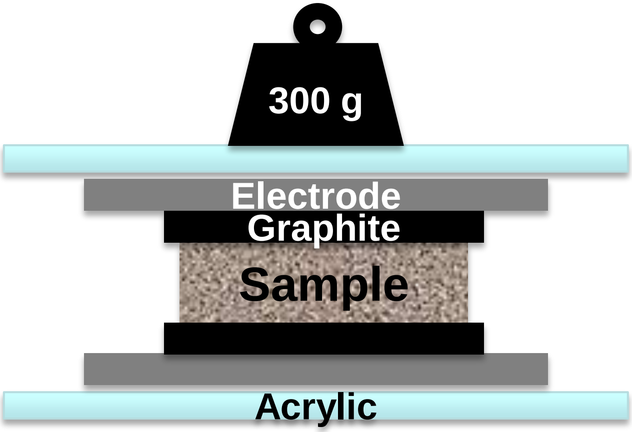
Process Variables:

- Tape casting or cast in a mold
- Drying time
- Humidity
- Sintering temperature
- Sintering time and ramp rate

Characterization of green and sintered ceramics:

- Measure shrinkage
- Measure density and porosity
- SEM (microstructure)
- Electrochemical impedance spectroscopy (permeability)
- Indentation (fracture strength)

Ionic Conductivity

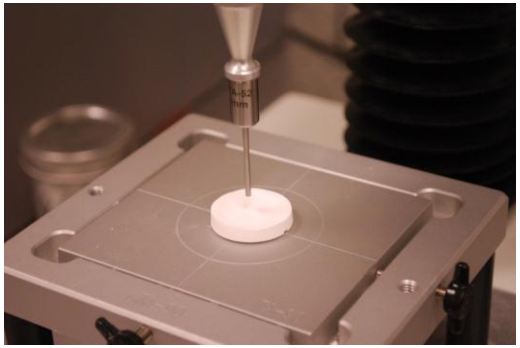


Impedance Spectroscopy

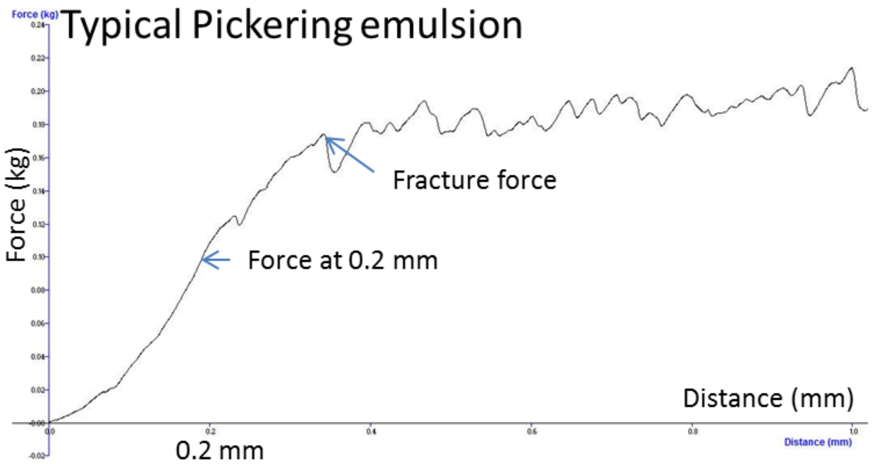
Sample filled with KCl + water solution
AC voltage applied across electrodes
Impedance measured vs AC frequency

$$\textbf{MacMullin \# } = \frac{\text{sample resistance}}{\text{solution resistance}}$$

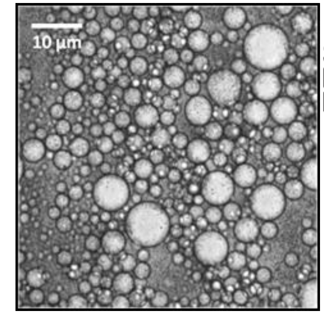
Fracture strength



TA.XT*Plus* Texture Analyzer
Wide range of probe shapes
Strain rates 0.01 - 40 mm/s



Emulsion Characterization



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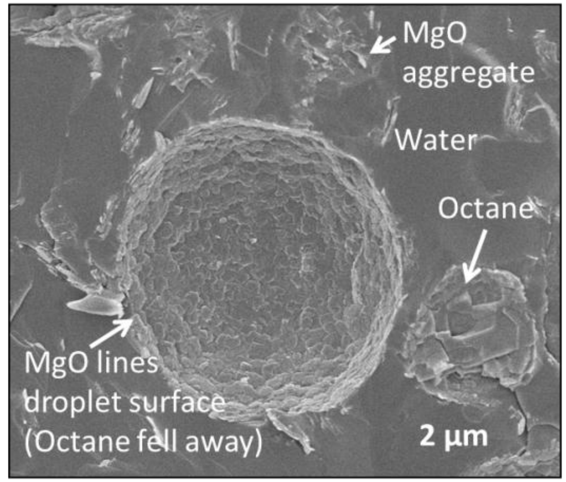
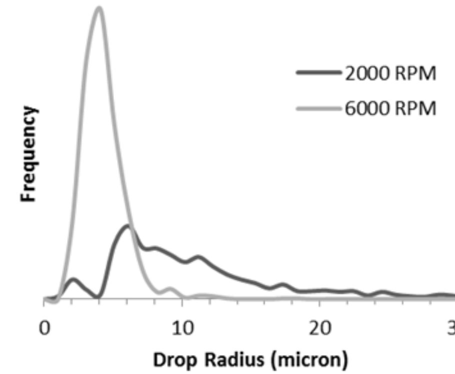
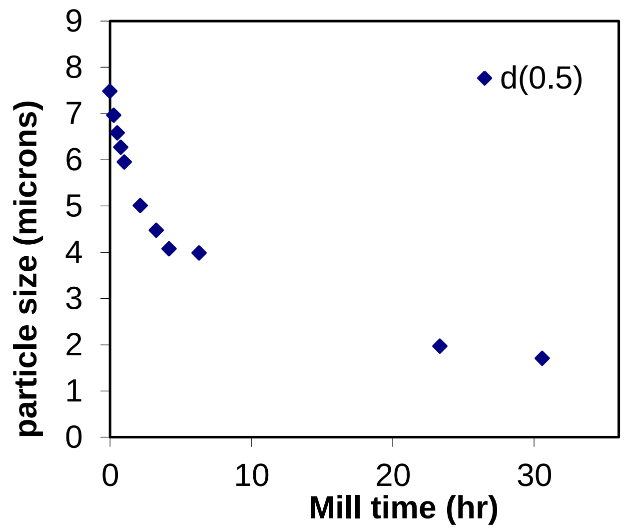
- Cryo-SEM shows that MgO particles do coat droplet surfaces
- Microscopy for droplet sizing
- Droplet size depends most strongly on mixing speed.
- Too much mixing energy (e.g. ultrasonic mixer) seems to knock the particles off the droplets and destabilize the emulsion

- Particle suspension were ball milled to disperse in solution and break up aggregates

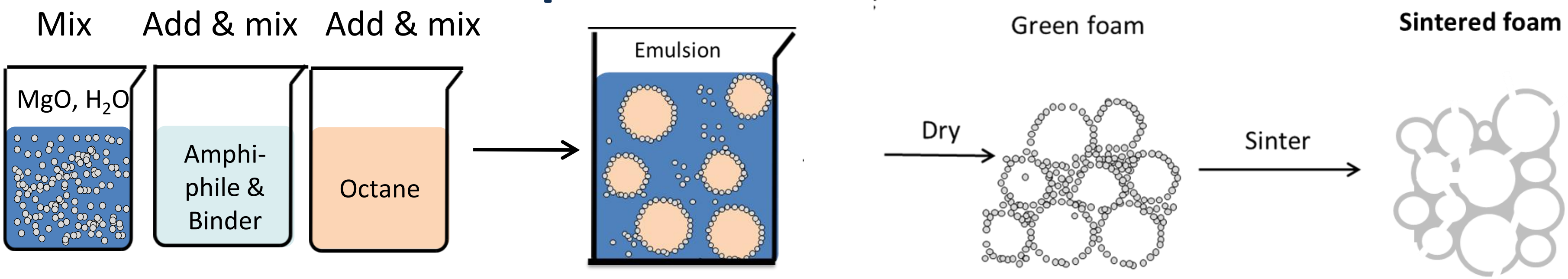




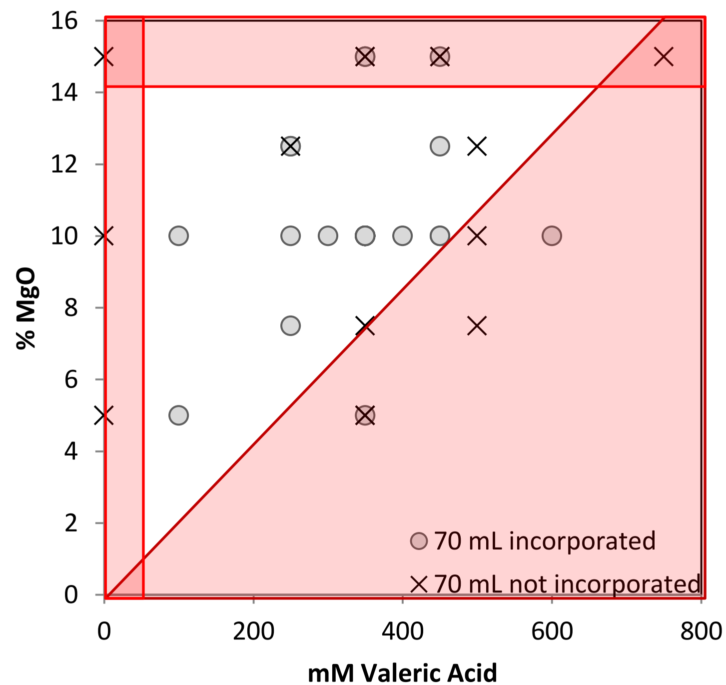


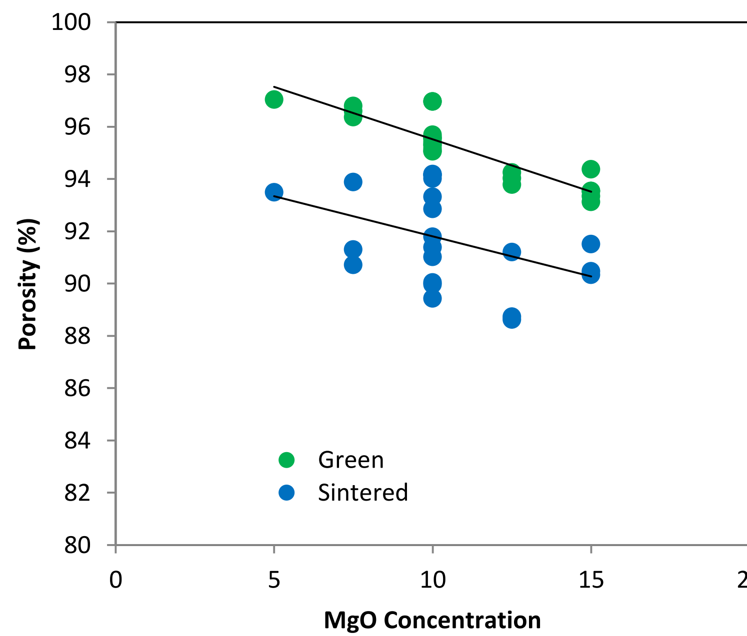
Cryo-SEM performed by Chris Frethem, Characterization Facility, U Minnesota

Emulsion Properties



- Valeric acid is important for stability of the emulsion

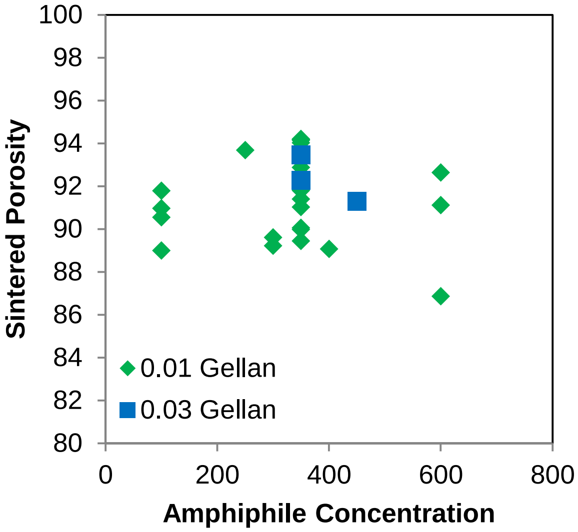


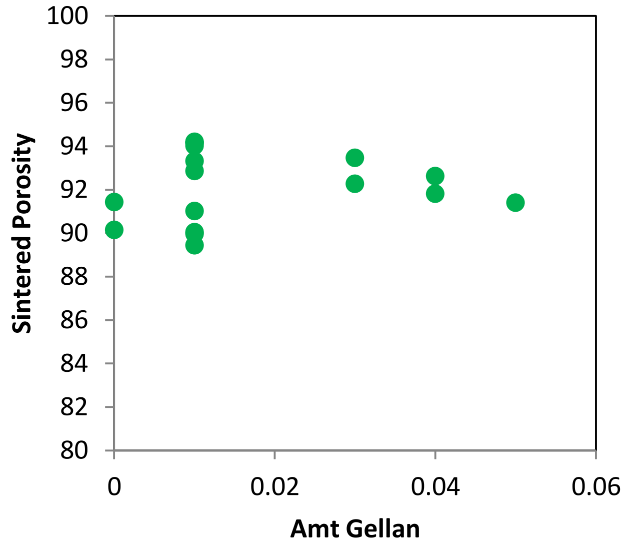


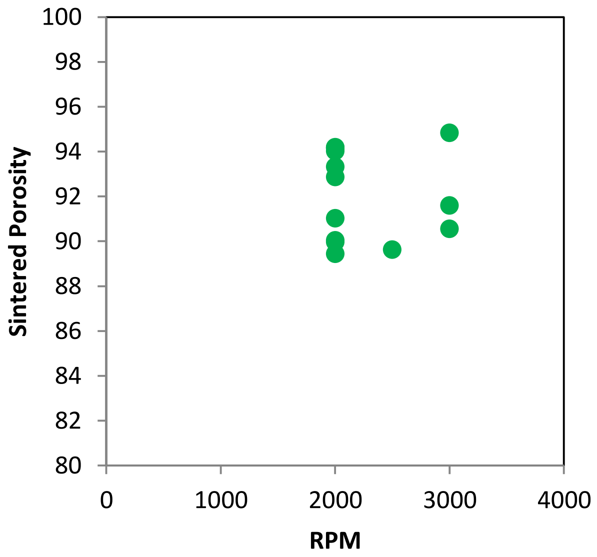
Emulsion Properties

- Basic recipe - %MgO, amphiphile, binder, octane, mixing speed
- Sinter with ?hr ramp and max temperature

- Many processing parameters, but many do not seem to affect the quality of the ceramic foam

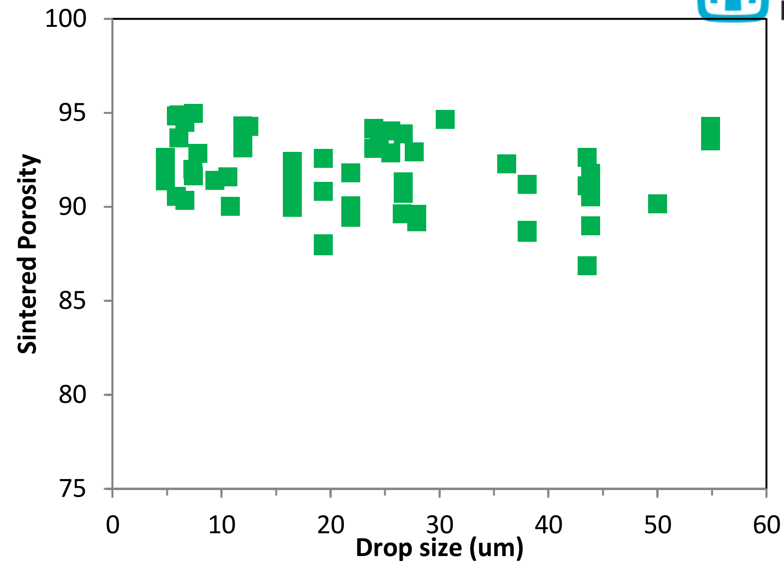


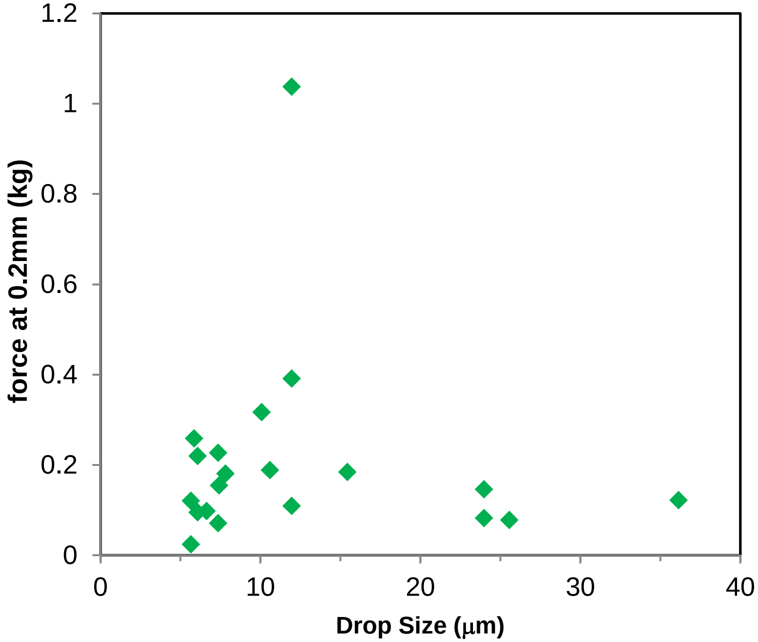


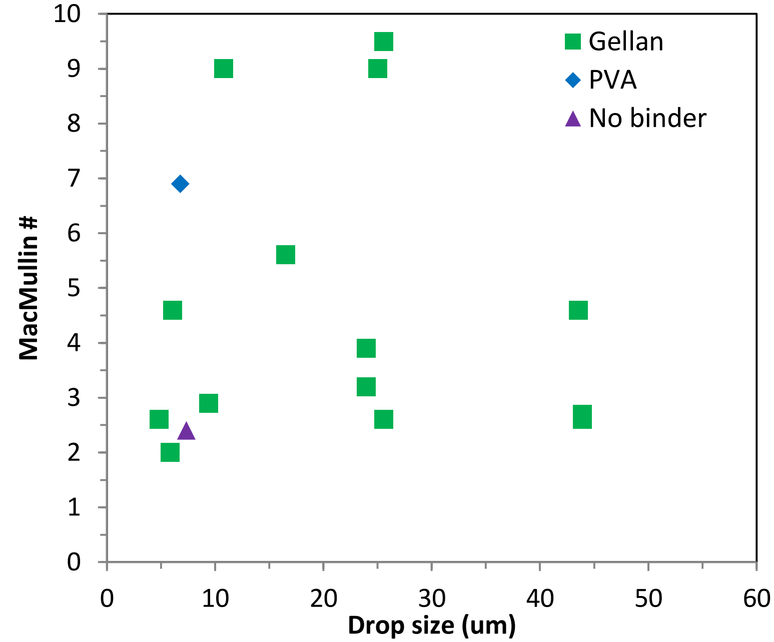


Drop Size

- We can manipulate oil drop size, but that doesn't seem to influence properties

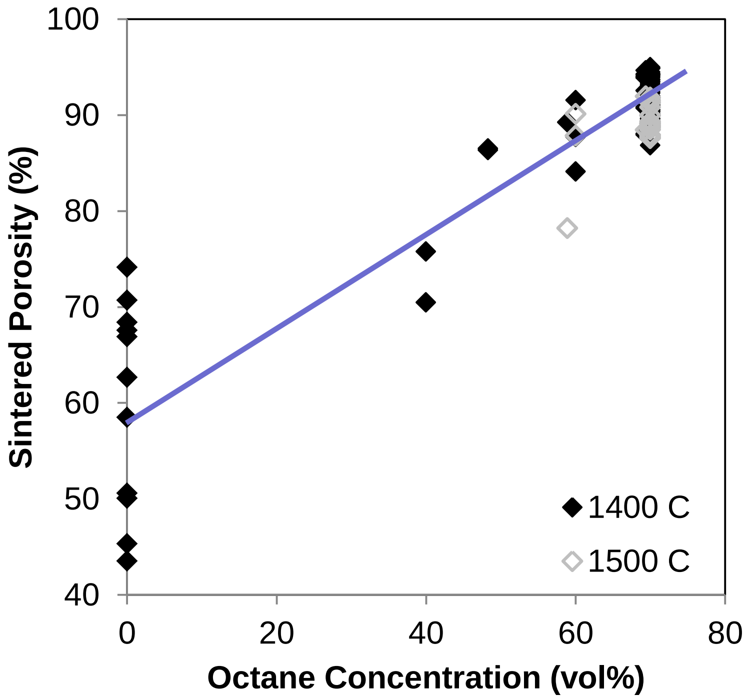


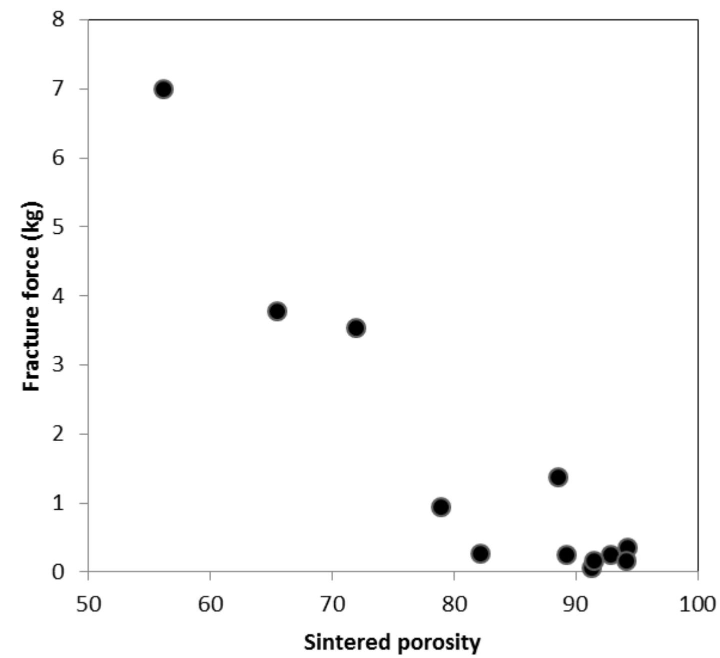




Controlling Porosity

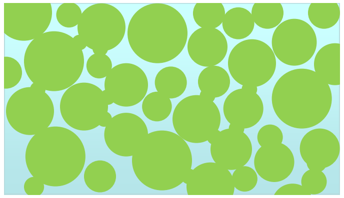
- Fraction of octane is the main control for sintered porosity and also strength of the resulting ceramic foams

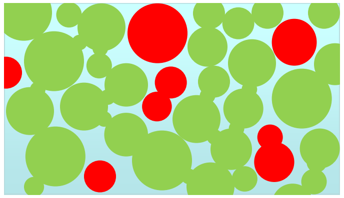




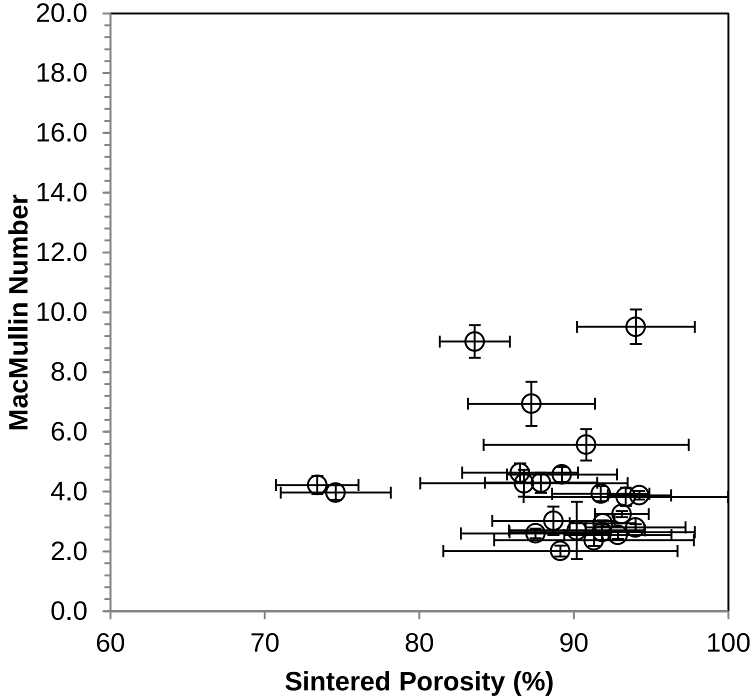
Ionic Conductivity

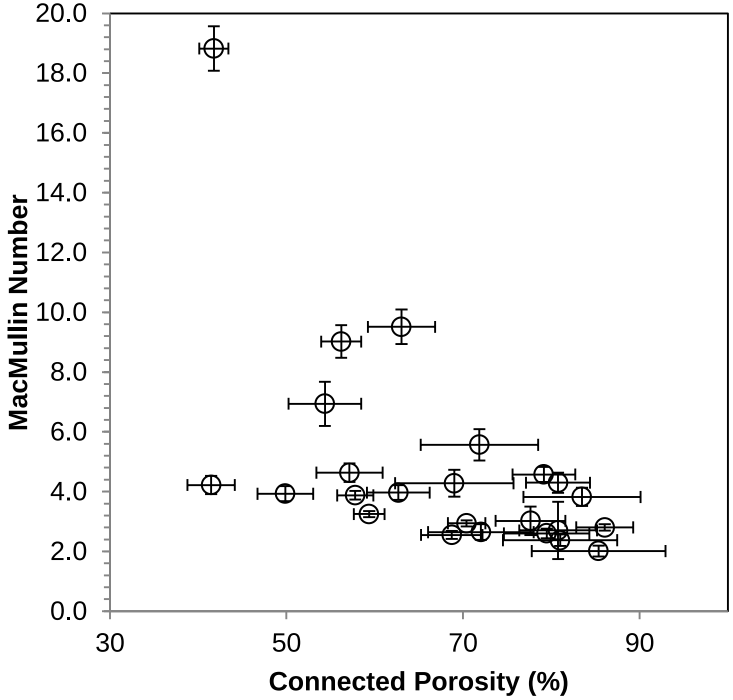
- Green Porosity → Sintered Porosity → Connected Porosity





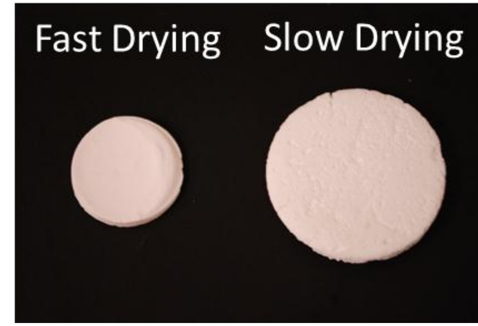
- Ionic Conductivity very sensitive to connected porosity



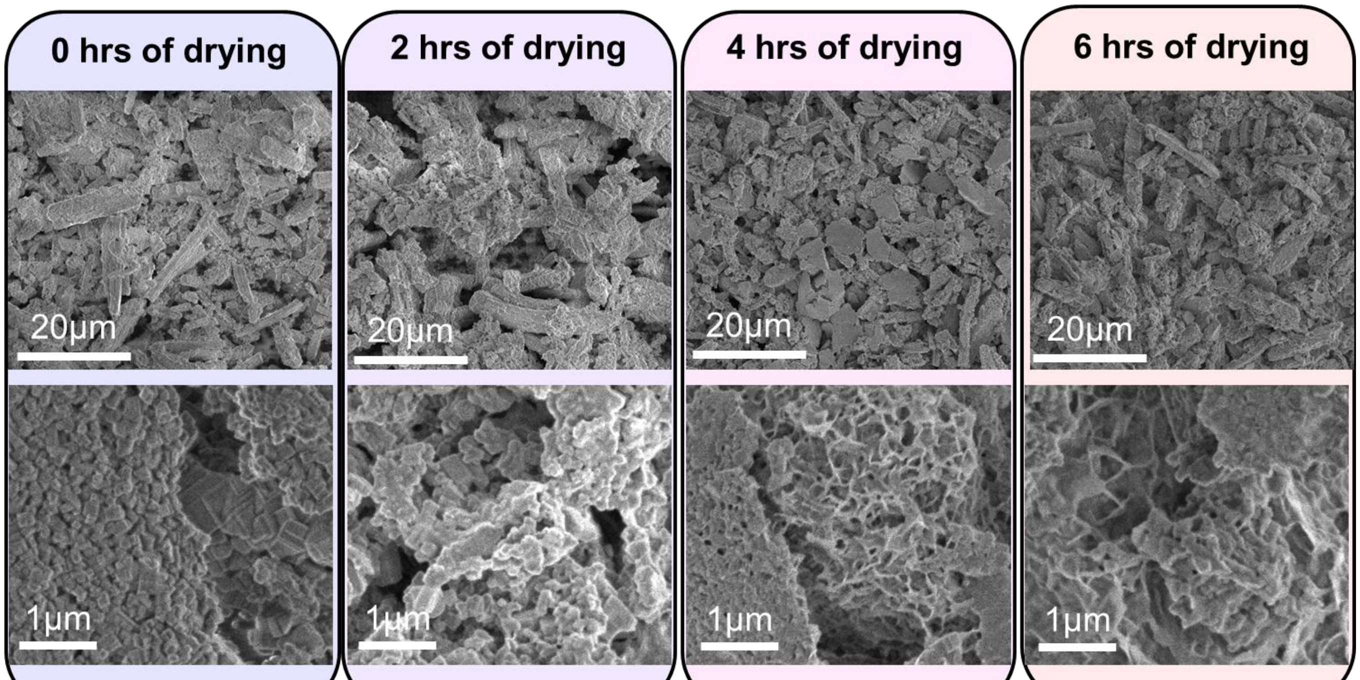


Microstructure Key to Permeability

- Pickering emulsions most stable with H_2O-based formulation, leading to MgO hydrolyzing to $Mg(OH)_2$
- Slow drying minimizes shrinkage, maximizes porosity, and allows brucite crystal formation
- MgO - H_2O gels with similar low MgO concentrations result in lower permeability than emulsions



Slow drying leads to less shrinkage = higher porosity



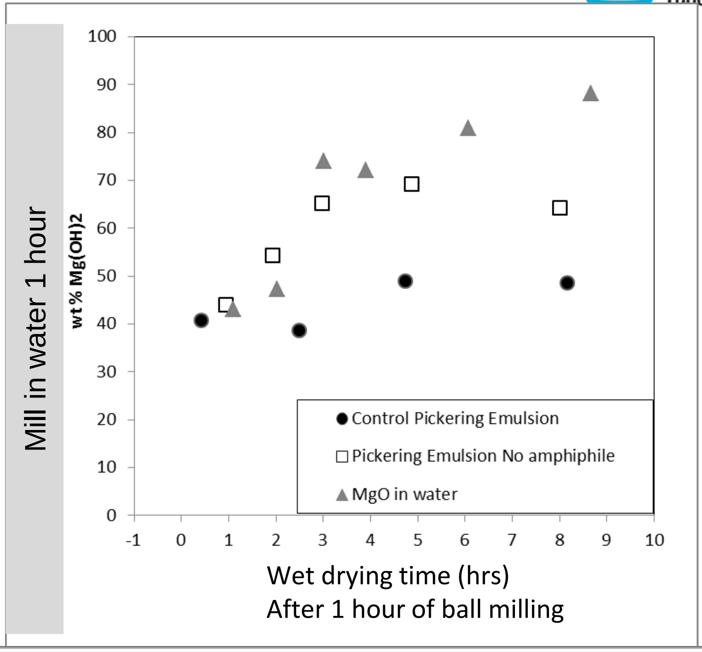
SEM images show emulsion microstructure evolution as it is allowed to dry for various amounts of time, forming brucite crystals (Unsintered)

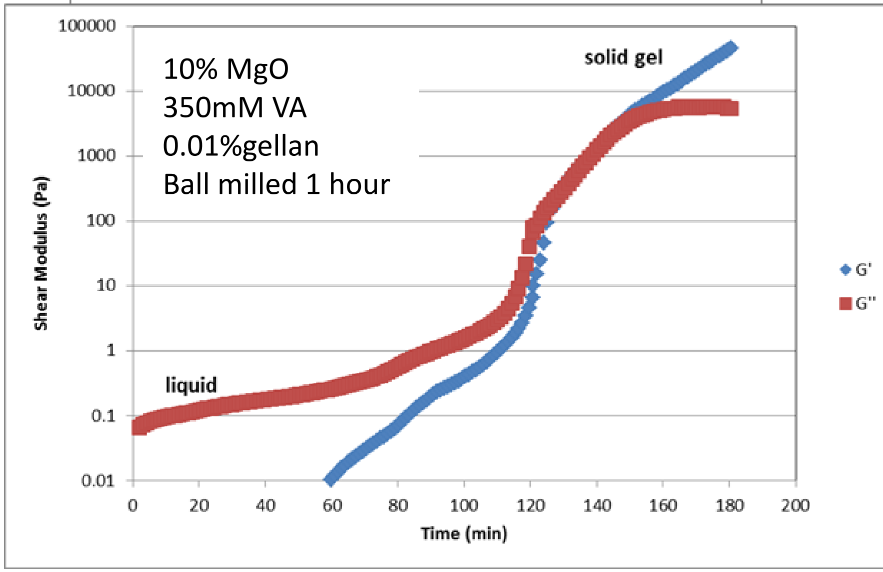
Brucite Formation

- MgO hydrolyzes to $Mg(OH)_2$
- Thermogravimetric analysis (TGA) quantifies amount of brucite
  - After 24 hrs ball milling MgO in water, 92 wt% brucite
  - After 1 hour ball milling MgO in water, 41wt% brucite; after left in a humid atmosphere for 8 hrs, 88 wt% brucite.

- Composition influences amount of brucite: Surface-active amphiphile inhibits formation
- Modulus of gel can increase orders of magnitude with time, even at very low fractions of MgO
- Self-standing gel can be molded without making a Pickering emulsion

- Brucite converts to MgO on sintering
  - Lower initial density – greater shrinkage





Sintering Shrinkage

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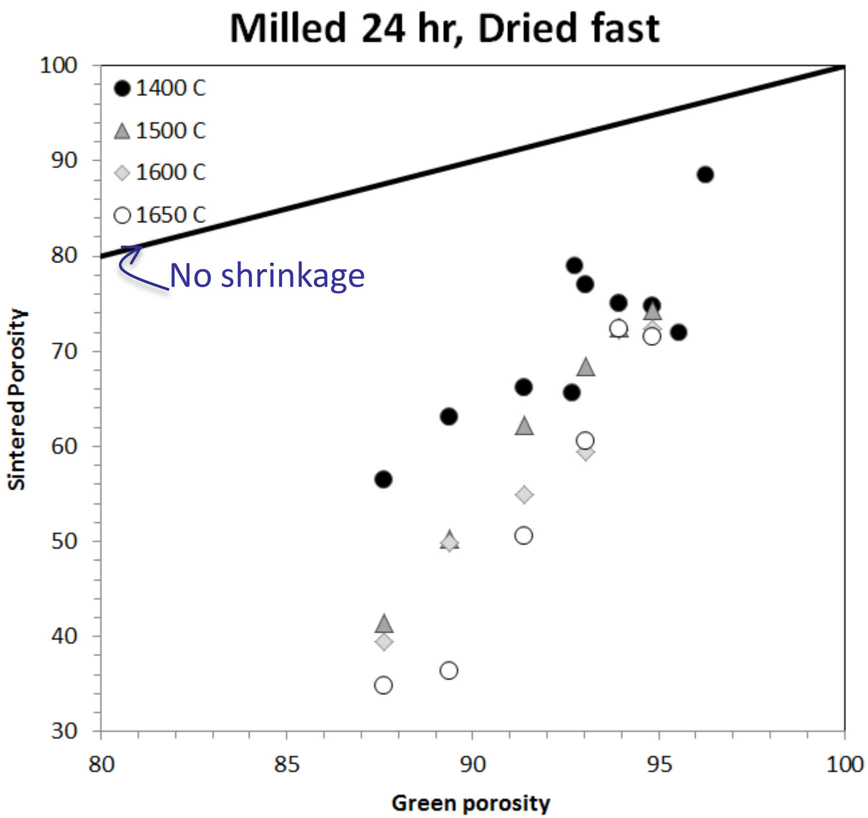
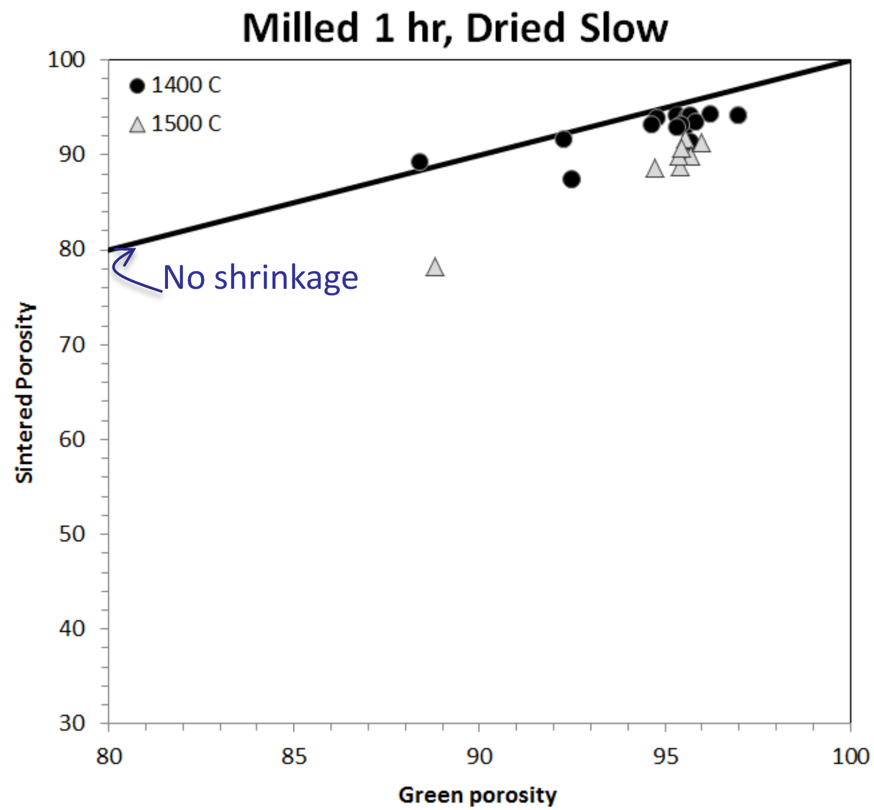
Higher temperatures = more shrinkage





Mostly ground brucite = lots of shrinkage

ρ (MgO) = 3.58 g/cm^3

ρ ($Mg(OH_2)$) = 2.39 g/cm^3

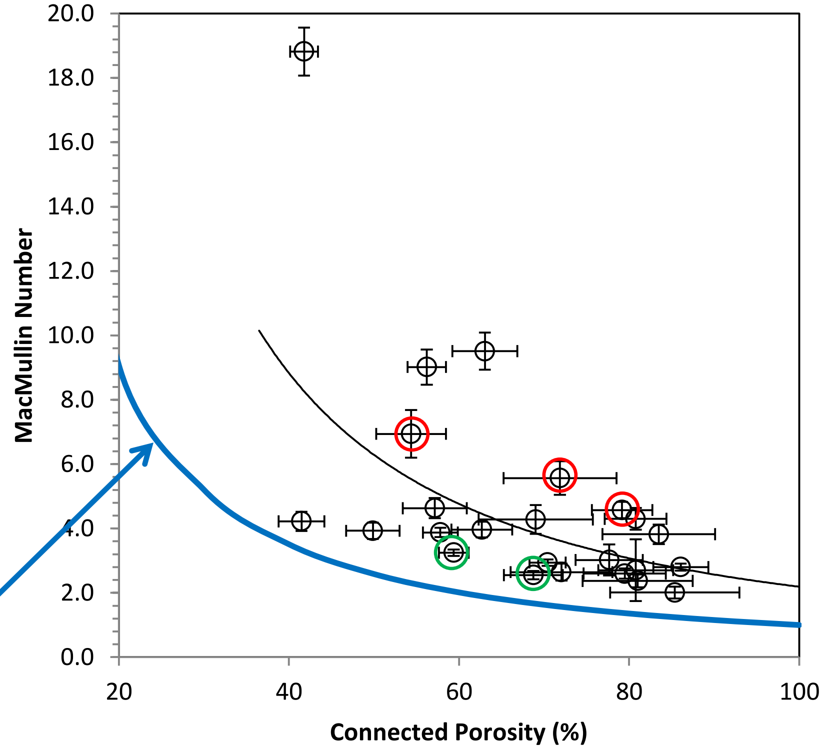
Some large-crystal brucite

Very low shrinkage on sintering

Varied microstructure

Ionic Conductivity

- Ionic Conductivity depends more closely on connected porosity

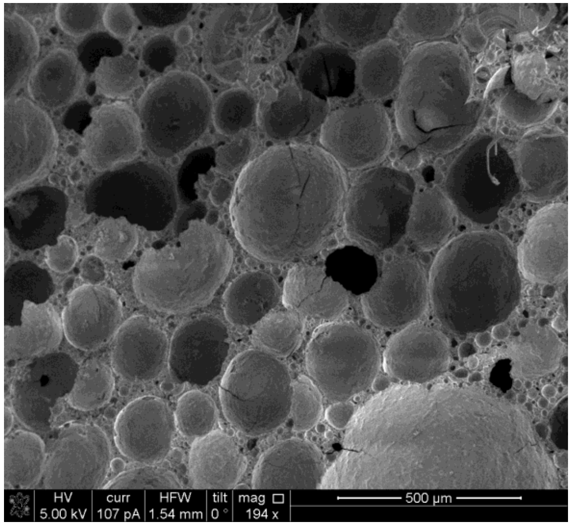


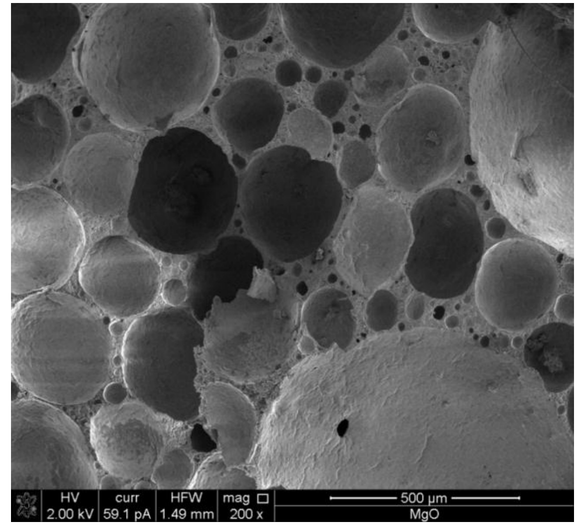
Ideal porosity with no tortuosity

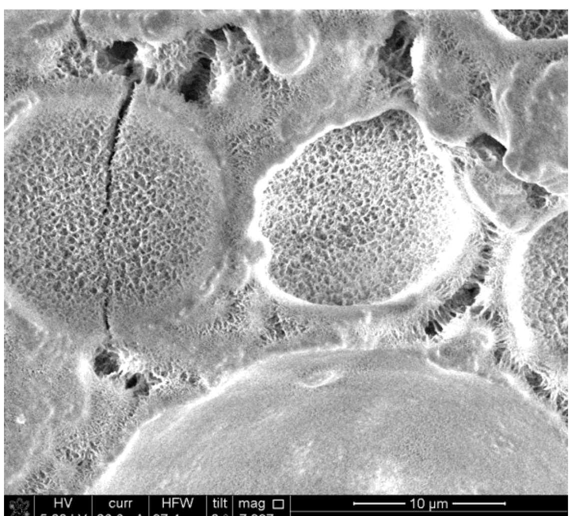
Relatively Good Ionic Conductivity

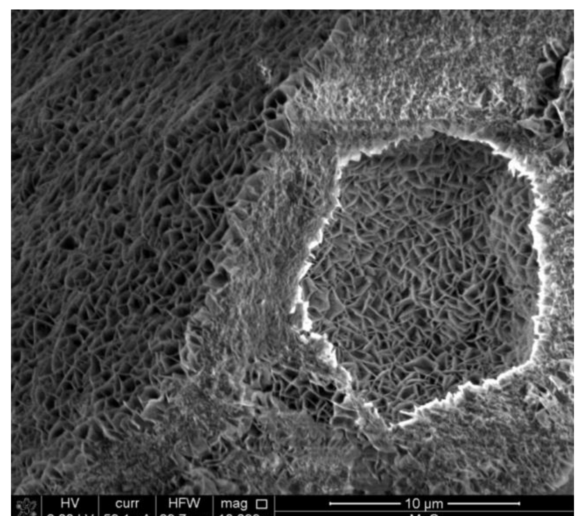
MM = 3.2 ϕ=59%

MM = 2.6, ϕ=69%



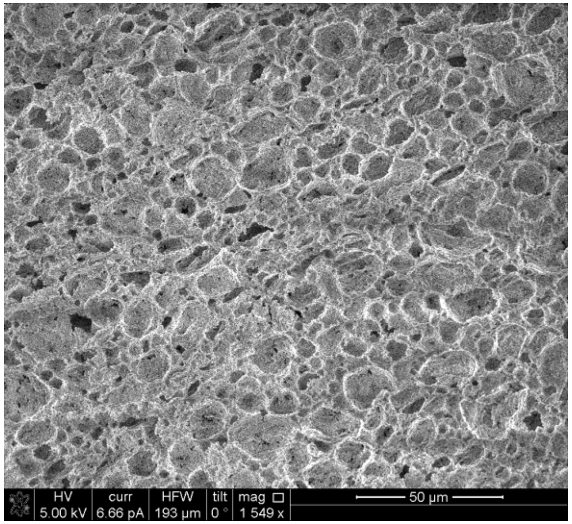


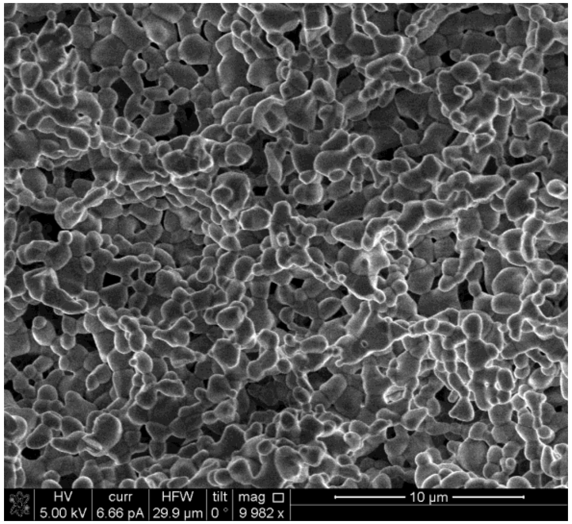




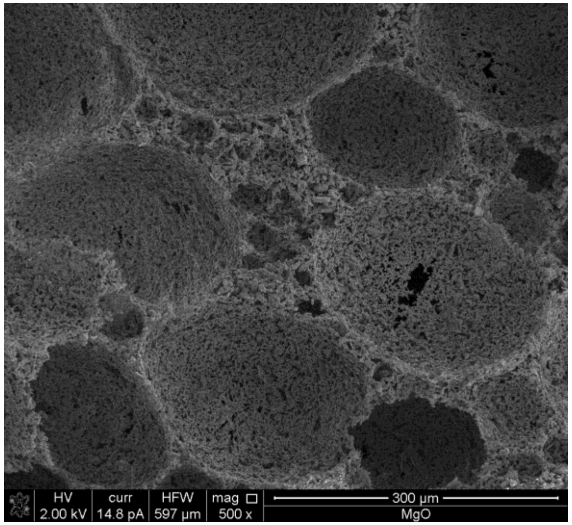
Relatively Poor Ionic Conductivity

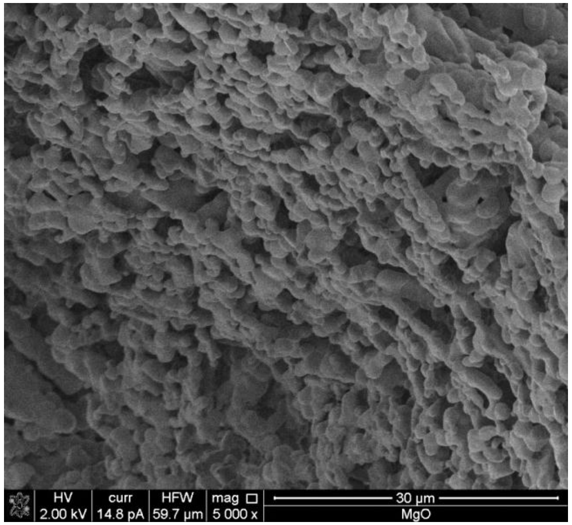
MM = 6.9, ϕ=54%



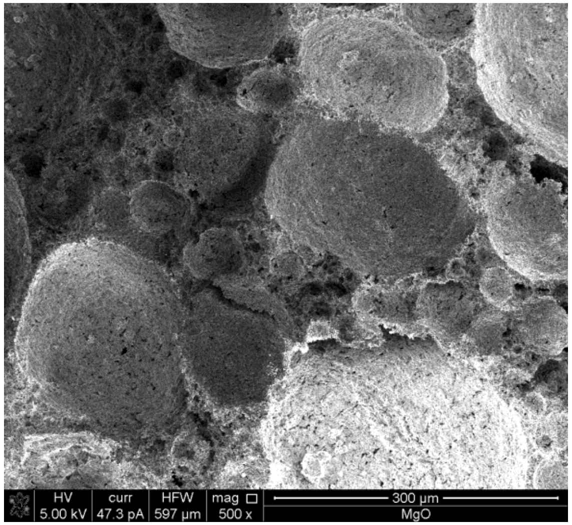


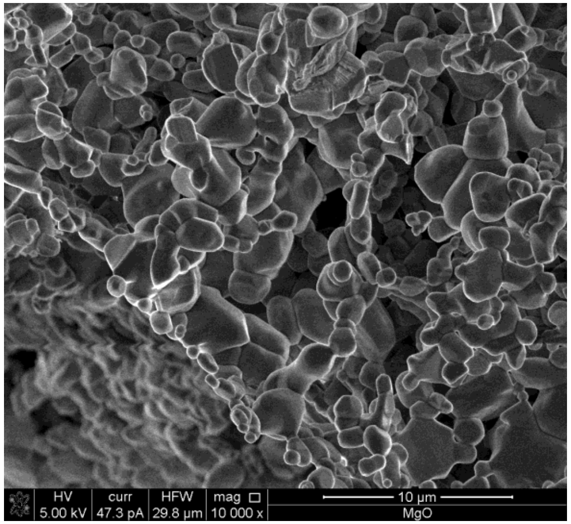
MM = 5.6, ϕ=72%





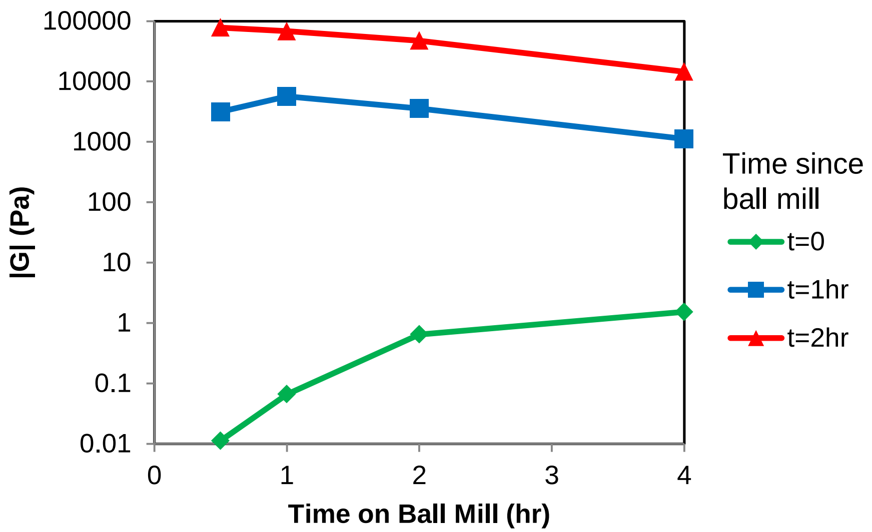
MM = 4.3, ϕ=81%

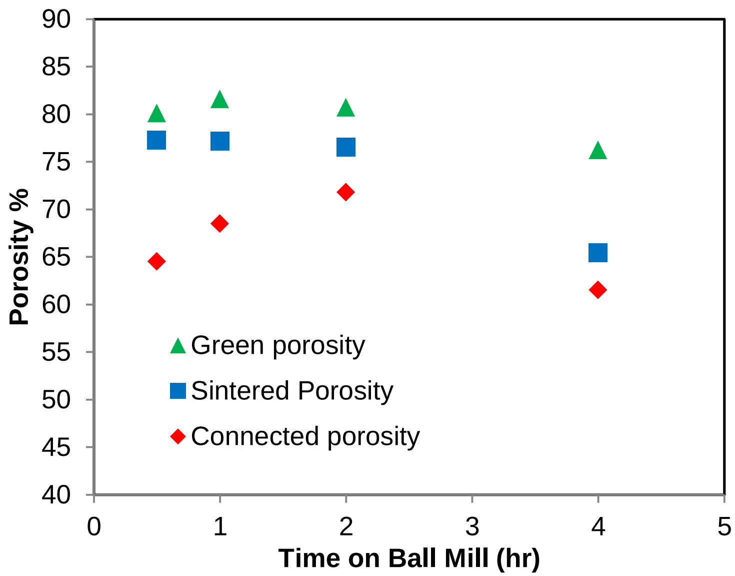




Optimize Microstructure

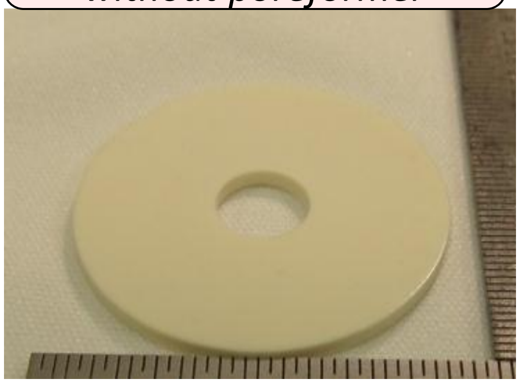
- Working with MgO suspensions to understand microstructure formation and control collected porosity & permeability
- Gelation is history dependent and thixotropic
- Ceramic properties as a function of milling conditions
  - 12.5% MgO in 0.1M HCl



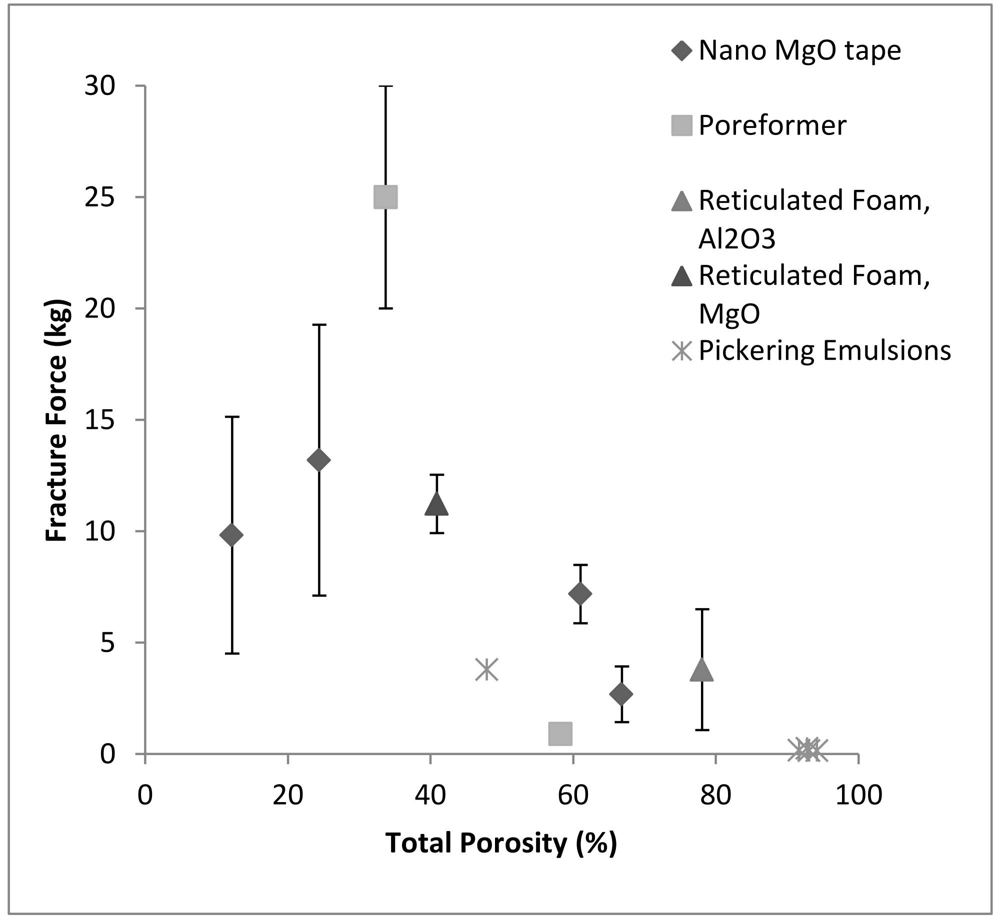


Fracture Strength Comparison of Various Foamed Ceramics

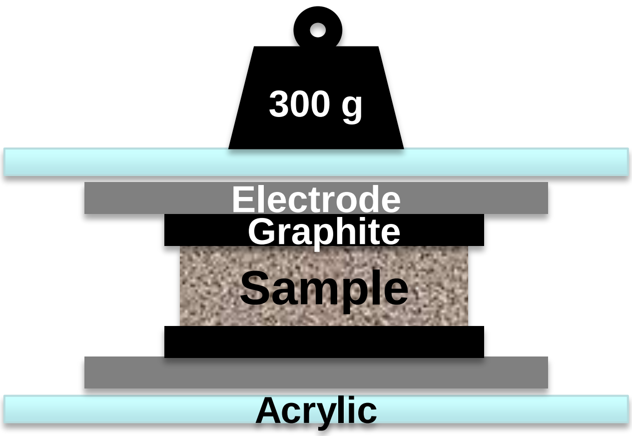
Tape cast with and without poreformer ◆

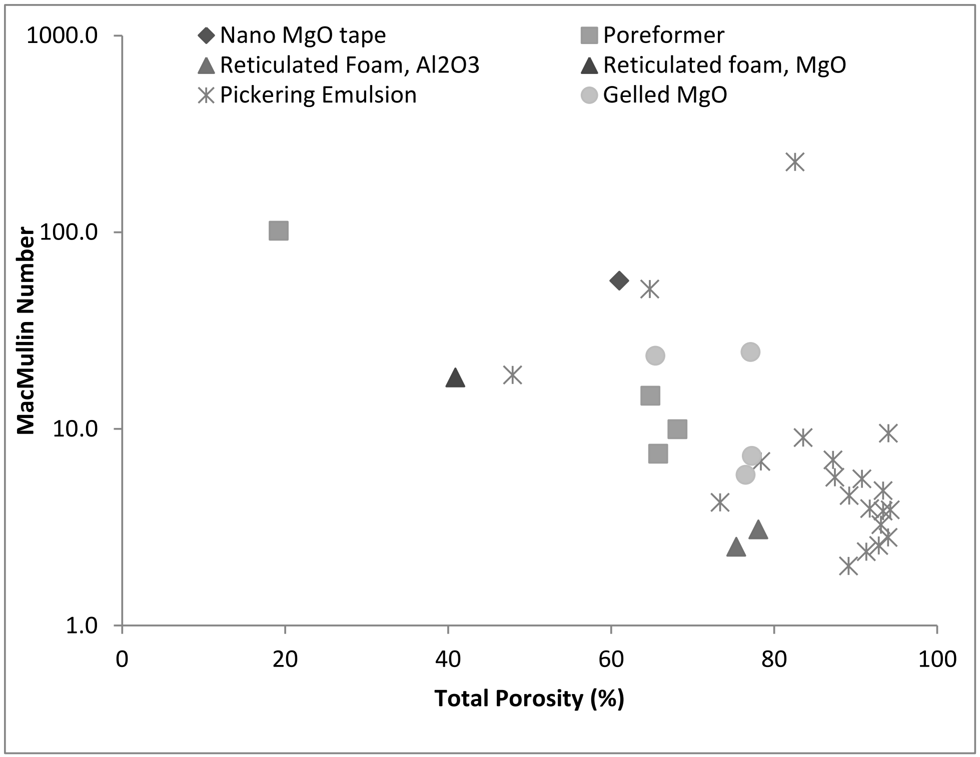


Reticulated foam ▲



Ionic Conductivity





Impedance Spectroscopy

Sample filled with KCl + water solution
AC voltage applied across electrodes
Impedance measured vs AC frequency

Lower impedance desirable

$$MacMullin\# = \frac{\text{Sample resistance}}{\text{Solution resistance}}$$

Summary*

Goal: Create and characterize an effective, MgO -ceramic scaffolding for use as a battery separator that can be processed in large batches, molded or coated, sintered, and back-filled with electrolyte.

- Developed MgO ceramic techniques
  - Highly porous, permeable, mechanically strong

Pickering emulsion ceramic foams and replicated reticulated foams are the most permeable

Numerous parameters influence performance

Brucite formation & Microstructure need to be optimized

- Future: Demonstrate performance of new MgO structure
  - Fill with electrolyte
  - Test in battery stack

Single cell tests will determine if mechanical strength and conductivity are sufficient

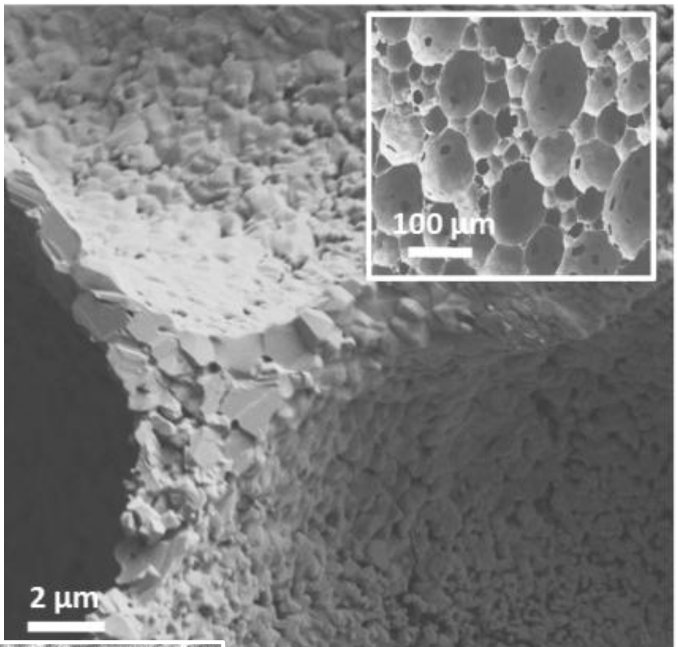
*The authors would like to acknowledge support from the Laboratory Directed Research and Development Program at Sandia National Laboratories.

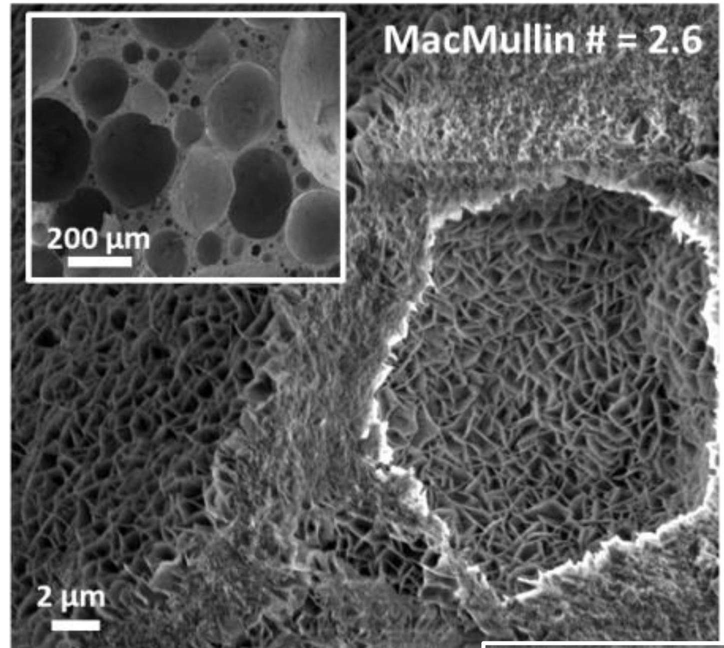
Effect of MgO

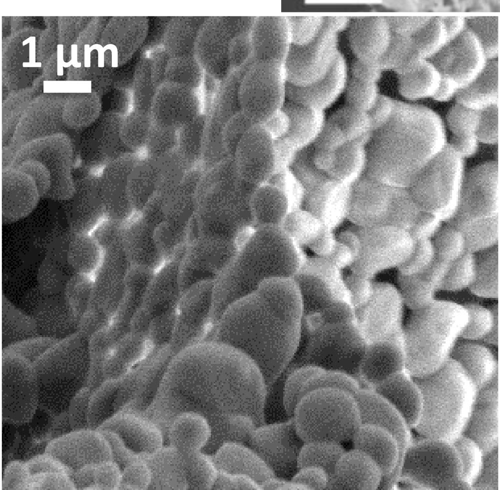
Microstructure Variations in Sintered Samples

24hr M

$Mg(OH)_2$ particle shape brucite







Macroscopic appearance