Creation and Characterization of Magnesium Oxide Macroporous Ceramics

SAND2011-7554C

Lisa Mondy, Christopher Diantonio, Tom Chavez, Lindsey Gloe, Anne Grillet, Christine Roberts, David Ingersoll

Sandia National Laboratories, Albuquerque, NM, USA

11th AIChE Annual Meeting
Minneapolis, MN
October 16-21, 2011

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Sandia National Laboratories

Overview

Goal: Produce *ceramic foams* to carry electrolyte and separate anode and cathode layers in batteries

- Highly porous
- Open celled
- Chemically compatible in a wide range of batteries → Magnesium Oxide (MgO)

Current Process:

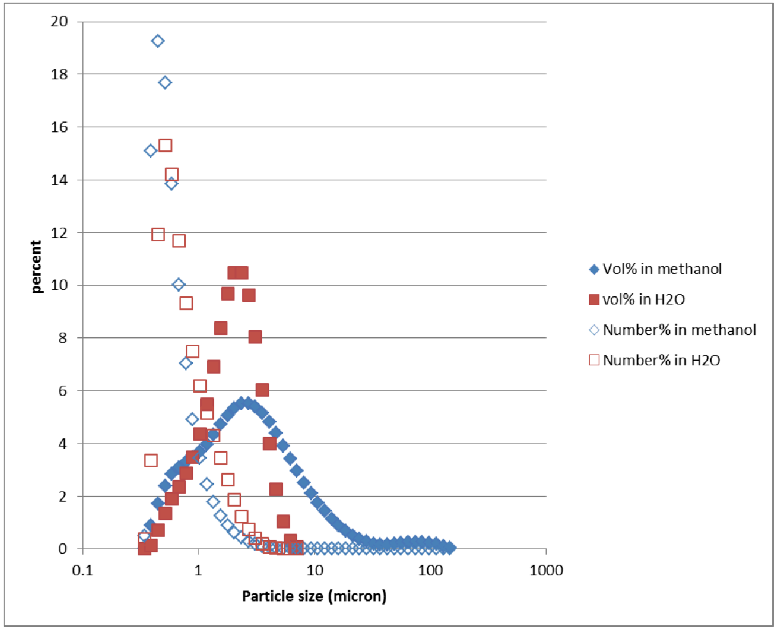
- Mix molten electrolyte and MgO powder, allow to cool to solidify electrolyte, regrind into a powder and press into a pellet
- Ceramic scaffold backfilled with molten electrolyte would add strength to pellet at high temperatures when electrolyte melts

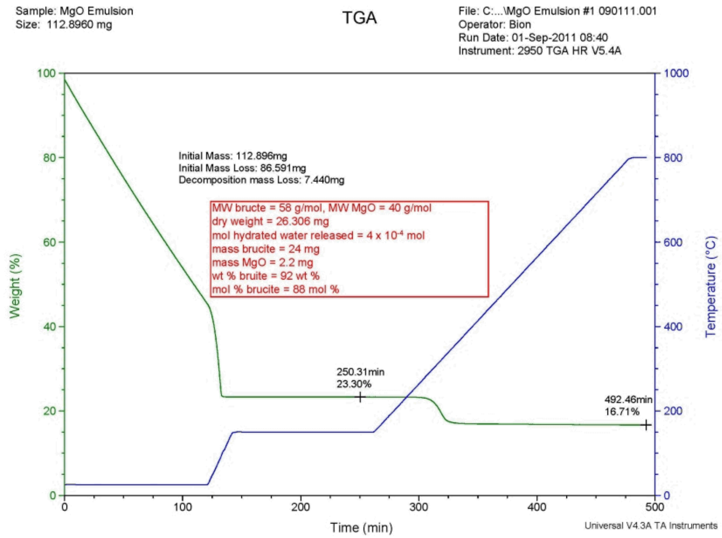
Outline:

- Issues with MgO
- Standard Ceramic Foam Processing
- Pickering Emulsions as Ceramic Template

MgO Hydrolyzes Easily

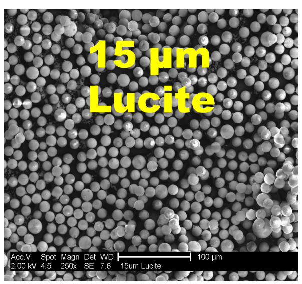
- Particles ball-milled to break agglomerates or to mix ceramic slip
- When ball-milled in H_2O, even micron-sized MgO particles hydrolyze to Brucite $Mg(OH)_2$
- Toluene-based ceramic slips work best
- Ball-milling in methanol works well

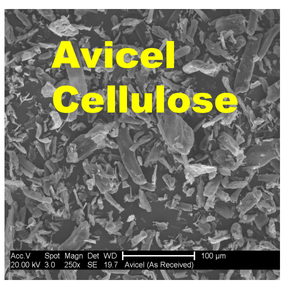


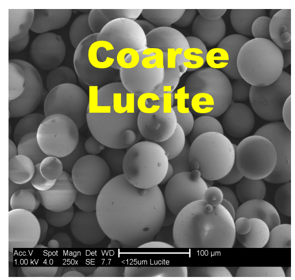


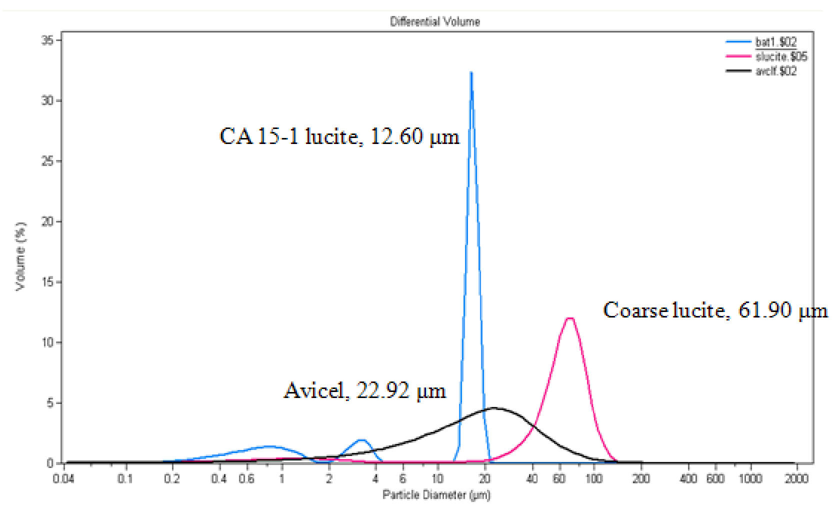
Standard Porous Ceramic Manufacturing Technique: Sacrificial Template Method

- Biphasic composite comprising a continuous matrix of ceramic particles and a dispersed sacrificial phase.
- Sacrificial phase extracted by heat during sintering to generate pores within the microstructure.
- Looked at submicron and nanocrystalline MgO mixed with 15-micron or 100-micron pore formers.





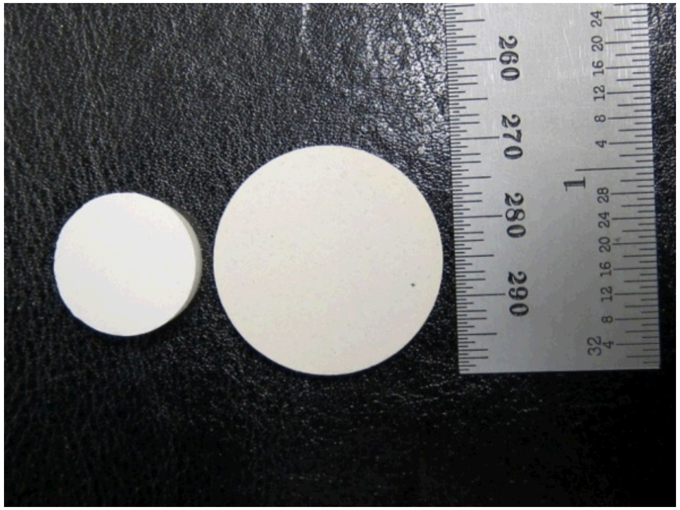




Sandia National Laboratories

Pressed powder

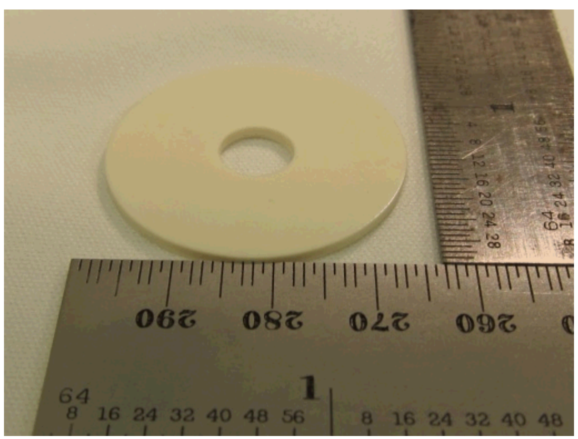
- With added pore former, we pressed and sintered MgO pellets
- No worries about slip solvent/pore-former compatibility
- But desire a way to manufacture many cheaply without the labor of pressing individual pellets



Nano-MgO (Inframat nano MgO Powder, 99.9%, 35nm) powder plus pore former creates porous, strong ceramic

Tape Casting

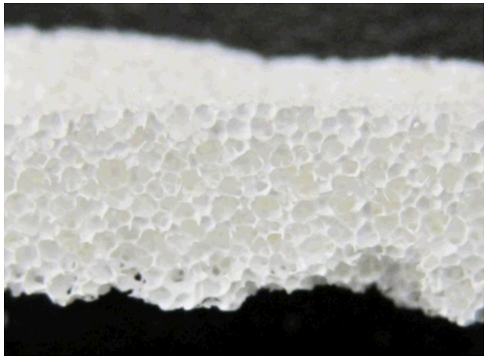
- Tape casting suspensions contain variations of nanocrystalline size MgO particles (Inframat), sub-micron crystalline size MgO particles (Inframat) and organic pore formers (Lucite and Avicel)
- B73305 Ferro tape cast vehicle
- Hypermer KD1 dispersant and toluene
- No significant degradation of the pore former from chemical attack noticed, even Lucite
- The suspensions varied between 10-20 wt% MgO and 4-8 wt% organic poreformer
- Resulting tape can be stacked, punched



20 layers of tape cast Nano-MgO (Inframat nano MgO Powder, 99.9%, 35nm) powder plus pore former creates porous, strong ceramic.

Replication Technique

- Foam is infiltrated with a ceramic suspension, dried, and sintered, which removes the original foam
- Only a thin layer of suspension remains on foam surfaces, therefore foam is replicated – open celled foams possible
- Urethane foams resistant to Toluene
- 25-50 wt% ceramic powder, 2-10 wt% polyvinyl alcohol (Fisher) and 0.5-1 wt% Dolapix (dispersant)



Sintered samples of replicated ceramic foams

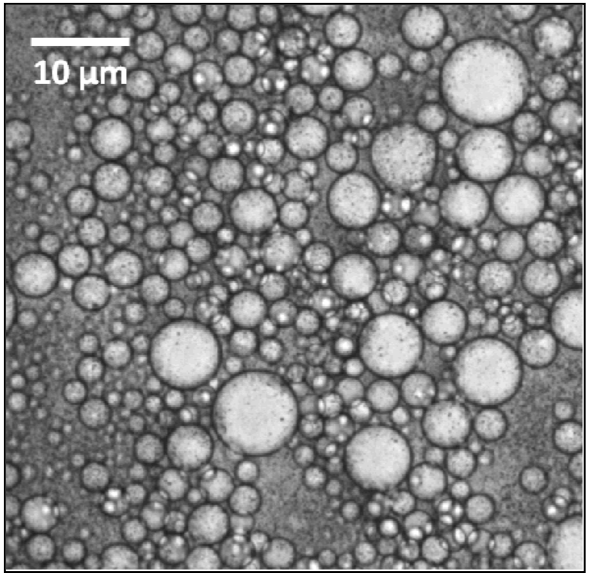
Sandia National Laboratories

Emulsion Templating

- After Akartuna et al. *Advanced Materials, Langmuir* 2008, ceramics are made from particle-stabilized oil/water emulsions.
- We substituted MgO for Al_3O_2
- After Hibner et al. *J. European Ceramic Soc.* 1997 and Gonzenbach et al. *Langmuir* 2006, we treated MgO particles with carboxylic and dicarboxylic acids.
- Untreated particles will still stabilize the emulsions, however, the treated particles allow much more of the dispersed phase to be incorporated. (Despite brucite)

Compound	$\log_{10}$ K for Mg^{2+}	I (m)	$\log_{10}$ K for Al^{3+}	I (m)
Methanoic	0.34	0.5	1.36	1
Ethanoic	0.51	0.1	2.04	0.1
Propanoic	0.54	0.1	1.69	1
Butanoic	0.53	0.1	1.58	1
Malonic	2.05	0.1	6.36	0.5
Butylmalonic	2.51	0	NA	

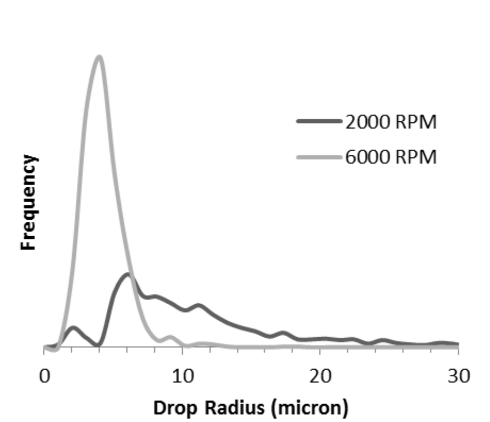
Complexation constants between the acids and Mg^{2+} , Al^{3+} for the reaction $[ML]_{(aq)}/[M^{x+}]_{(aq)}[L-]_{(aq)}$.



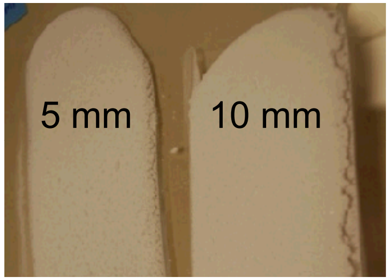
Particles surface treated with valeric acid go to droplet interfaces to create Pickering emulsions.

Parameters Explored to Optimize Emulsion Processability

- Wetting of particle controls migration to interface:
  - Amphiphile type, concentration
  - pH
- Composition:
  - Initial particle fraction in water
  - Oil fraction in emulsion
  - Other immiscible systems (methanol replacing water)
- Mixing technique
  - Ultrasonic mixer (too much energy!)
  - Cowles mixer speed, duration
- Drying
  - substrates
  - addition of polymers to prevent cracking
  - rate



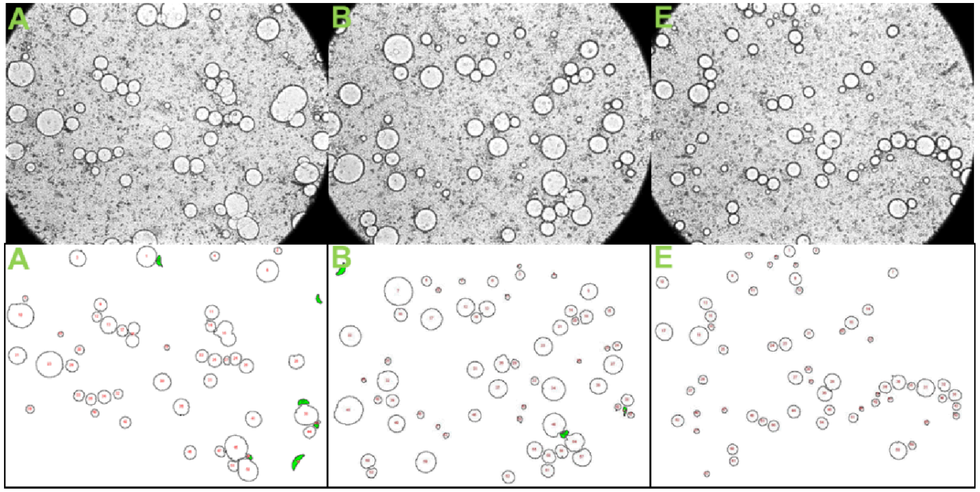
Initial droplet size depends most strongly on mixing speed.
Emulsion contains 0.3% PVA and 350 mM propionic acid.



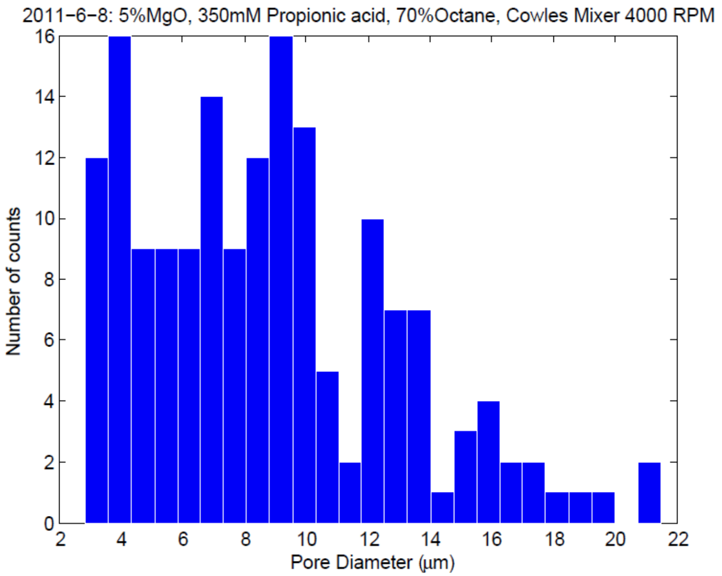
Ultrastable emulsions can be tape cast or formed..

Droplet Size Analysis

- Size analysis from images of diluted sample on slides
- Image analysis done in commercial software packages (MatLab or ImagePro)



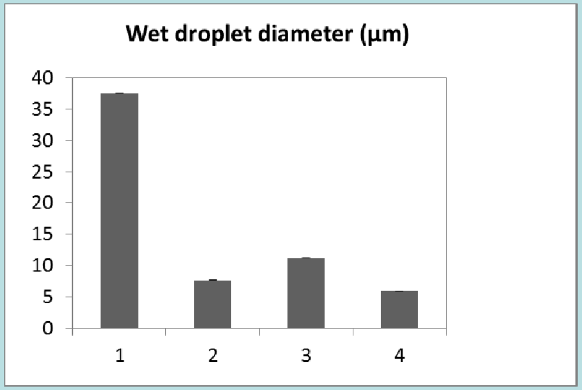
20x microscope images. Emulsion diluted for better microscope image

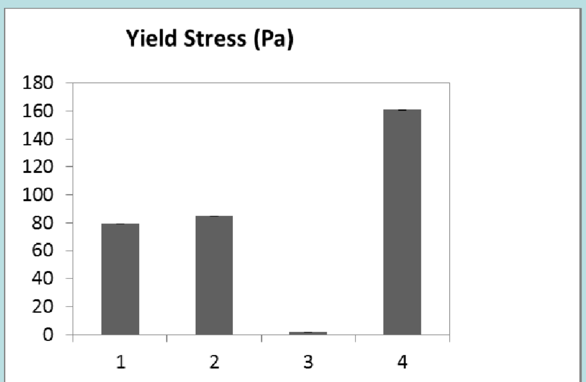


Mechanical Properties Measurements

Quantification of mechanical properties of green emulsion-based ceramics will help us understand effects of processing and optimize for our application

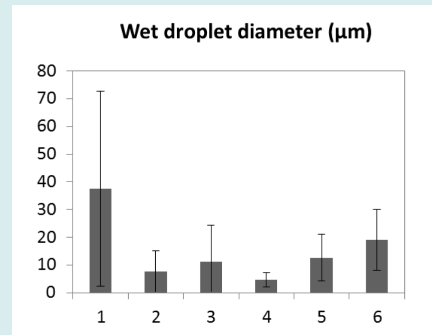
Droplet size alone does not indicate "goodness"

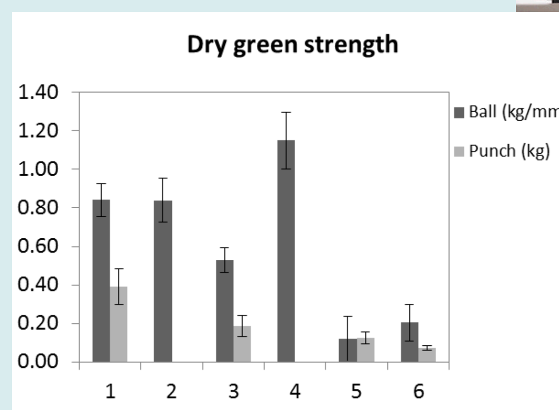




TA ARES-G2 Rheometer

Used to determine yield stress as an indication of stability





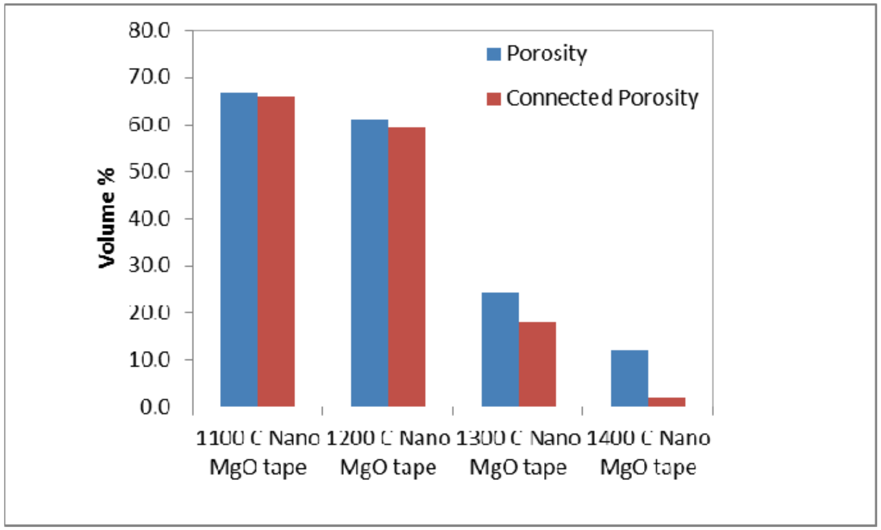
TA.XT*Plus* Texture Analyzer

Used to indicate the hardness

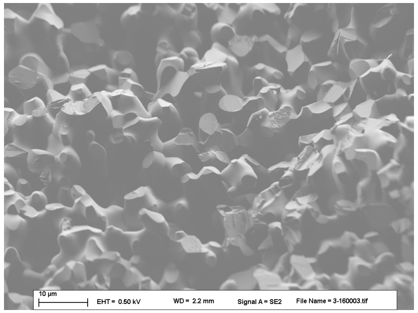
Sandia National Laboratories

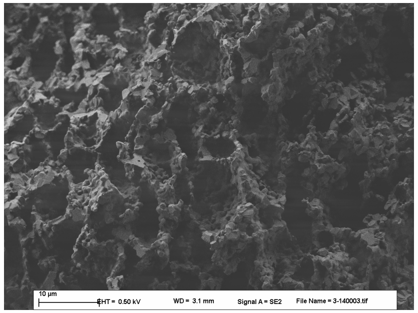
Effects of Sintering

- Sintering studies have just begun
- As expected, in general, the lower the sintering temperature the more connected porosity remains
- Slips/emulsions using smaller particles can be sintered at lower temperatures.



Traditional tape cast samples show clear effect of sintering temperature





SEM of emulsion samples sintered at 1600C above and 1400C below

Comparison of Methods to Date

Sample Type	Highest Total Porosity (volume %)	Highest Connected Porosity (volume %)
Pressed MgO/pore former	37	20
Traditional tape cast MgO/pore former	67	66
Emulsion	75	75
Foam replication	Not tested yet	

Summary

- Variety of techniques show promise in creating high porosity, open celled, MgO ceramic foams
- Work in progress to optimize methods for our applications
- Emulsion templating promising but not as mature
- A variety of diagnostics will help mature emulsion technique
- Next steps with emulsion templating:
  - Use nano-scale particles
  - Develop non-aqueous emulsion systems
  - Refine drying/sintering techniques
  - Optimize formulations including polymeric binder

Sandia National Laboratories