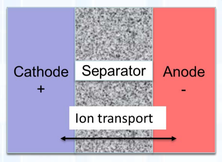
SAND2013-3186P

Design of Macroporous Ceramic Battery Separators

Christine Roberts, Lindsey Hughes, David Barringer, Lisa Mondy, Anne Grillet, Stephanie Fitchett, Chris Diantonio, Tom Chavez & David Ingersoll

Challenge:

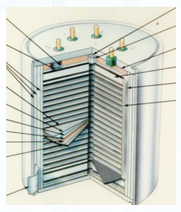
- Polymer lithium ion battery separators are subject to thermal runaway
- Molten salt battery separators are expensive to manufacture and need to be thick to be mechanically strong



Goal:

Create and characterize an effective magnesium oxide (MgO) thermal battery separator

- Separator must be highly porous, permeable, and mechanically strong
- Separator will be coated, sintered, and filled with electrolyte.
- Performance of separator will be tested in a battery stack

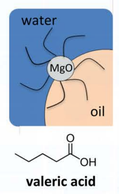


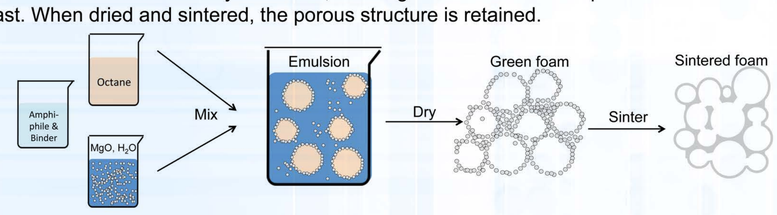
Method:

Pickering emulsions will be dried and sintered to produce highly porous foams. Formulation and processing parameters will be explored to optimize performance. Results will be compared to some traditional methods of creating porous ceramics.

Control of Ceramic Foam Microstructure:

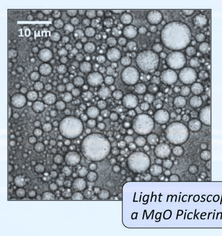
The creation of a ceramic foam using Pickering emulsions is a multi-step process, offering many parameters that have impact on the final microstructure and performance. Pickering emulsions are created following the work by Akartuna et al.[1] where short chain amphiphiles are used to modify the wetting behavior of the magnesium oxide so the particles are most stable at the interface of the octane-water emulsion. The resulting emulsion has a substantial yield stress, allowing it to be molded or tape-cast. When dried and sintered, the porous structure is retained.





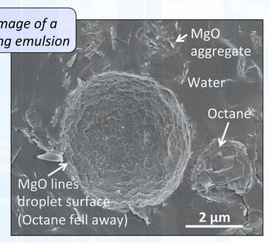
Formulation Process Variables:
- MgO particle size & concentration,
- Mixing time & speed
- Amphiphile chain length & concentration
- Binder type & concentration
- Octane amount

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

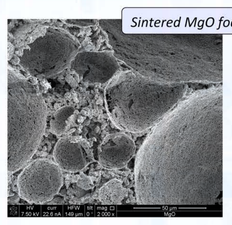


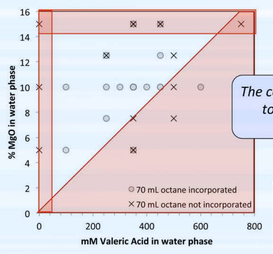
Light microscopy image of a MgO Pickering emulsion.

CryoSEM image of a MgO Pickering emulsion

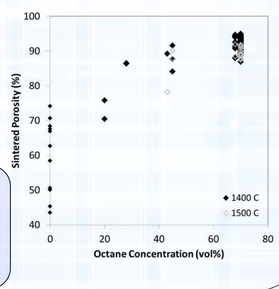


Sintered MgO foam





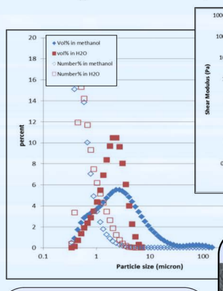
The correct ratio of valeric acid to MgO is required for a stable emulsion.

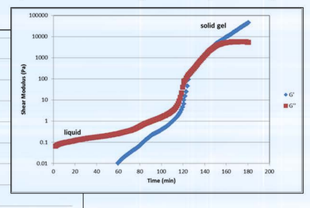


A multi-variable design of experiments concluded that most processing variables do not statistically affect foam porosity. The most effective processing variable to control porosity is the octane amount.

Effect of Brucite Formation on Microstructure:

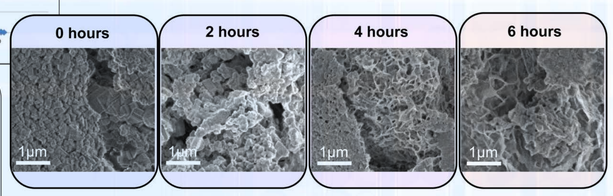
Relative humidity can be used to influence the amount of time it takes for the emulsions to dry. As the magnesium oxide is in contact with water, it hydrolyzes to brucite, $Mg(OH)_2$. The amount of brucite in the green foam greatly influences the drying and sintering shrinkage, as well as product strength and porosity.

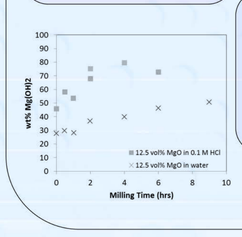




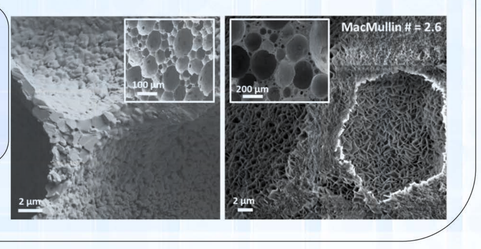
As magnesium oxide is initially dispersed into water, hydrolysis of MgO into brucite is apparent. Fragile brucite breaks into smaller particles than MgO that is ball milled in methanol. The transition can also be seen in the rheology of the suspension. After two hours, the suspension gels as brucite makes a percolated network in the water.

The brucite reaction is also apparent in the shape of the ceramic particles in the dried emulsion. Right we show green samples that were dried for various amounts of time.





The brucite particle shape is sometimes retained, even after sintering the samples. Samples with more brucite shrink more on sintering.

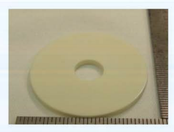


Comparison to Traditional Porous Ceramic Processing Techniques:

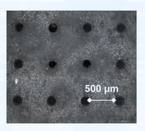
The performance of ceramic foams manufactured from Pickering emulsions are also being compared to other approaches to porous ceramic manufacturing techniques.

Pressed pellet with added poreformer

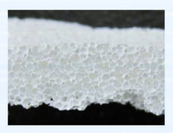
Tape cast with and without poreformer added



Tape cast with punched array of holes

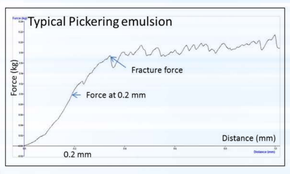


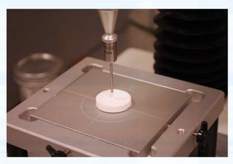
Reticulated foam

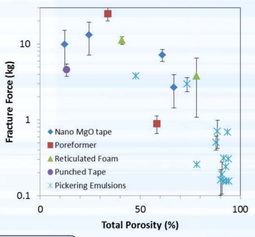


Fracture Strength of Sintered Samples:

The fracture strength is measured by a Texture Technologies TA.XT Plus texture tester using a 2 mm diameter probe



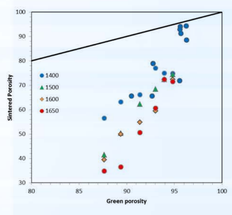


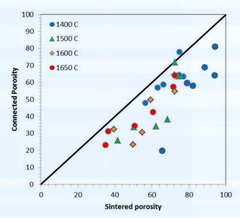


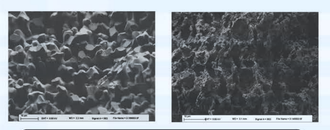
The fracture force of all ceramic is highly dependent on the total porosity

Effect of Sintering Temperature:

Sintering temperature has a big impact on the final structure of the ceramic foam. Higher temperatures reduce the foam porosity as the particles are increasingly consolidated.



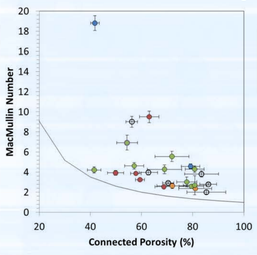




SEM of emulsion samples sintered at 1600 °C (left) and 1400 °C (right)

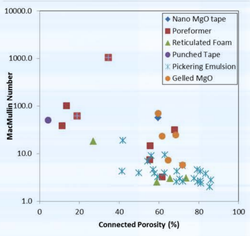
Ionic Conductivity:

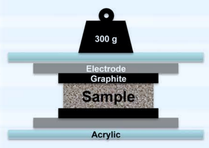
One important measure of the permeability of the ceramic foams is the ionic conductivity. The ceramic foams are soaked in conductive KCl solutions and then the impedance is measured as a function of frequency. Where the frequency response is in-phase with the applied AC current, the resistance is measured. Results are reported in terms of the MacMullin number which gives the resistance of the sample relative to the pure salt solution.



Sintered Pickering emulsion samples with flake like structures (red) are more conductive than otherwise (green). The ideal case for each porosity is shown as a line.

Pickering emulsion samples have relatively low MacMullin numbers as compared to porous ceramics made by other traditional methods.

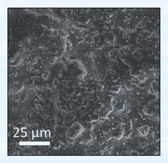


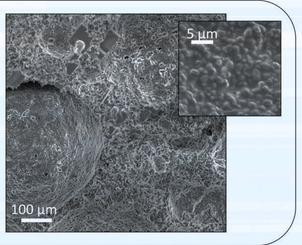


Backfill of Samples with Electrolyte:

Electrolyte must be added after the samples are sintered.

Room temperature filling methods fill pores in tape cast samples effectively (right), but access to large pores in Pickering emulsion samples (far right) becomes blocked. High temperature filling methods are being developed to circumvent this issue.





Conclusions:

- Particle stabilized emulsions show great promise as a manufacturing route for ceramic separators.
- Separator porosity and strength are sufficient for use in batteries
- Hydrolysis of magnesium oxide can produce samples with close to ideal permittivity
- Work is ongoing to demonstrate that new separator designs can be filled with electrolyte and function in a battery.

Selected References:

1. Akartuna I, Studart AR, Tervoort E, Gaukler LI. *Advanced Materials*. 2008; 20(24):4714.
2. "Highly Porous Ceramic Foams from Magnesium Oxide Stabilized Pickering Emulsions", Langmuir, *In preparation*.
3. "Highly Porous Ceramic Foams from Magnesium Oxide Stabilized Pickering Emulsions", AIChE extended abstract, October 2012, Pittsburg, Pennsylvania.
4. "Creation and Characterization of Macroporous Ceramics for Use as Molten Salt Battery Separator Layers", Power Sources Conference Proceedings, June 2012, Las Vegas, Nevada.

Acknowledgements:

We are grateful to Chris Frethem of the University of Minnesota Characterization Facility for cryoSEM images and Martin Nemer for helpful discussions.

This work is supported by the Division of Chemical Sciences, Geosciences, and Biosciences, the Office of Basic Energy Sciences, the U. S. Department of Energy.

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SAND2013-XXXXP Sandia Creative Group 284-2905 LW-04-13

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