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Role of microstructure and manufacturing in transport properties of highly porous ceramics

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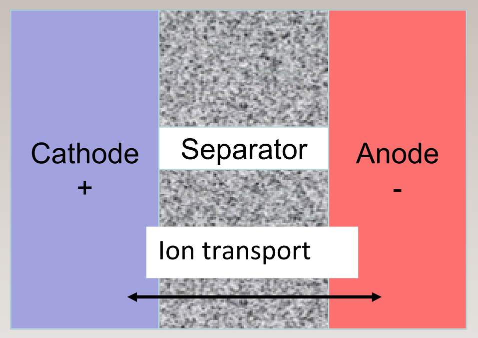
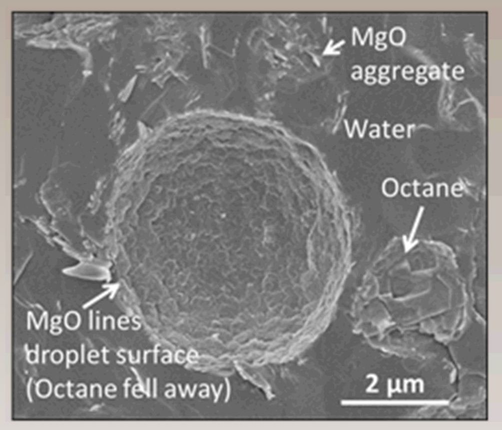
Goal:

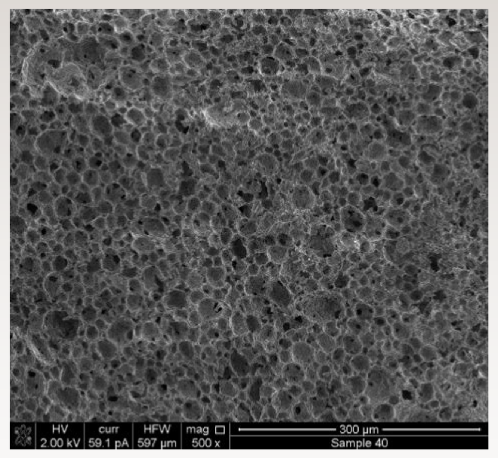
Produce *sintered ceramic foam battery separators* to electrically isolate the anode & cathode layers electrodes while allowing free ion transport

Current battery separators:

- Polymer separators for Lithium Ion batteries are susceptible to thermal runaway (i.e. Boeing 787)
- 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







Highly porous and permeable ceramic foams are useful for many applications ranging from catalyst supports, acoustic insulation, filtering molten metal alloy, tissue engineering scaffolds and high temperature insulation. One route for manufacturing ceramic foams pioneered by Akartuna et al. (2008) is to make concentrated Pickering emulsions stabilized by ceramic micro- or nano-particles which are then dried and sintered.

Pickering Emulsions

- We are focused on manufacturing MgO ceramic foams
- MgO particles are treated with carboxylic and dicarboxylic acids to make them neutrally wetting
- Resulting emulsion so stable that the liquids can be dried and leaving a particle scaffold
- Particle structure is sintered to create a ceramic
- Can also create ceramic foams from the colloidal gel of MgO suspensions
- **Ceramic foams with porosity up to 94%**

Process Variables:

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

Process Variables:

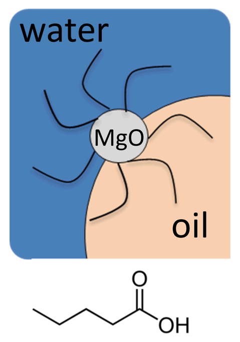
- Tape casting or cast in a mold
- Drying time
- Humidity
- Sintering temperature
- Sintering time and ramp rate

Characterization of emulsions:

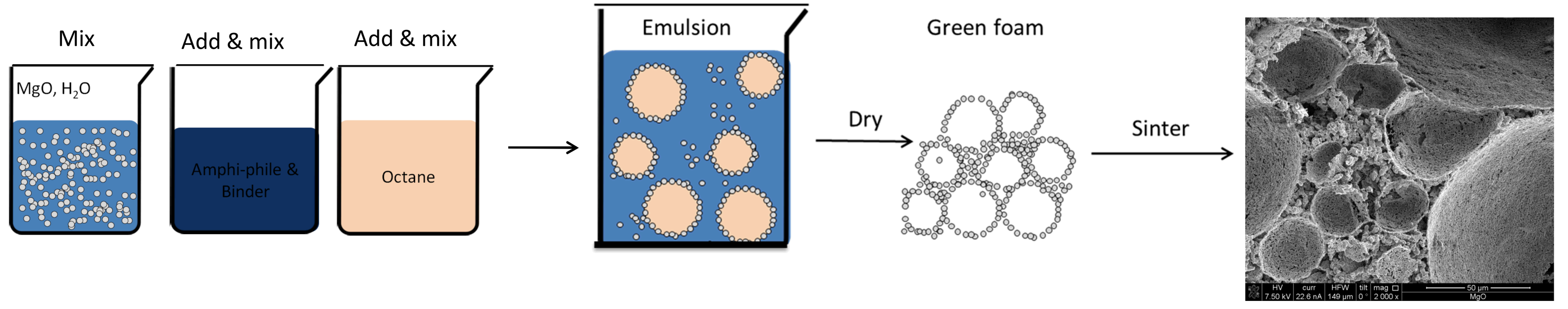
- Light scattering (MgO aggregate size)
- Thermal gravimetric analysis (TGA) for brucite amount
- Microscopy for droplet size
- Cryogenic scanning electron microscopy (SEM) for emulsion microstructure

Characterization of green and sintered ceramics:

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

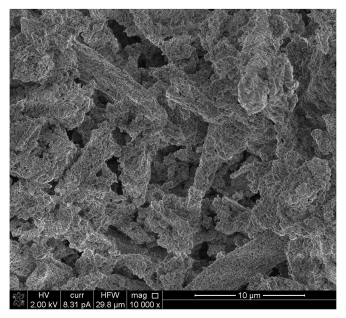


valeric acid

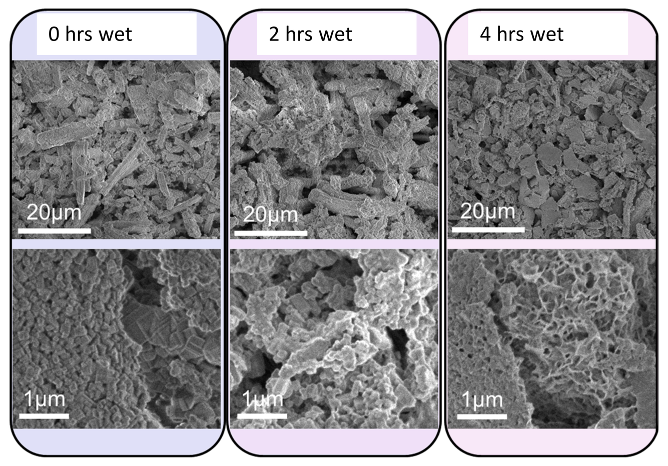


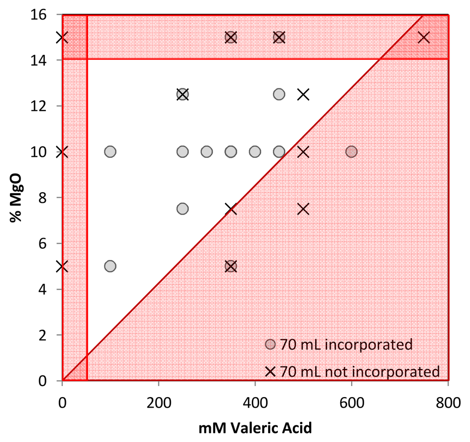
MgO suspensions form colloidal gels due to brucite conversion

- Makes a good ceramic foam too!

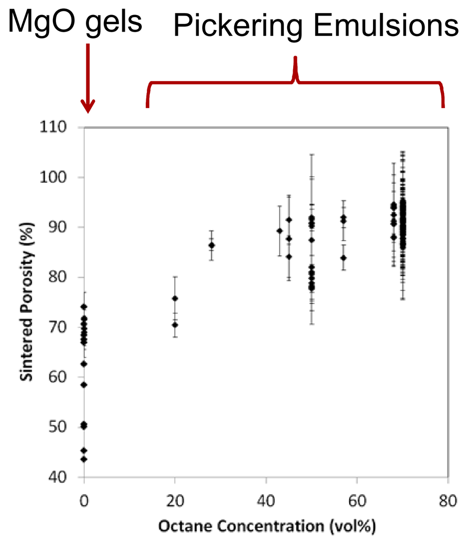


- Pickering emulsions most stable with H_2O-based formulation, leading to MgO hydrolyzing to $Mg(OH)_2$
- Slow drying minimizes shrinkage, maximizes porosity, and allows brucite crystal formation



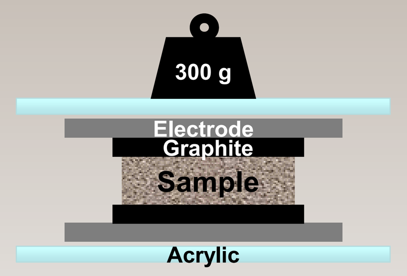


Stable Pickering emulsions can be made over a broad range of MgO concentrations with a balanced valeric acid concentration.



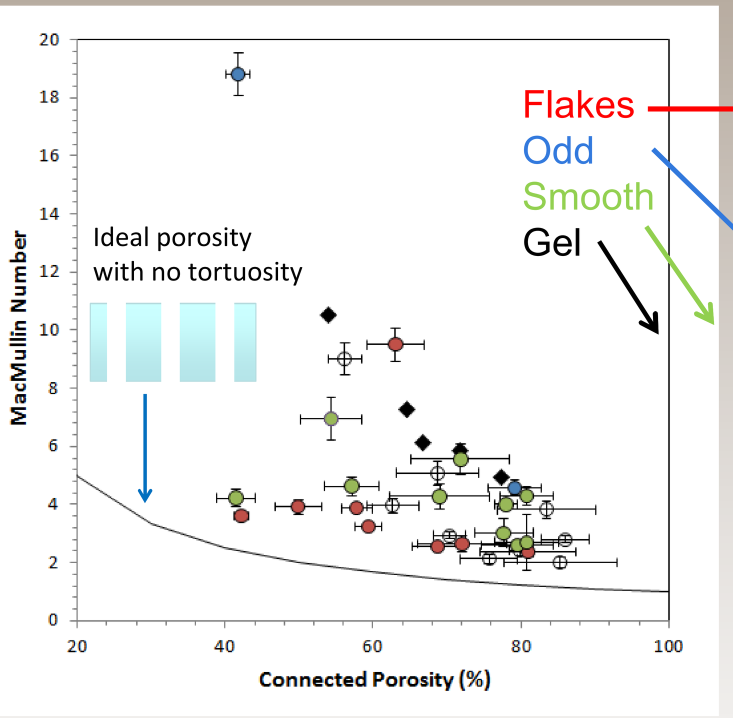
Performance

Ionic Conductivity



Impedance Spectroscopy

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

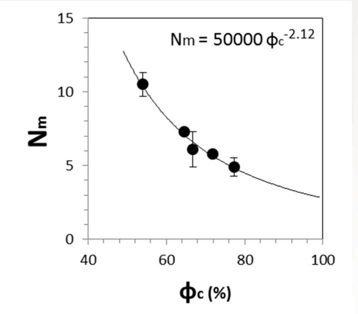


MacMullin # $N_m = \frac{\text{sample resistance}}{\text{solution resistance}}$

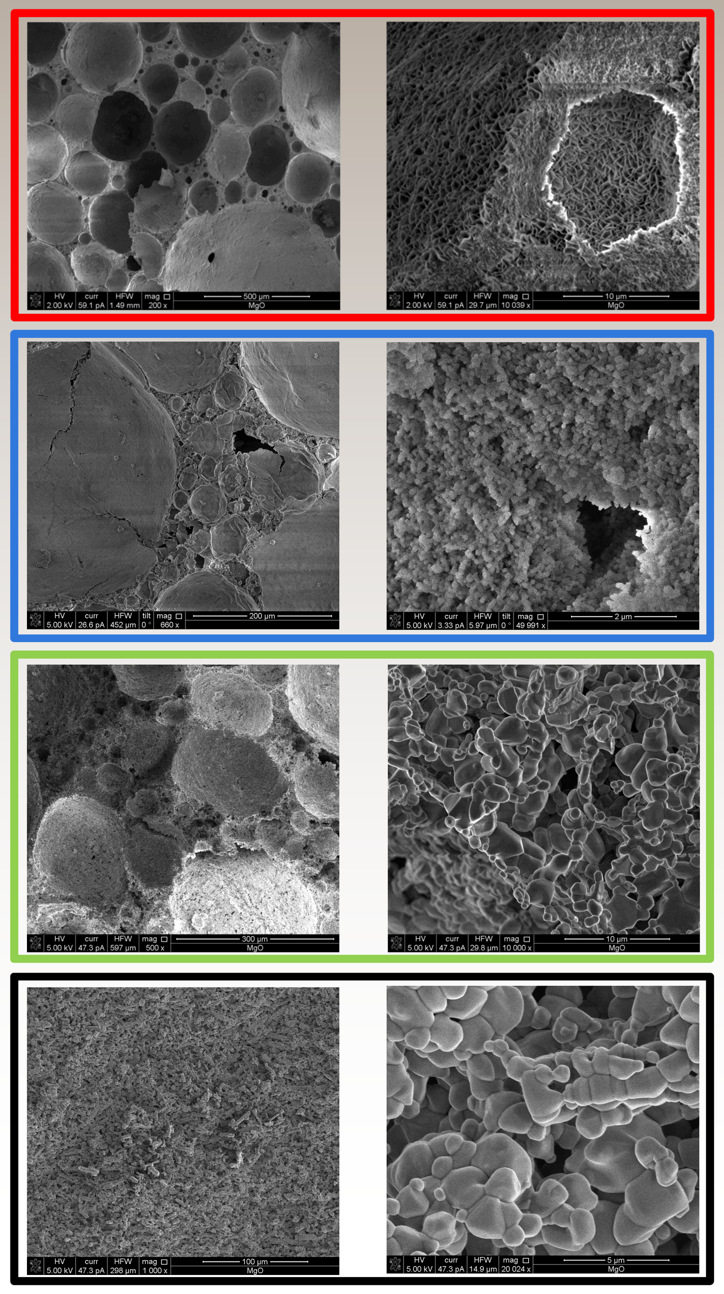
Archie's law (Archie, 1942) for MgO gel ceramics

$$N_m = a\phi_c^{-m}$$

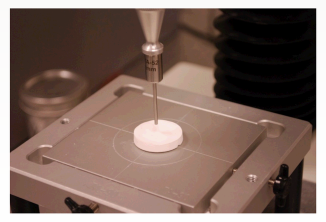
With no tortuosity m would be 1 (Dullien, 1975). In common materials, 1.3 < m < 2.5.
Gel porosity is very tortuous!



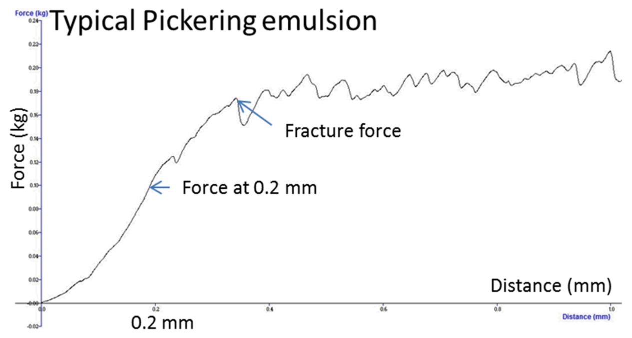
MgO Microstructure



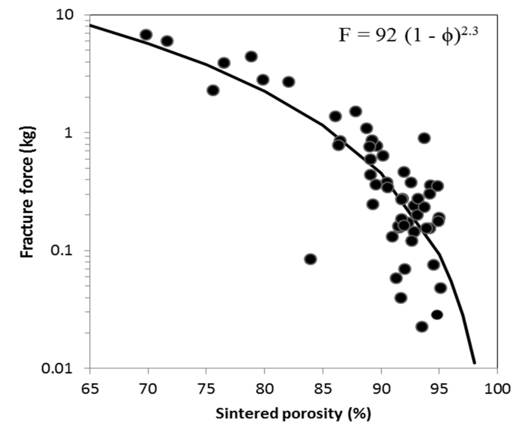
Fracture strength



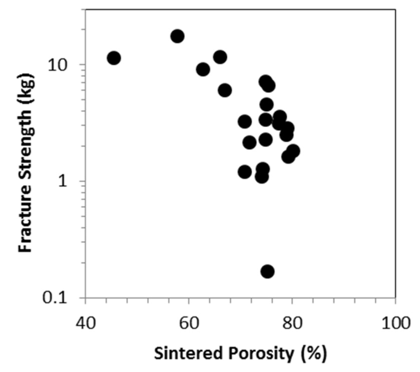
TA.XT*Plus* Texture Analyzer
2mm cylindrical indentation probe



Fracture force of Pickering emulsion foams is consistent with strength of closed cell foams Rice (1998)

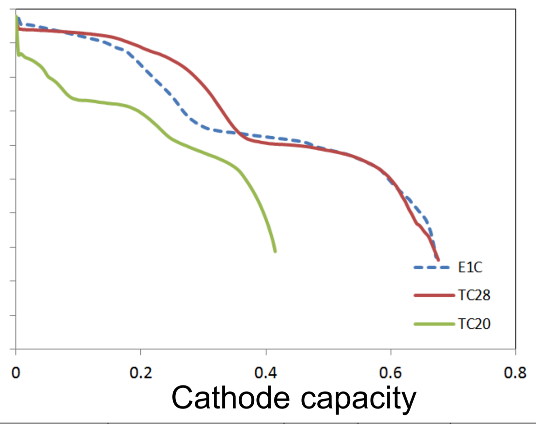


Gel ceramic foams tend to be stronger though less porous

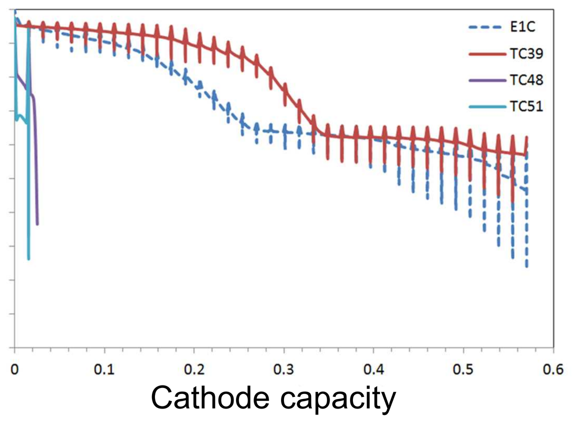


Battery Testing

For use in a battery, the ceramic foam must be filled with the electrolyte. Several methods from aqueous deposition to vacuum impregnation were tried. In particular the large pores in the emulsion samples were very difficult to fill with electrolyte. Gel ceramic foams were easier to fill with electrolyte and compare well to existing molten salt technology in single cell testing. However the cell impedance is noticeable higher as evidenced in the pulse discharge curves.



ID	Notes	Filling method	h (mm)	Before fill	After filling		
				Total porosity	vol% MgO	vol% elect	vol% pores
TC28	12.5% MgO	LiCl/KCl aqueous	1.39	84	16	30	53
TC20	12.5% MgO + gellan	LiCl/KCl aqueous	0.67	73	27	47	27
E1C	vol%s after melting	Pressed pellet	0.42		20	80	0?



ID	Notes	Filling method	h (mm)	Before fill	After filling		
				Total porosity	vol% MgO	vol% elect	vol% pores
TC39	12.5% MgO + gellan	LiCl/KCl aqueous	0.97	84	22	37	41
TC48	17.5% MgO, extra salt on top	LiCl/KCl aqueous	0.466	63	37	80	-17
TC51	17.5% MgO, sample not flat	LiCl/KCl aqueous	0.453	68	32	35	33
E1C	vol%s after melting	Pressed pellet	0.42		20	80	0?

References

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NNSA National Nuclear Security Administration
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