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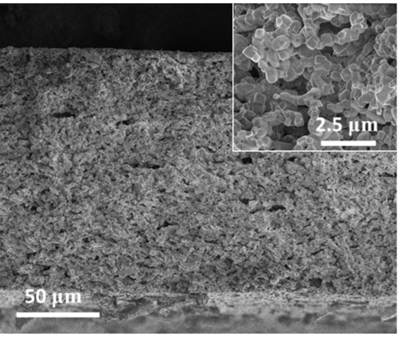


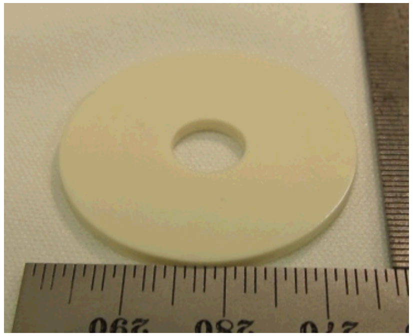

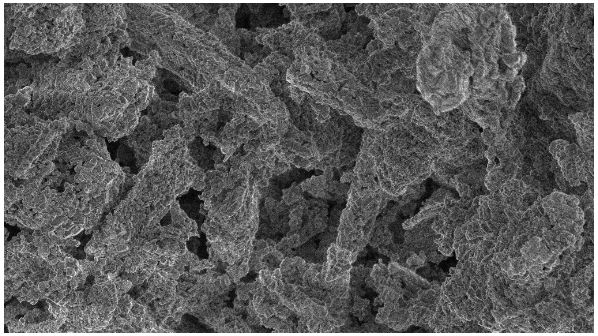

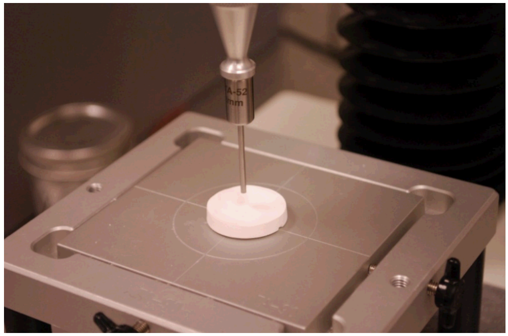

# New Macroporous Ceramic Pellets for use as Thermal Battery Separator Layers

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U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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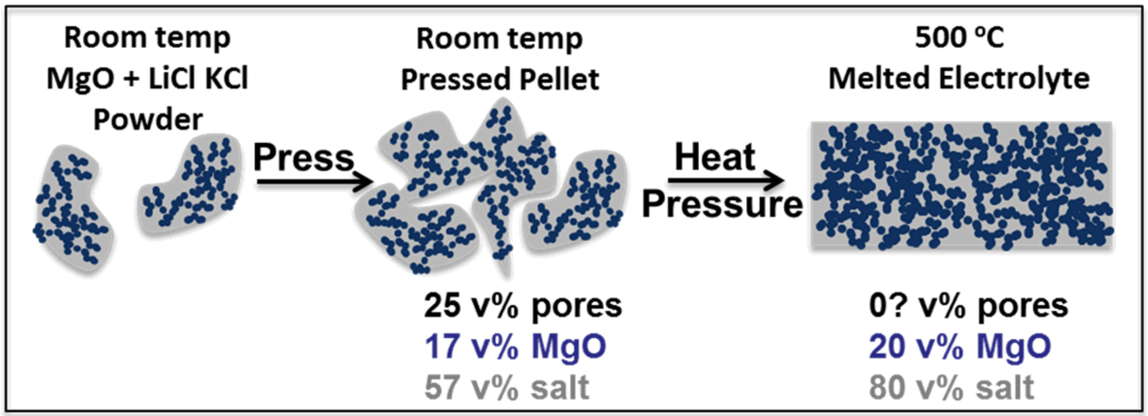
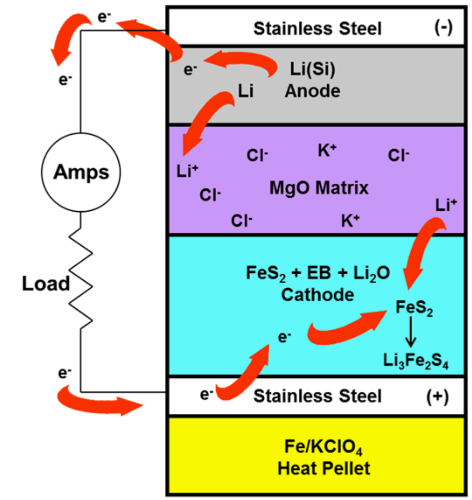
# Motivation

Current thermal battery separator technology




Pressed, porous pellet of electrolyte (LiCl/KCl salt) + Binder (MgO)

- Pressing operation : circular shapes, slow
- Pellet compresses, densifies on activation/melting salt
  - See talks 25.4, 28.1
- MgO properties significantly dictate performance, limit pellet thickness

# Goal:

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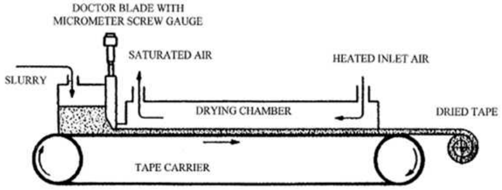
New porous ceramic that will be coated, sintered, and filled with electrolyte to serve as a separator in thermal batteries

- Performance
  - Porous and permeable to electrolyte
  - Robust enough to withstand battery closing force (~500 psi)
  - Chemically compatible with batteries (MgO)
  - Not dependent on MgO properties

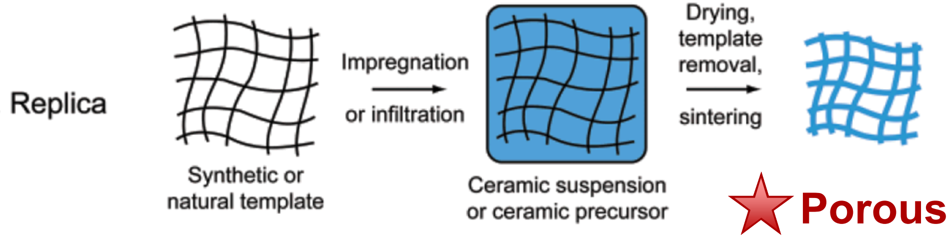
- Processability
  - Ability to be coated, dried, and removed from substrate
  - Sintered and cut to a flat shape
  - Backfilled with electrolyte
  - Robust enough to be handled

Lab-Cast Model TC-71LC



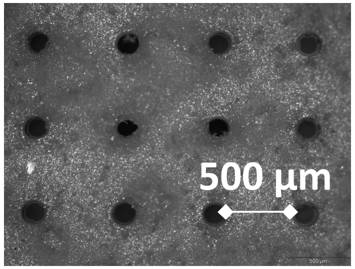
# Unsatisfactory fabrication methods

- Reticulated foam filled with ceramic slip




★ **Porous; not thin**

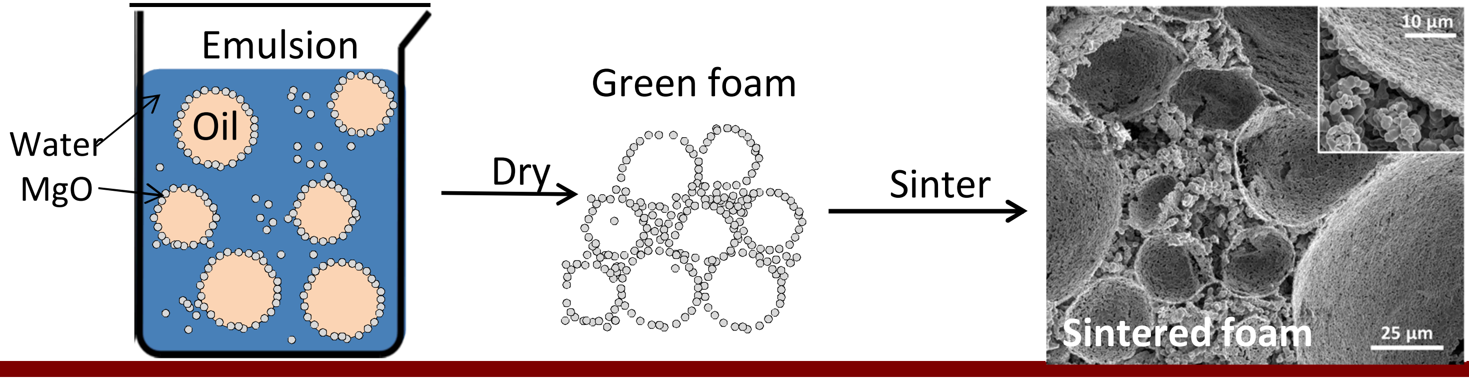
- Tape cast sample with punched hole array




★ **Strong; not porous**

- Dried Pickering emulsion

★ **Porous and strong; not flat, bad salt fill**

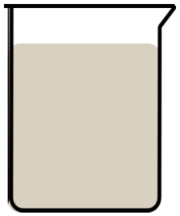


# Accepted fabrication methods

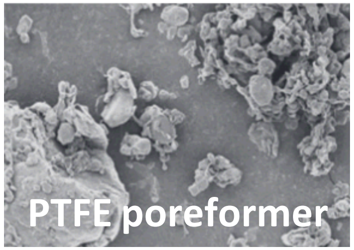
## Tape casting with poreformer burnout (“poreformer”)

- Mix ingredients in a turbula mixer, coat onto substrate

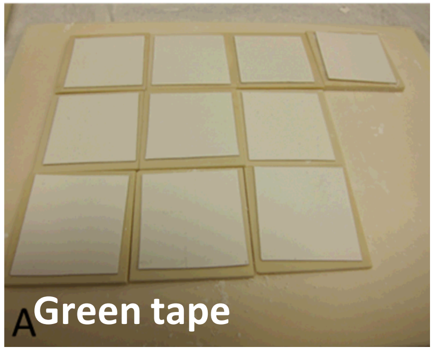
Toluene

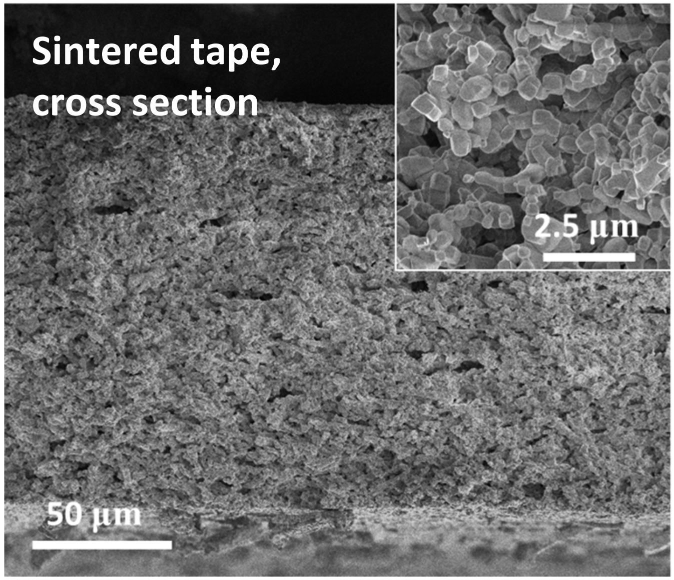


MgO




- Green tape is removed from substrate, layered, sintered
  - PTFE poreformer burns away, leaving pores

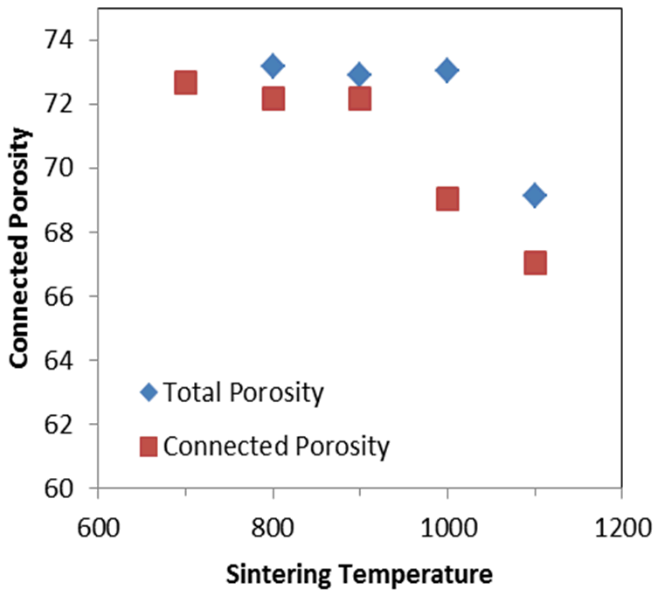



- Sintered tape is laser cut into circles

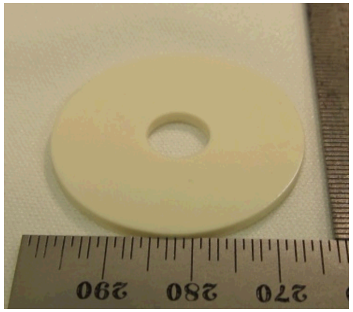
# Explored poreformer sample processing variables

- Poreformer concentration
  - 40 vol%, 50 vol%, and 70 vol% (total poreformer/total solids)
- Sintering temperature
- Sample thickness depends on number of layers laminated
  - 0.6 mm – 1.2 mm thickness, 1 inch diameter, center hole optional




Total porosity ranges from 20 vol% to 73%

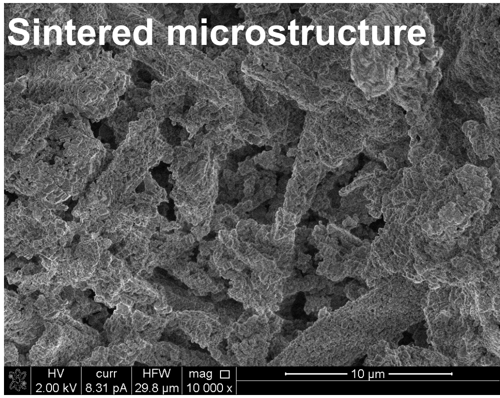
Current technology: Salt fraction = 80 vol%(?) when melted

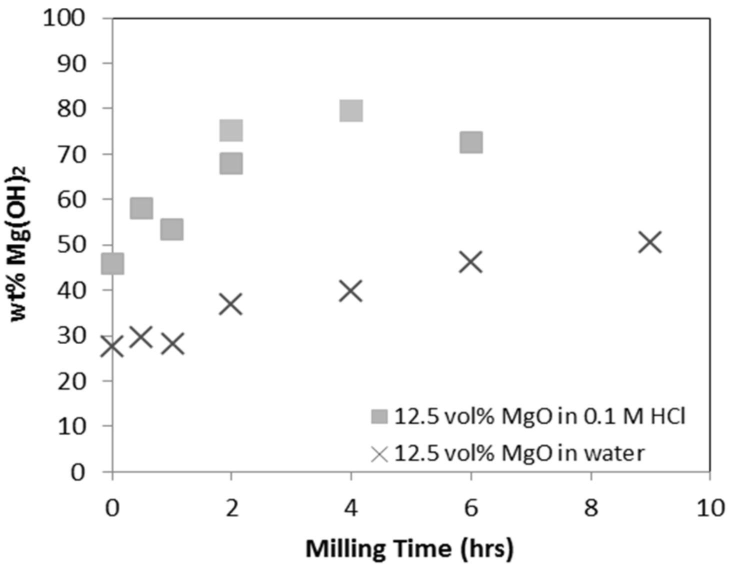


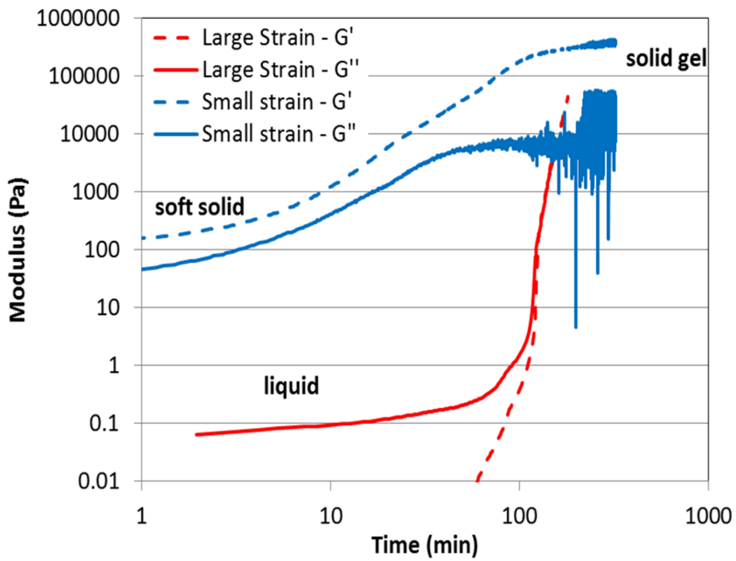
# Accepted fabrication methods

## Tape cast of aqueous, gelled MgO ("gelled")

- MgO hydrolyzes to brucite $Mg(OH)_2$ when added to water
  - $MgO + 2H_2O \leftrightarrow Mg(OH)_2 + OH^-$
  - In basic solutions, brucite destabilizes and aggregates
- MgO + water + gellan or PVA (time sensitive)
  - Tape cast -> dried -> sintered-> laser cut into shapes
  - $Mg(OH)_2$ converts to MgO upon sintering



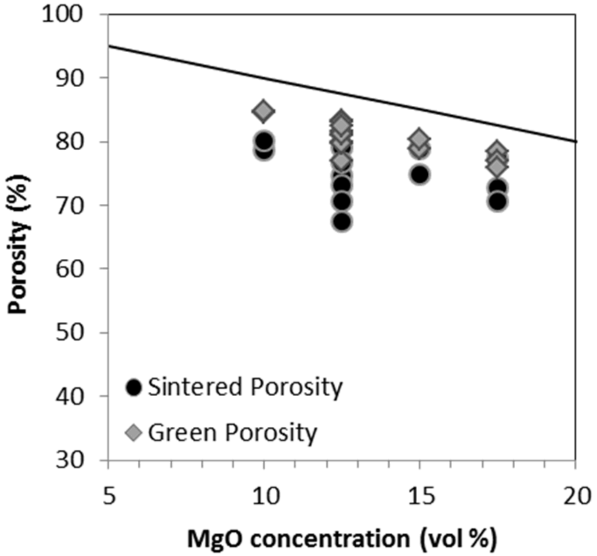



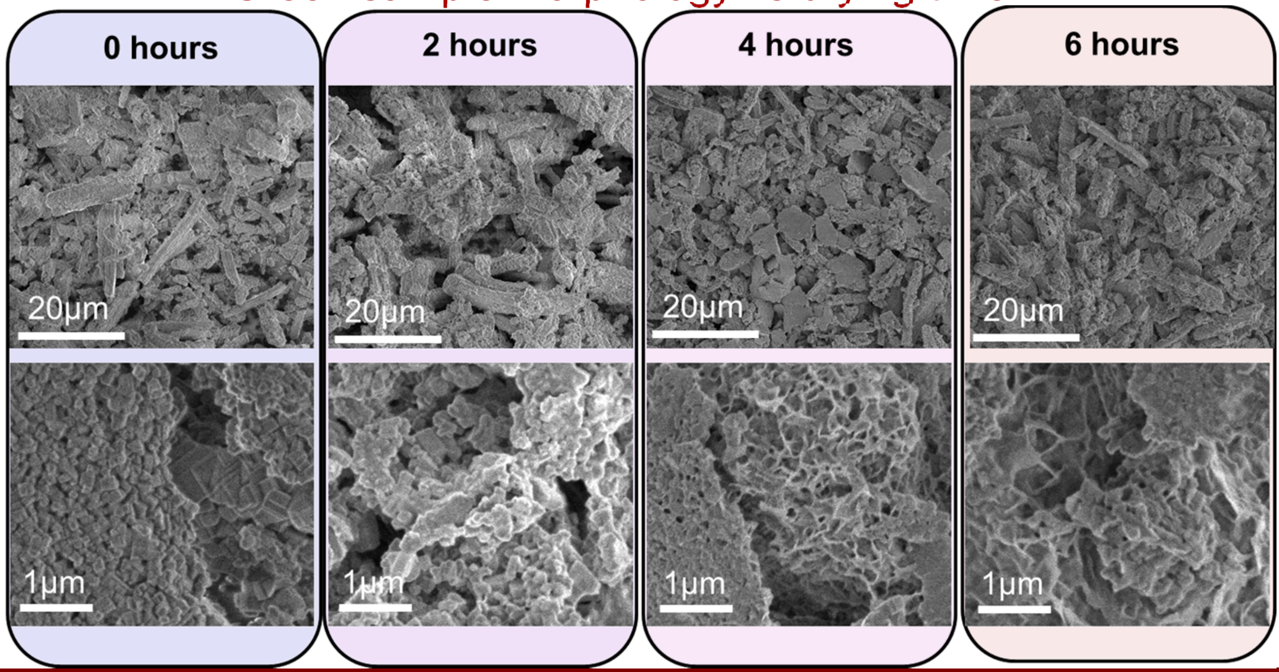
# Gelled sample processing variables

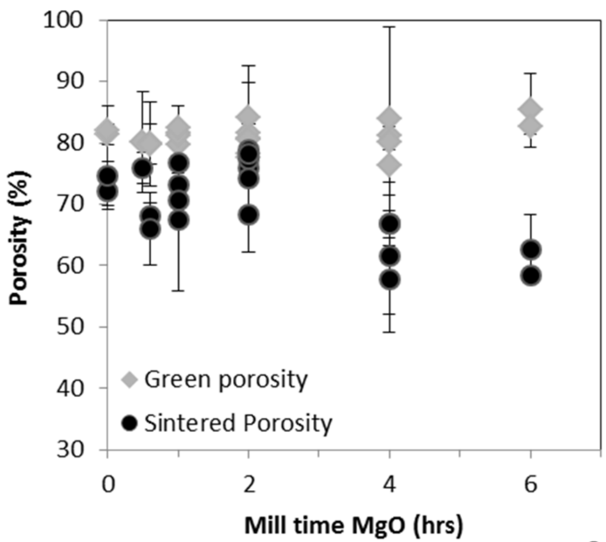
- MgO concentration in initial slip
- Mixing time of slip, drying time
- PVA, gellan concentration (no effect on ϕ)

Samples as thin as 0.4 mm made,
Total porosity up to 84 vol%



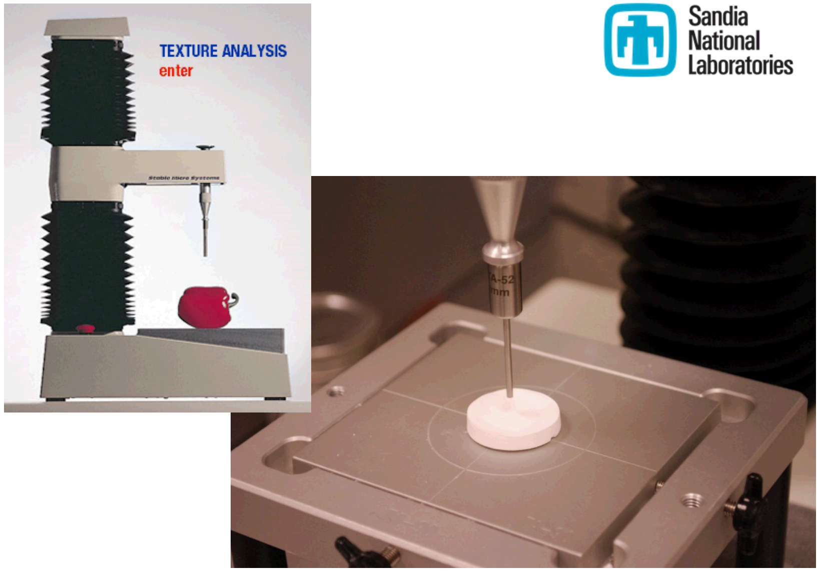

Green sample morphology vs drying time

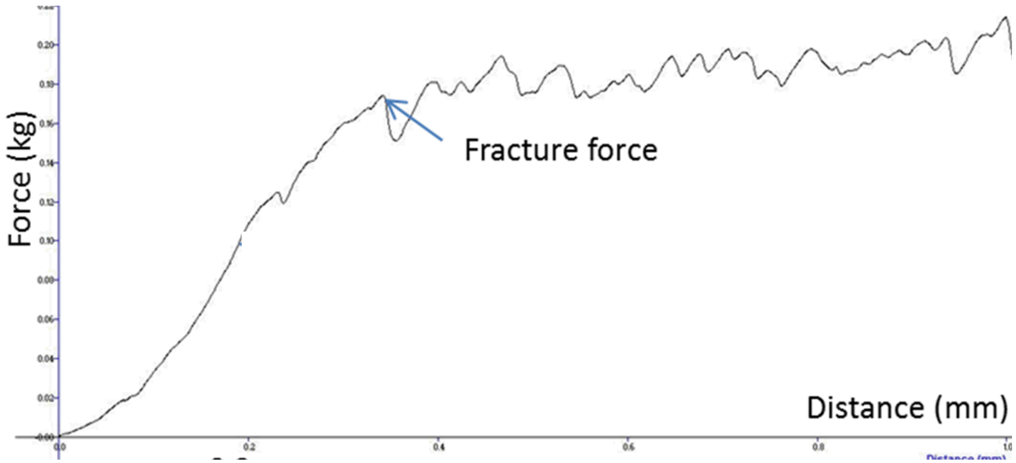


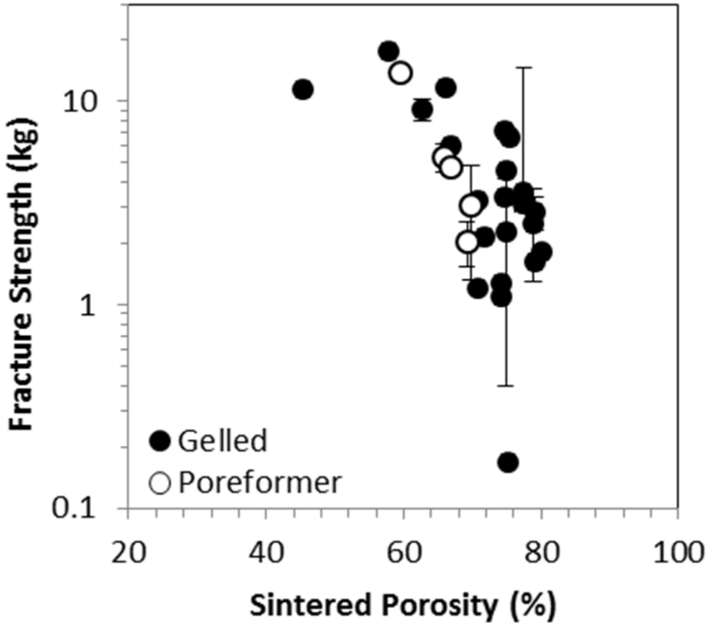



# Fracture strength

- Measured with a texture tester
  - 2mm diameter post
  - 2 kg ~ 900 psi
- Worst case scenario



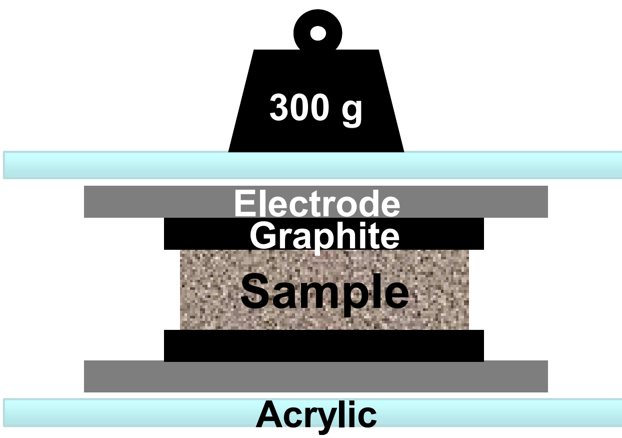



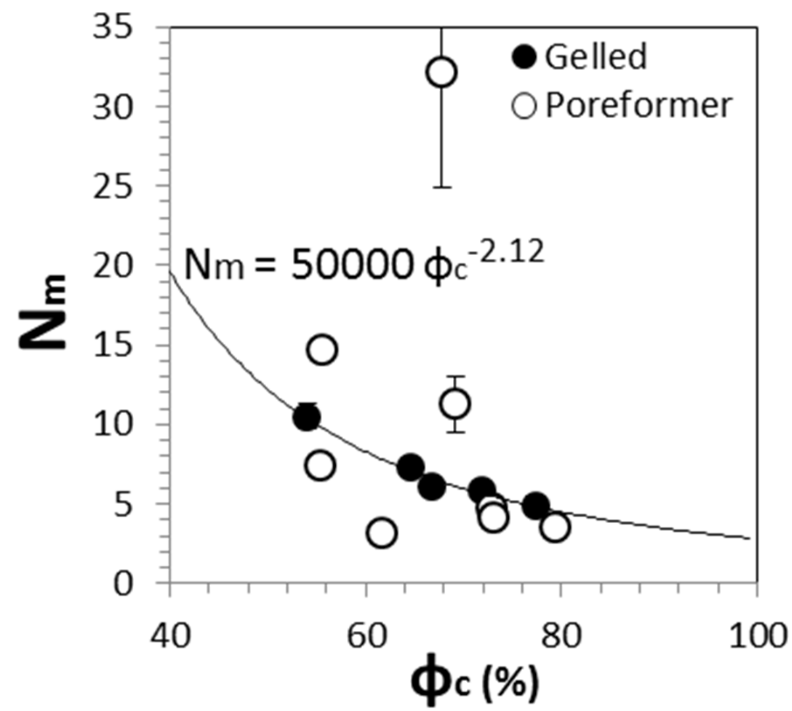



# Sample Impedance

- Procedure:
  - Fill sintered samples with water + KCl
  - AC voltage applied across electrodes
  - Impedance measured vs AC frequency
- Compare to Li Ion batteries $N_m$ = 6-12[1]
- Archie's Law[2,3] $N_m = a\phi_c^{-m}$
  - 1.3 < *m* < 2.5 in common materials

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



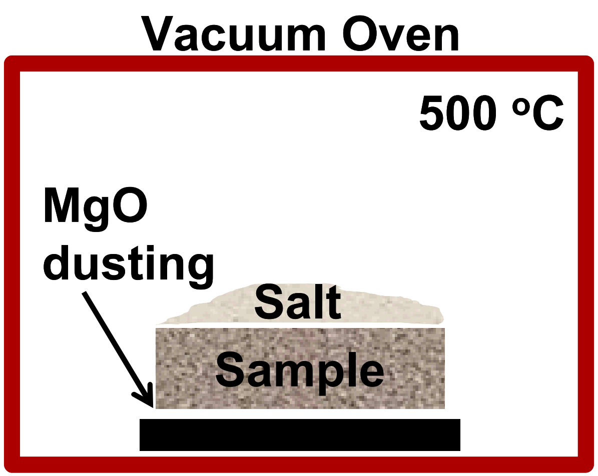





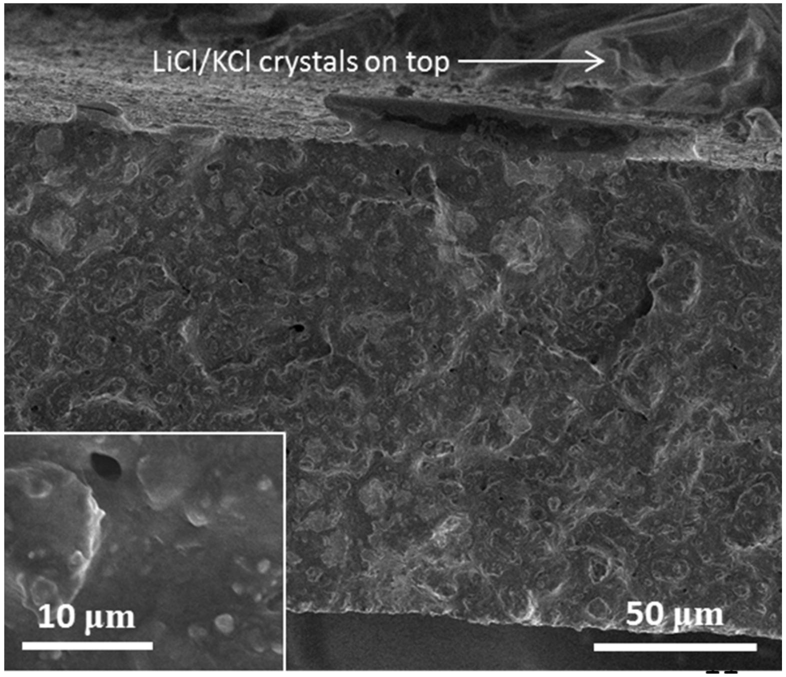
[1] Arora, P., Zhang, Z.J., "Battery separators." Chem. Rev. vol 104,pp 4419–4462, 2004.
[2] Archie, G.E., 1942. "Trans AIME" 146, 54–62. [3] Balberg, I., 1986. Phys. Rev. B 33, 3618–3620.

# Electrolyte filling methods

- Electrolyte: LiCl/KCl eutectic composition
- Challenges:
  - Unfilled samples are brittle
  - Salt: 352 °C melting point, deliquescent
- Multiple methods tried
  - Best filled >70% of porosity regularly

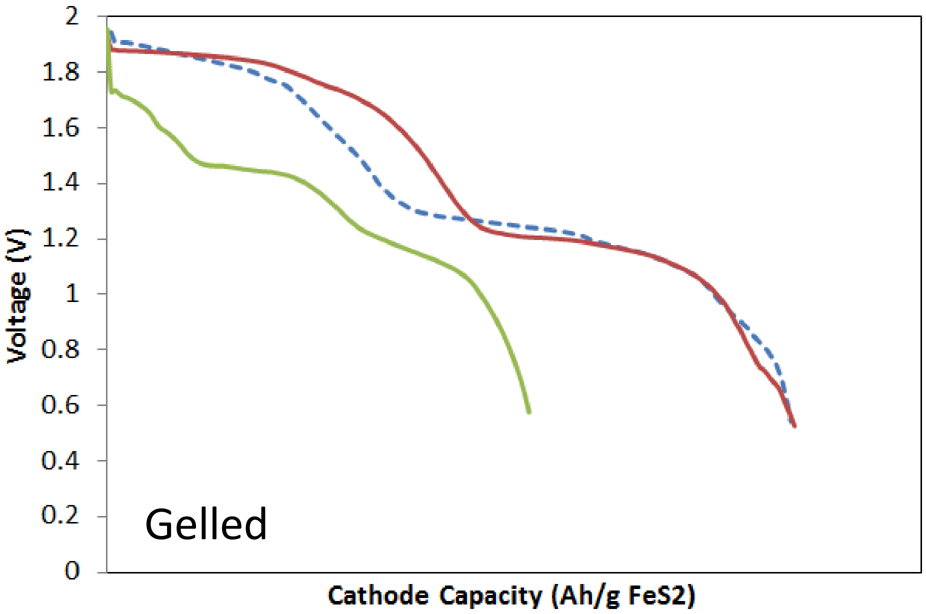


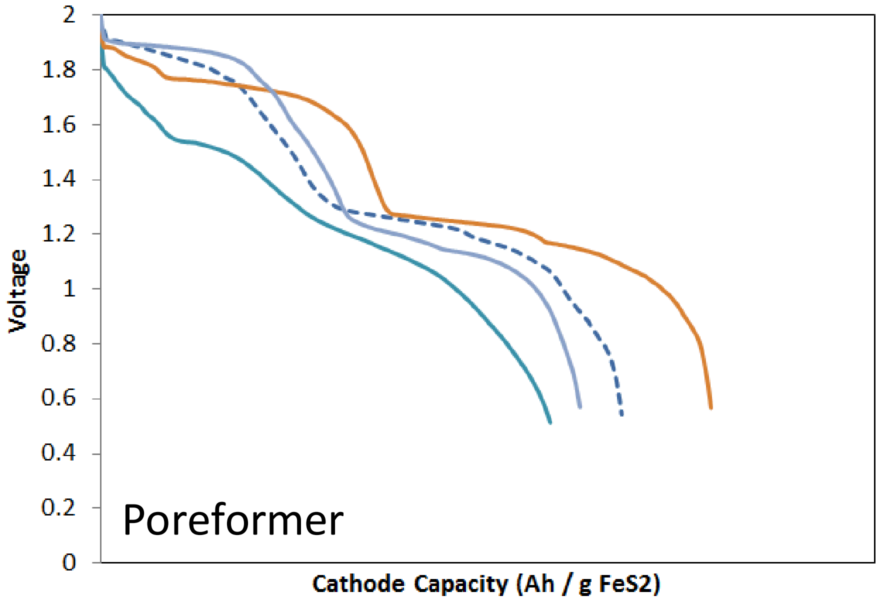

Poreformer sample filled with electrolyte



# Single Cell Performance: Constant current

1 inch diameter cell: FeS2 + Separator material cathode, LiSi anode
500 °C, 8 psi axial load
50 mA/cm² constant current

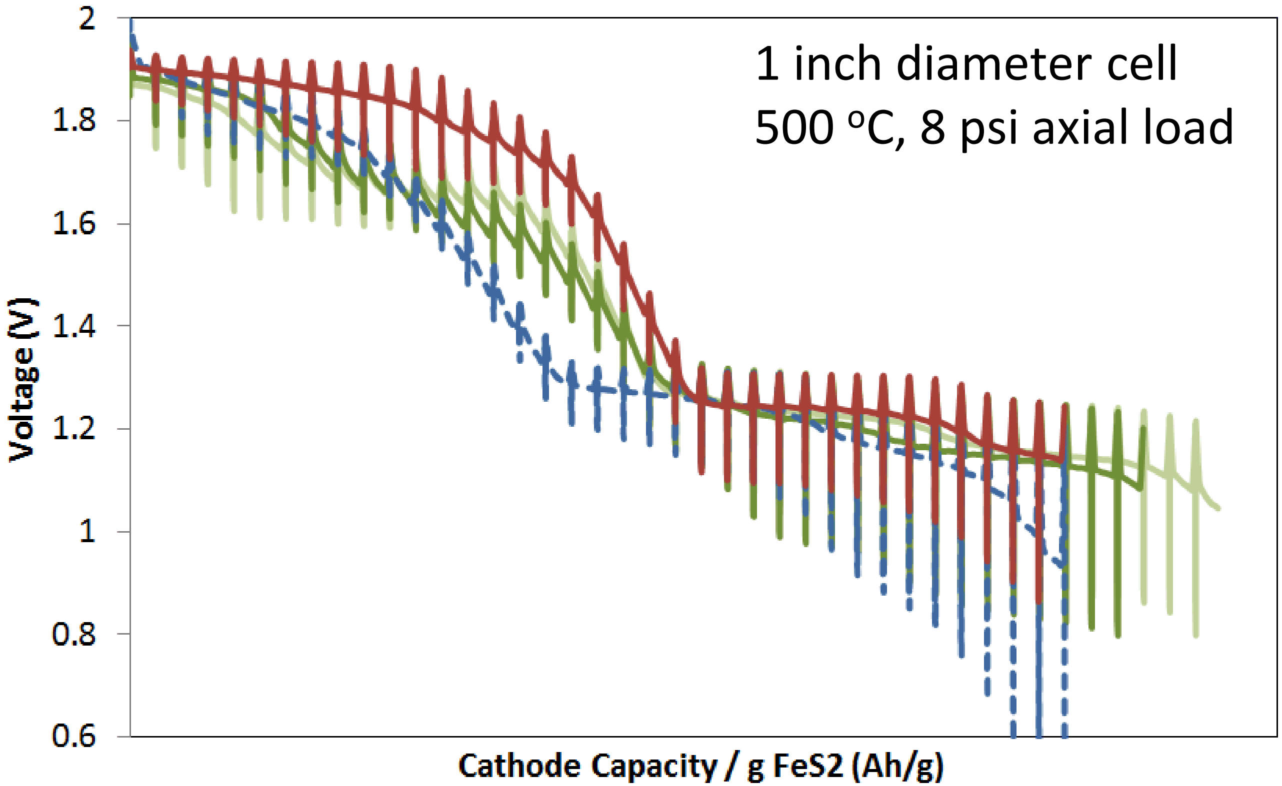


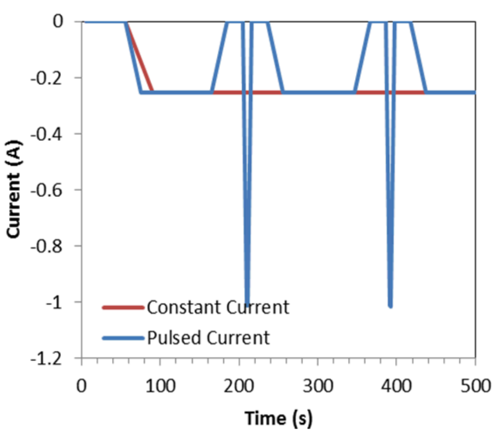




| Sample | h (mm) | Vol % MgO | Vol% Elect | Vol% pore |
|---|---|---|---|---|
| Control | 0.42 | 20? | 80? | 0? |
| Red | 1.39 | 16 | 30 | 53 |
| Green | 0.67 | 27 | 47 | 27 |

| Sample | h (mm) | Vol % MgO | Vol% Elect | Vol% pore |
|---|---|---|---|---|
| Control | 0.42 | 20? | 80? | 0? |
| Orange | 1.06 | 28 | 48 | 24 |
| Lt blue | 0.48 | 29 | 62 | 9 |
| Teal | 1.02 | 31 | 34 | 36 |

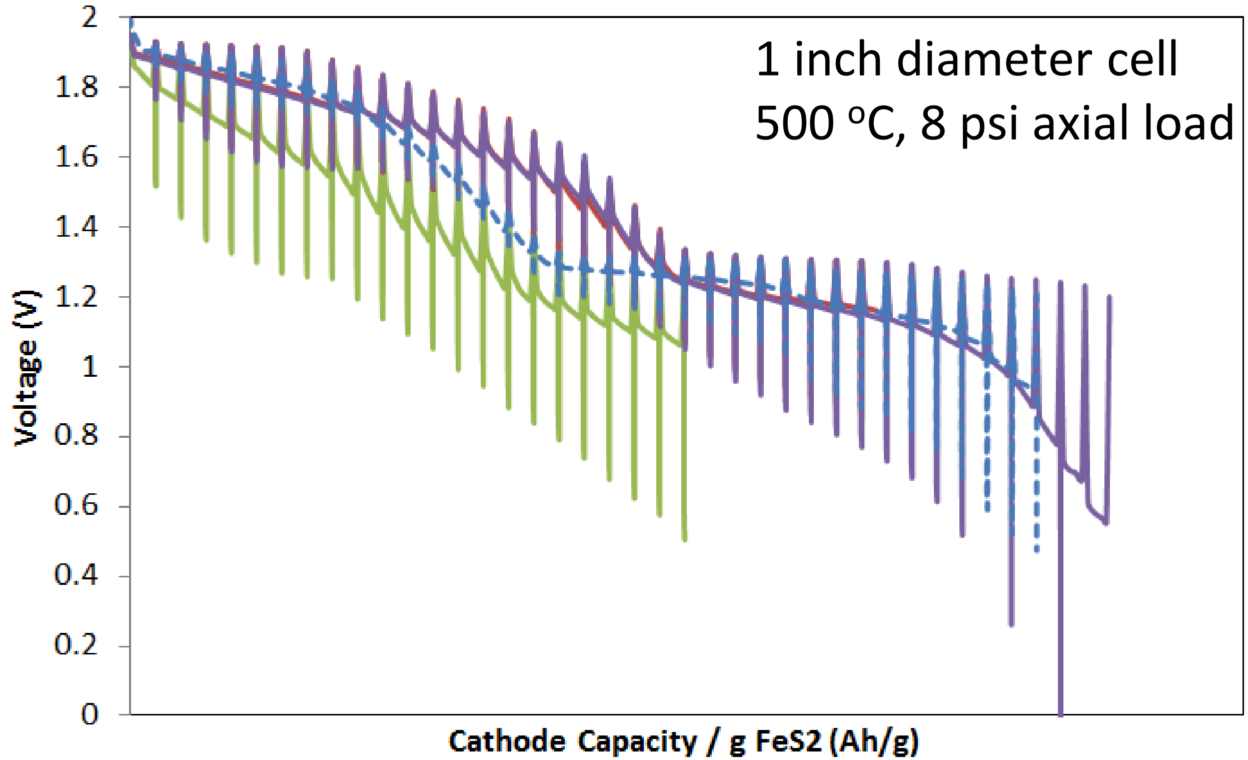
# Pulsed Cell Performance: Gelled

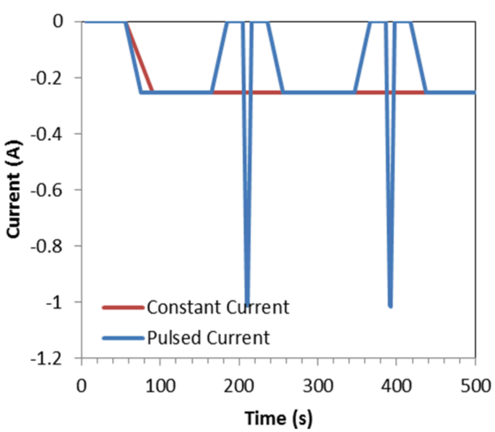



| Sample | h (mm) | Vol % MgO | Vol% Elect | Vol% pores |
|---|---|---|---|---|
| Control | 0.42 | 20? | 80? | 0? |
| Red | 0.97 | 22 | 37 | 41 |
| Green | 0.79 | 18 | 35 | 47 |
| Light green | 0.78 | 24 | 37 | 39 |

# Pulsed cell performance: Poreformer




| Sample | h (mm) | Vol % MgO | Vol% Elect | Vol% pores |
|---|---|---|---|---|
| Control | 0.42 | 20? | 80? | 0? |
| Red | 0.97 | 27 | 57 | 17 |
| Purple | 0.78 | 24 | 56 | 16 |
| Green | 1.03 | 30 | 35 | 35 |

# Next Steps

- Sample optimization
  - Gelled samples: flat sintering
  - Poreformer samples: robust when thin, porous
  - Filling methods
  - Consistency
- Fabrication, testing at the battery level

# Acknowlegements


- Bob Fox, Linda Johnson – help with single cell testing
- Adrian Wagner - sample laser cutting
- Discussions with Karen Waldrip, Chris Apblett, Michael Russel over electrolyte filling methods
- This project was funded under LDRD project # 151359