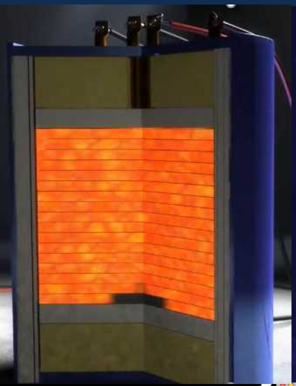
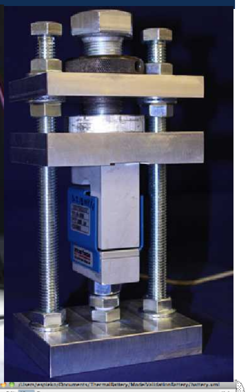
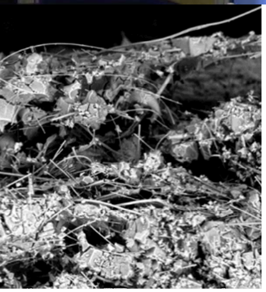
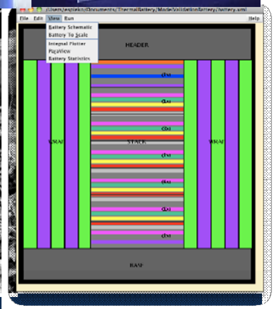
SAND2017-11696C









Molten Salt Batteries: Mechanics and Electrolyte Transport 670g

Christine C. Roberts, Martin B. Nemer, Mark Stavig, Alexander Headley, Ryan Solich, Scott A. Roberts

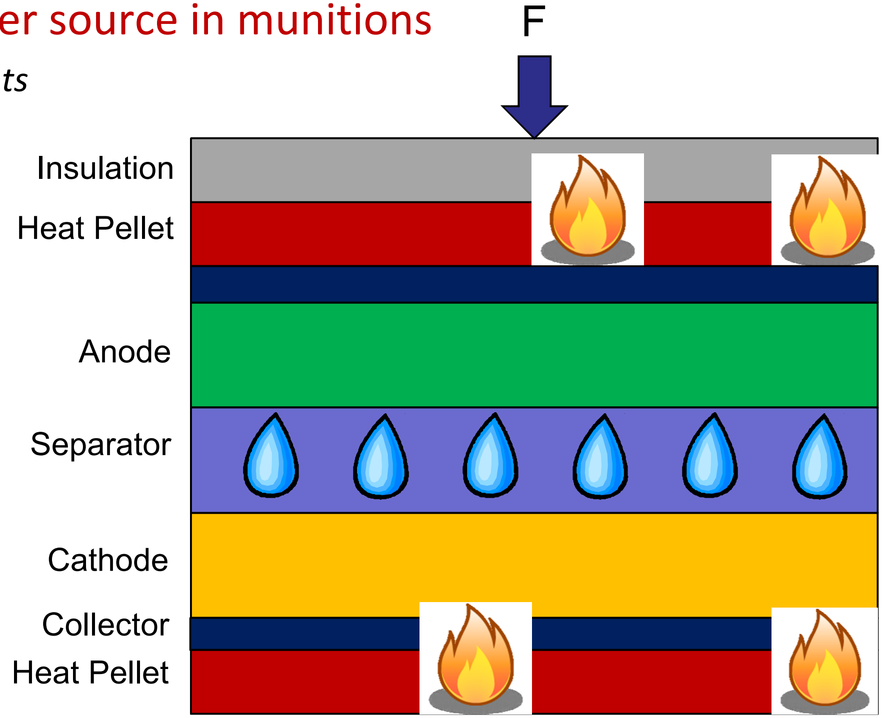
Lithium and Beyond: Fundamental Advances in High Performance Batteries 1
AICHE Annual Conference
November 2, 2017, 10:10

Sandia National Laboratories is a multi-mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA-0003525

Introduction to Thermal Batteries

Thermal batteries: workhorse primary reserve power source in munitions

Only Thermal Batteries (TBs) can meet the demanding requirements for power, energy, size, weight, reliability, shelf-life, mechanical robustness, insensitivity to environments, etc

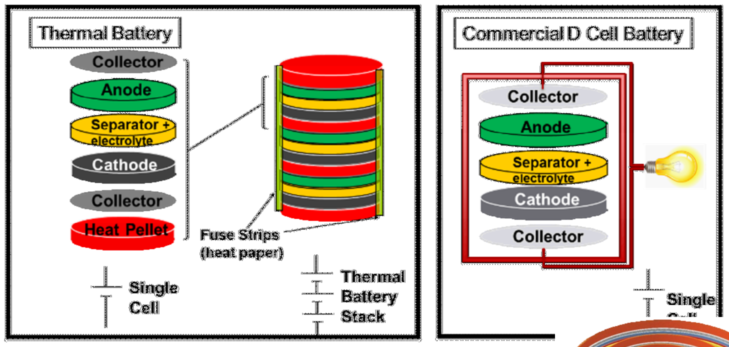


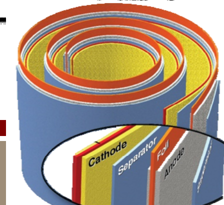
Battery activation is a complicated, multi-step process

- Electrolyte frozen below 352 °C (long shelf life)
- Activation: pyrotechnic heat pellets
  - Battery operational temp approx 550 °C
  - Separator supported by MgO network

Battery design: a true multiphysics problem

- Thermal: rise time, run time, thermal decomposition, system-level interactions
- Mechanical: Shock, vibration, Separator and insulation deformation Porous flow of electrolyte
- Electrochemical: Predictable current loads, voltages to protect down-circuit electronics





Control over temperatures, voltages, mechanical robustness indirectly through design parameters

(heat balance, pellet composition, closing force,…)

Guidotti, 2006, J. Power Sources, 161 (2)

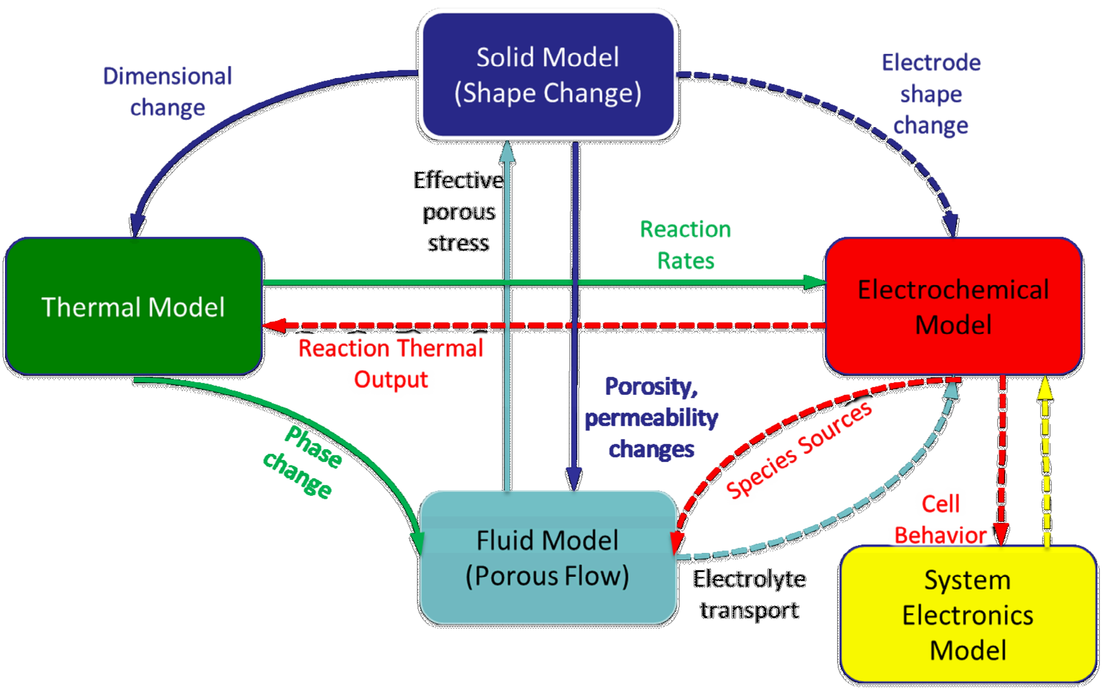
Sandia TABS predictive design tool

TABS Sandia National Laboratories

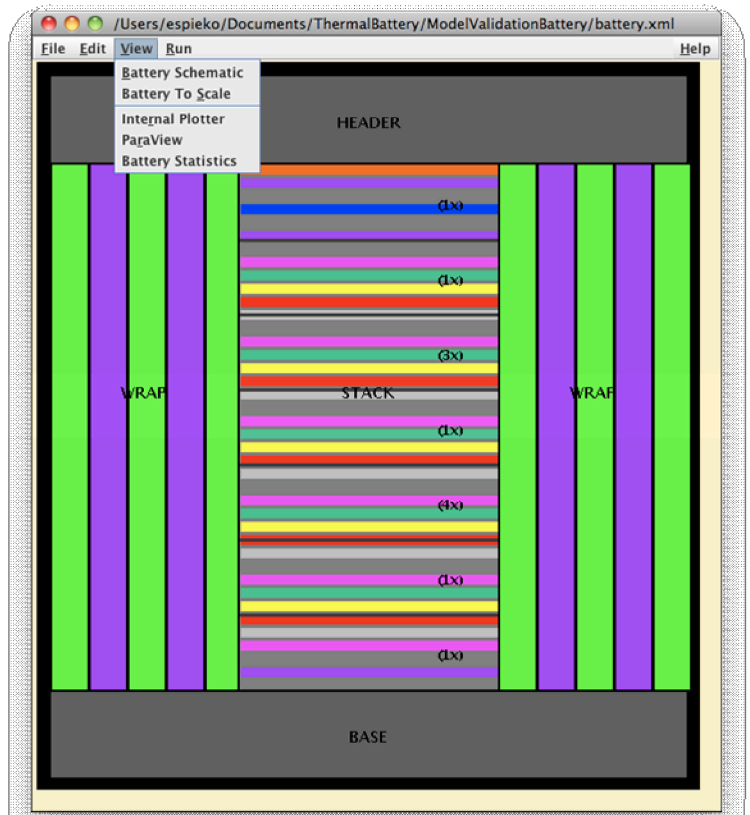
Thermal batteries are one shot devices

Thermally Activated Battery Simulator

- Physics solved by Sierra/Aria
- User-friendly GUI: runs on desktops of battery design engineers



SIERRA/Aria

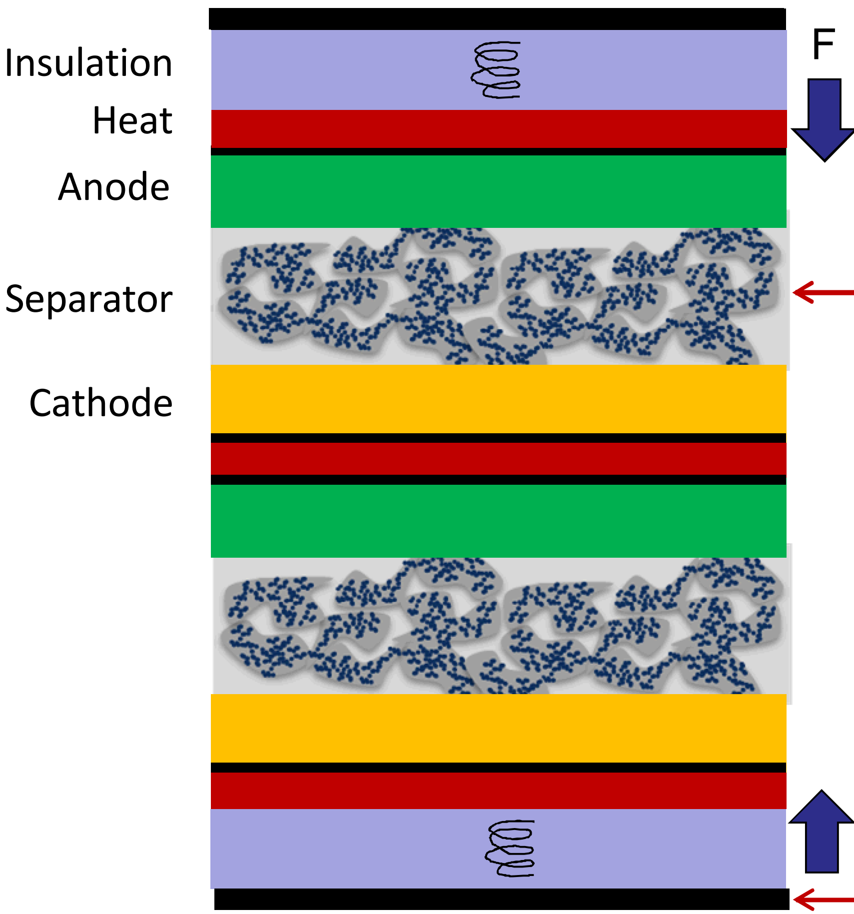


Screen capture image of TABS GUI interface

Model-based design and qualification is much faster and cheaper than iterative prototyping in the lab

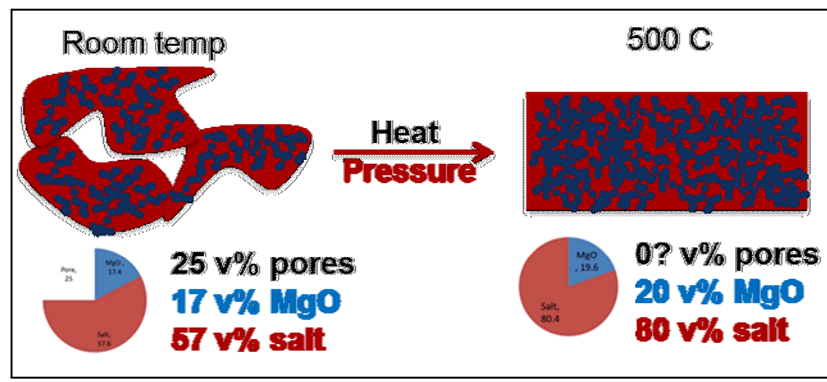
Mechanical Changes in Thermal Batteries

Room Temperature



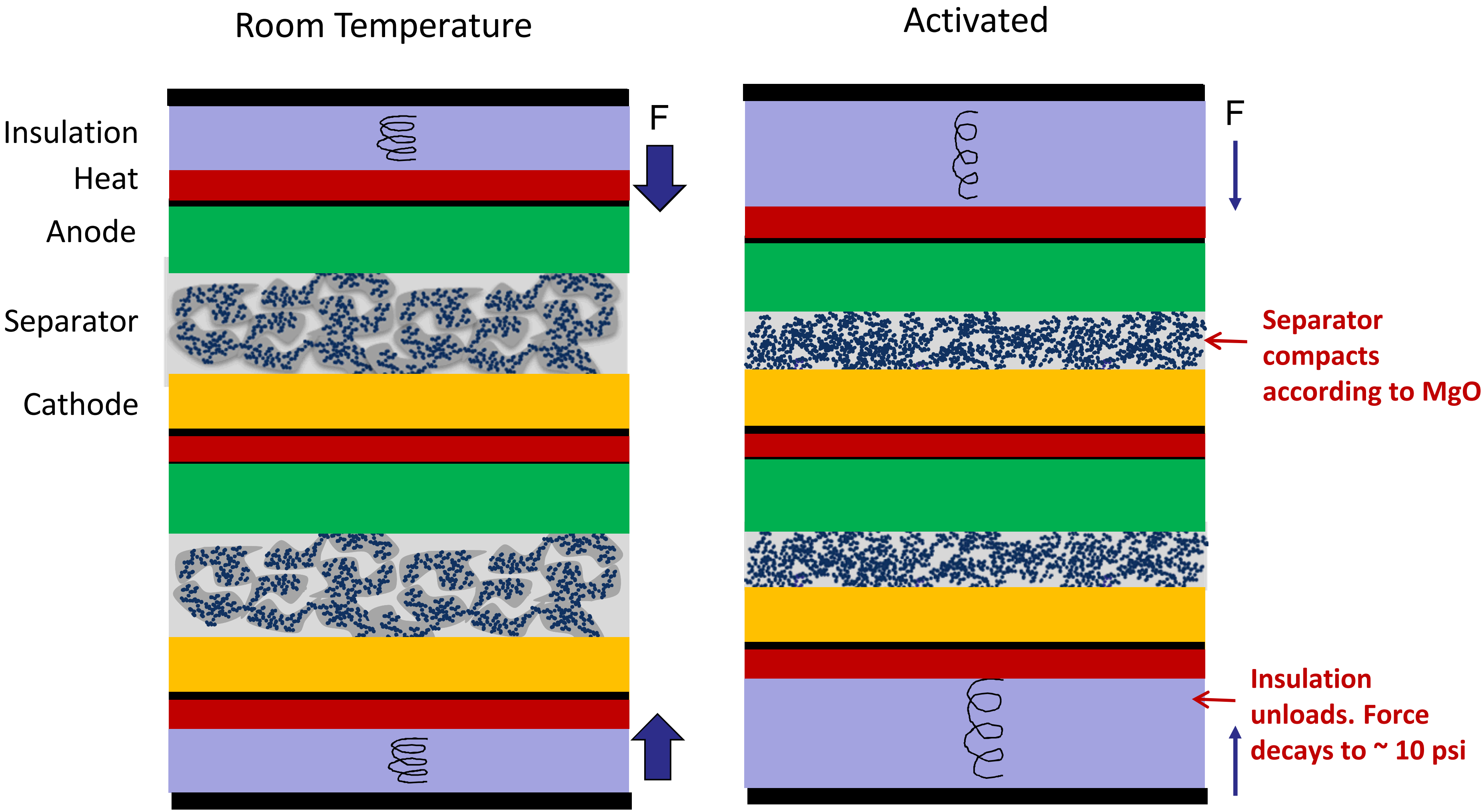
Battery packaged under 100's of psi

Separator initially porous



Battery can = constant strain for stack

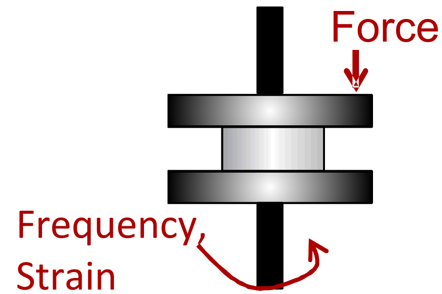
Mechanical Changes in Thermal Batteries

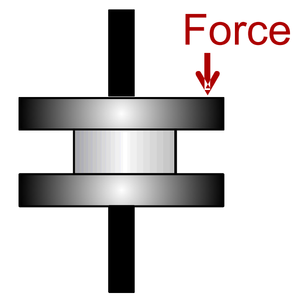


Force on active battery is determined by interplay between insulation, separator.

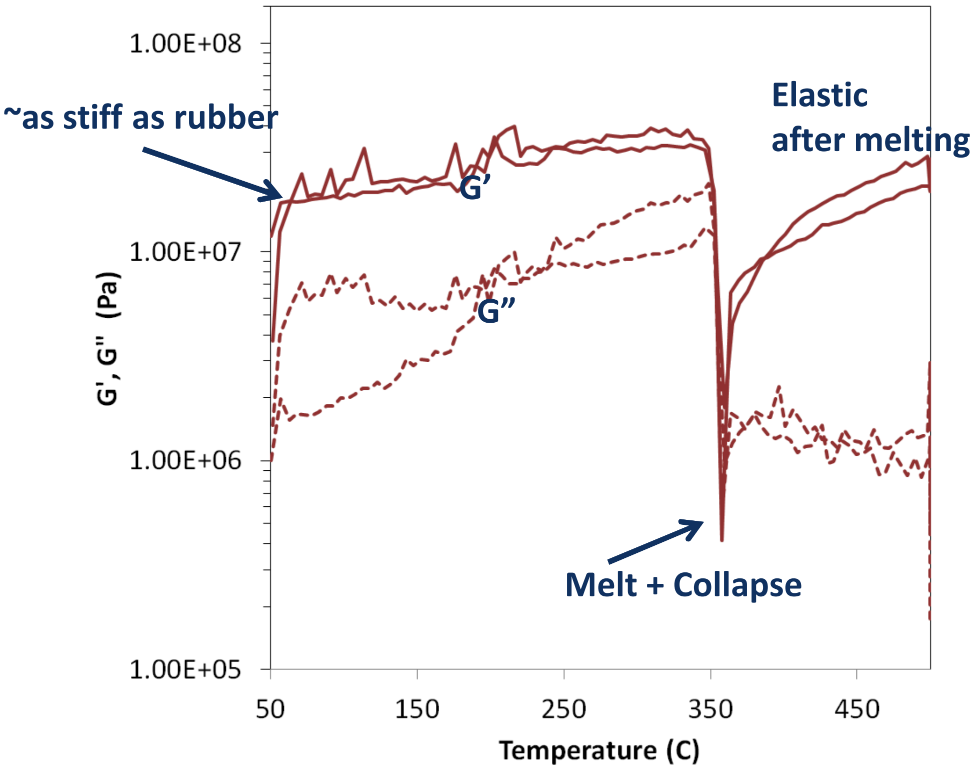
Characterizing separator deformation

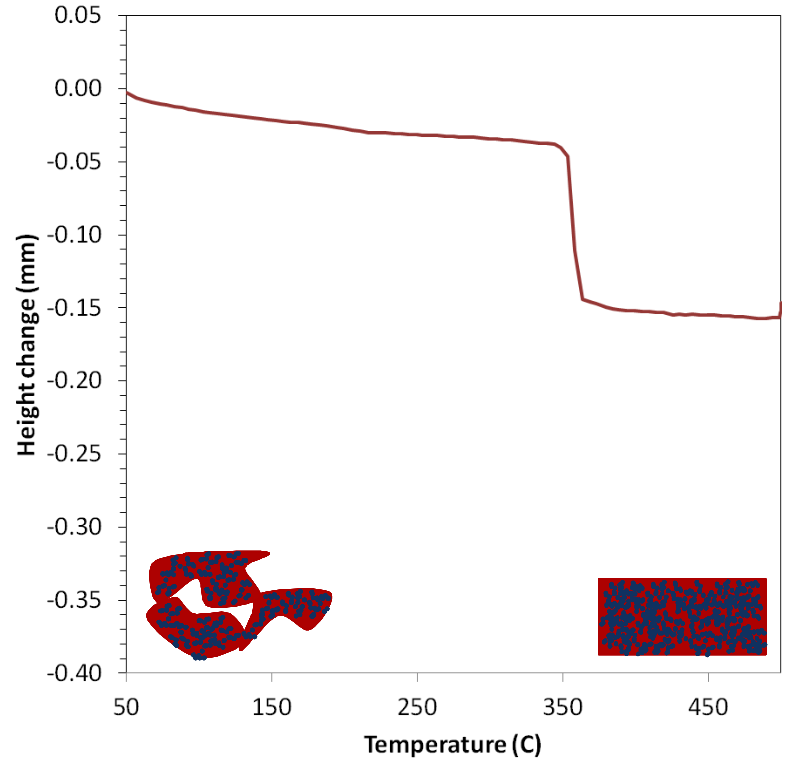
- Separator: ARES G2 rheometer, Anton Paar MCR 502
  - 500 °C maximum temperature
  - Dry nitrogen air flow
  - Measures:
    - **Shear modulus, G**
      G' = in phase, solid-like component
      G" = out of phase, liquid-like component
    - **Height change of pellet**
    - **Image analysis: diameter change**
  - Confirmed using Q800 DMA
- Insulation: Instron
  - Room temperature and high temperature measurements
  - Measures:
    - **Compressive modulus, E**





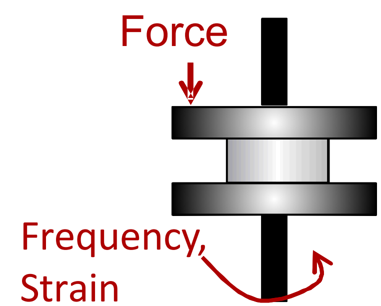
Separator Deformation During Melt



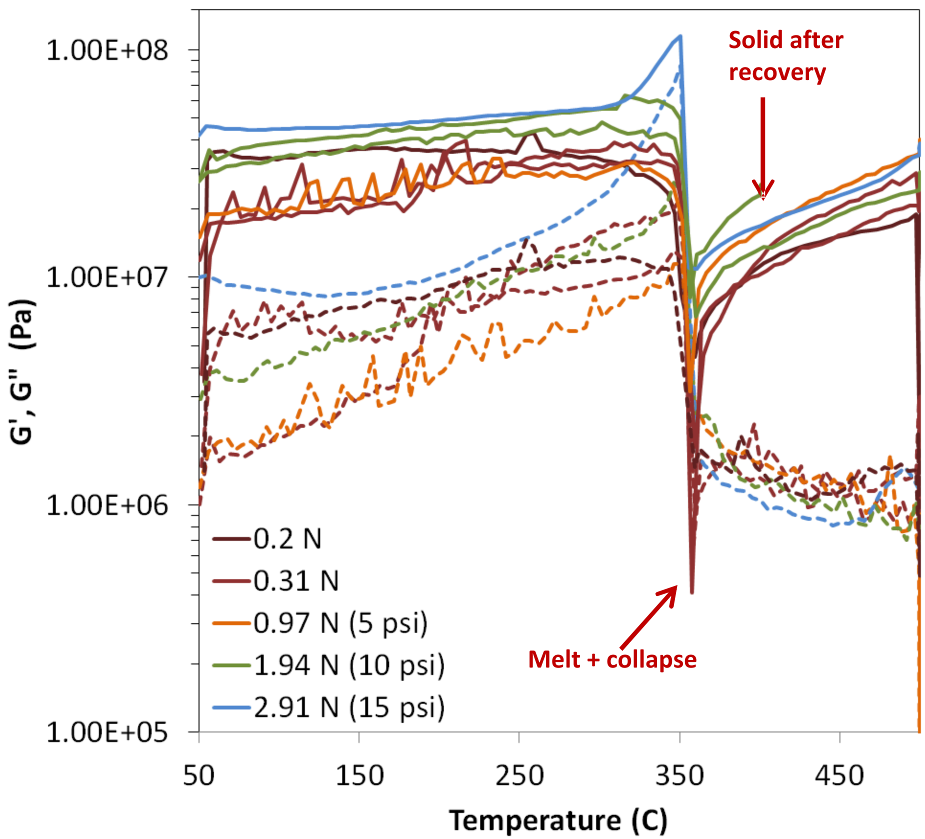


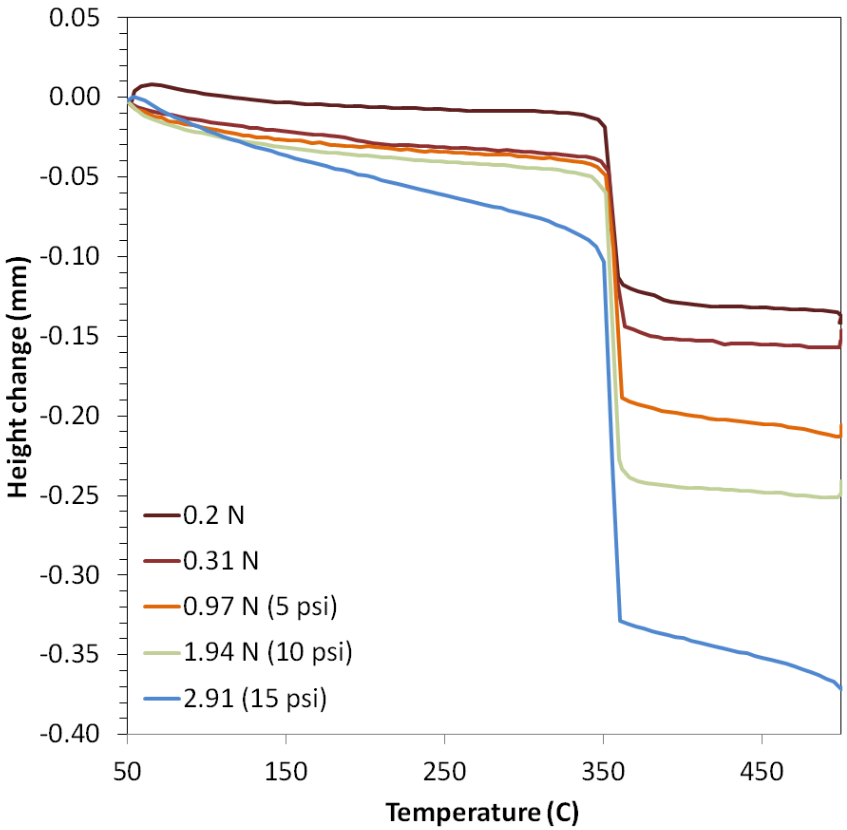
6 mm diameter separator pellets (1mm thick)
ARES G2 Rheometer

Elastic+viscous shear modulus
0.05% strain, 5 °C/min temperature ramp,
0.31N compressive force



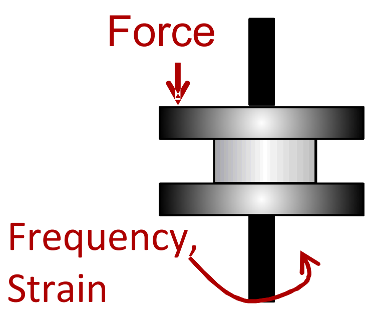
Separator Deformation During Melt



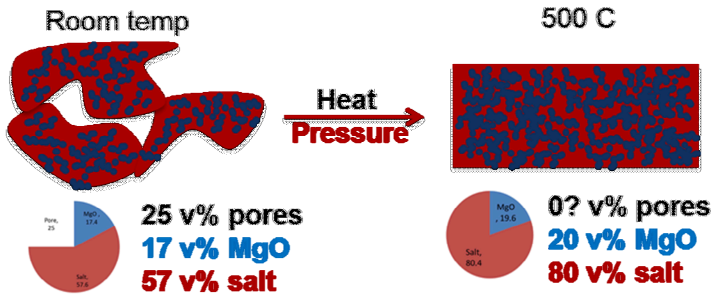


6 mm diameter separator pellets (1mm thick)
ARES G2 Rheometer

Elastic+viscous shear modulus
0.05% strain, 5 °C/min temperature ramp



Effects on diameter

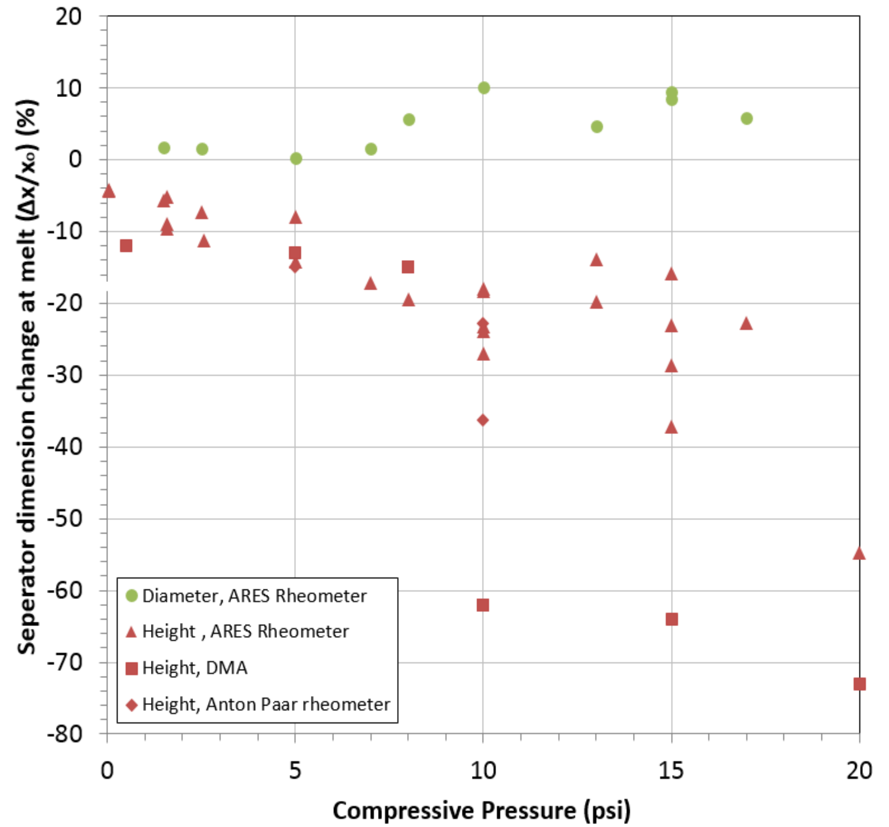


When the electrolyte in the separator melts, the MgO particles densify to create a stress-supporting network

- Thickness and modulus of separator depends on the compressive force under which it was melted

Two deformation regimes observed

- Initial deformation decreases thickness only (lose porosity)
- Further compression causes diameter of separator to expand.
  - Increasing concentration of electrolyte promotes yield
  - When pores are gone, remaining materials are incompressible: must be volume-conserving



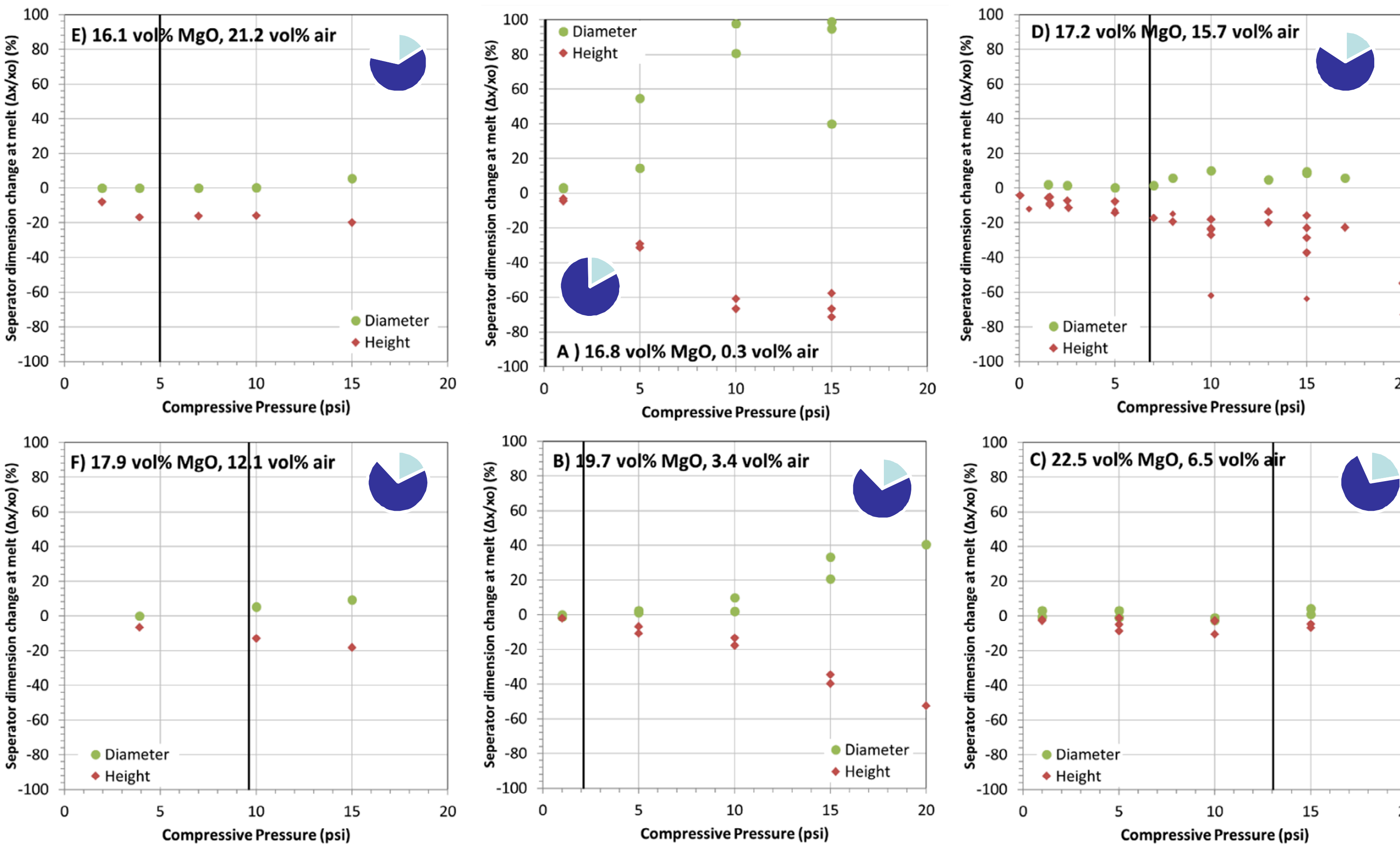
Too much deformation, and the electrolyte will leak, shorting the battery
Too little deformation, and the separator will have high ionic resistance

Deformation vs. Separator Composition

In general, samples with greater concentrations of MgO deform less in height.

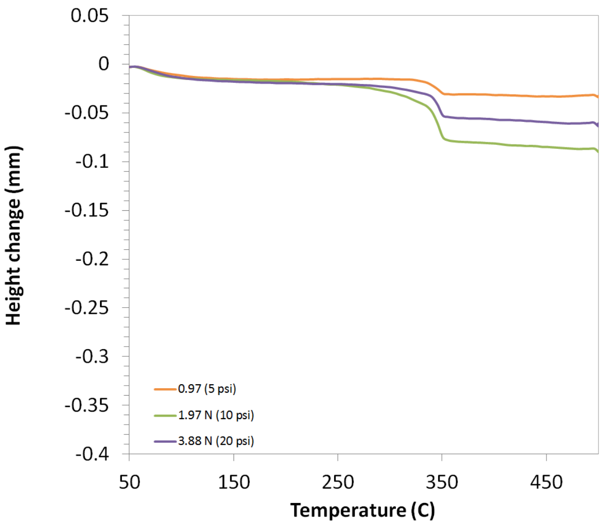
Concentration of electrolyte strongly affects diameter expansion (yield)

Vertical lines: prediction of when no porosity exists in separator due to deformation



MgO
Electrolyte
Air (white)

Effects of Cathodes

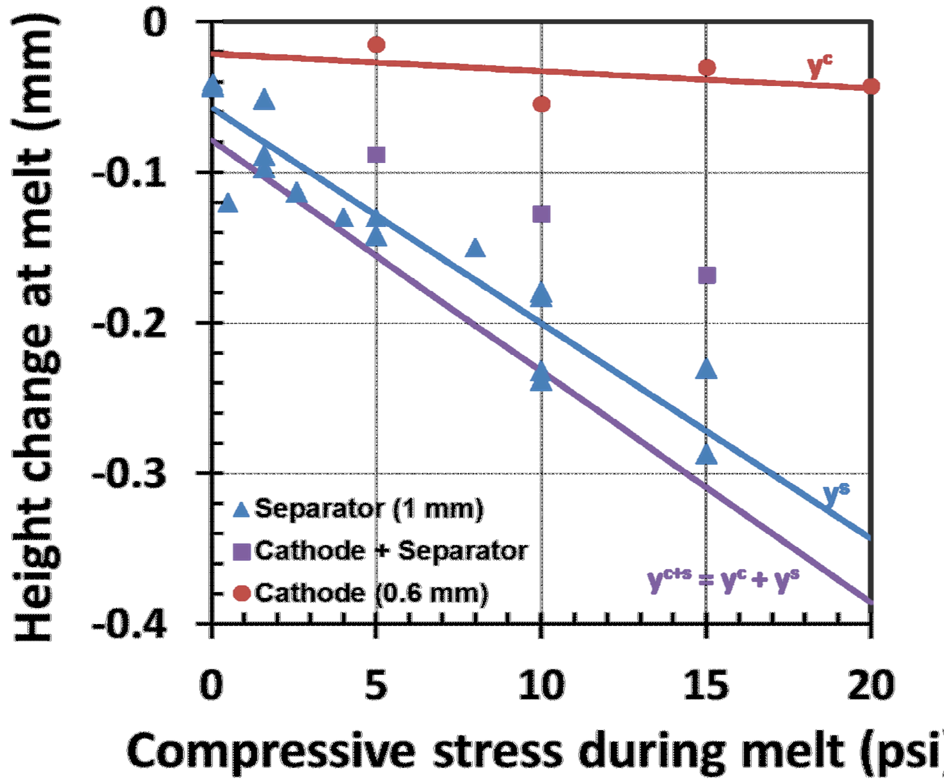


Cathode: 0.5 mm thick, 25 wt% separator matl.

Cathode height change is approximately 5% at melt due to collapse of electrolyte.

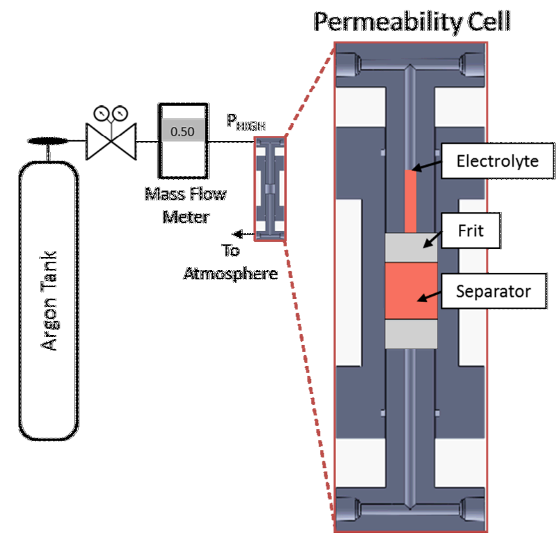
When a separator is layered with a cathode, the deformation is less than the sum of their individual deformations

Electrolyte flow into the cathode reduces the saturation of the separator, causing it to deform less.



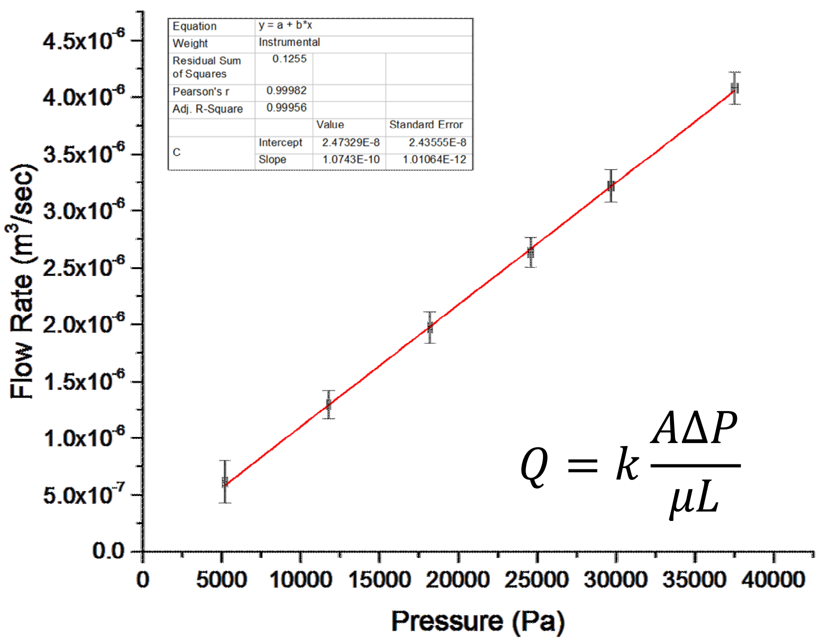
Densification affects electrolyte permeability

Permeameter designed to independently control MgO density and gas (N_2) pressure

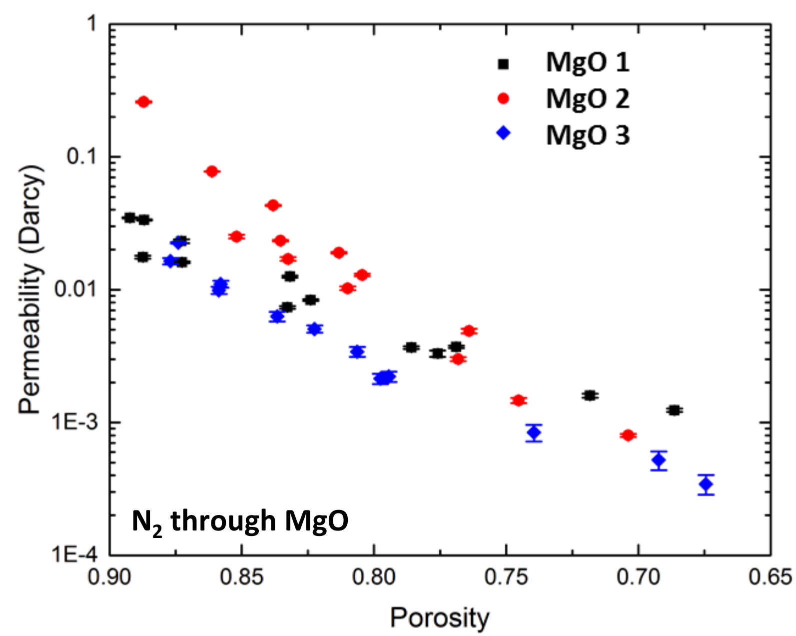


N_2 permeabilities of three separate MgO powders being considered for thermal batteries were measured vs. density

- Orders of magnitude difference in permeability observed across powders at a given porosity
- Porosity in active thermal battery separator depends on design factors like powder microstructure and closing force

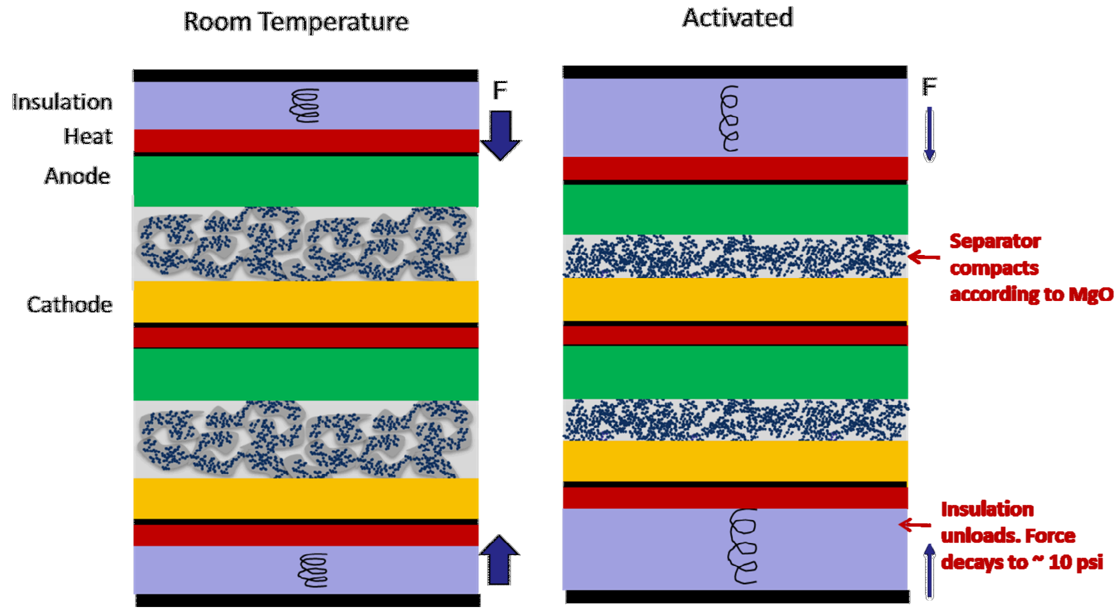


$$Q = k\frac{A\Delta P}{\mu L}$$



Insulation Mechanical Behavior

Insulation acts like a spring in the battery to prevent slipping in mechanical environments.



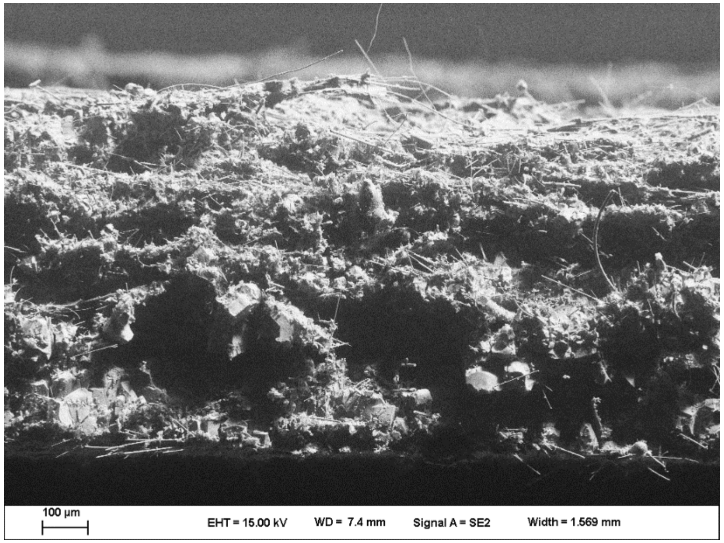
Insulations include (axial) Fiberfrax and Min-K boards, (radial wrap) Fiberfrax paper

Two main questions for battery design:

- By how much does the stress relax in compressed axial insulation during storage?
- When the battery is activated and the strain on the insulation is relaxed, what is the remaining stress imposed on the electrochemical stack?

Axial Insulation Materials

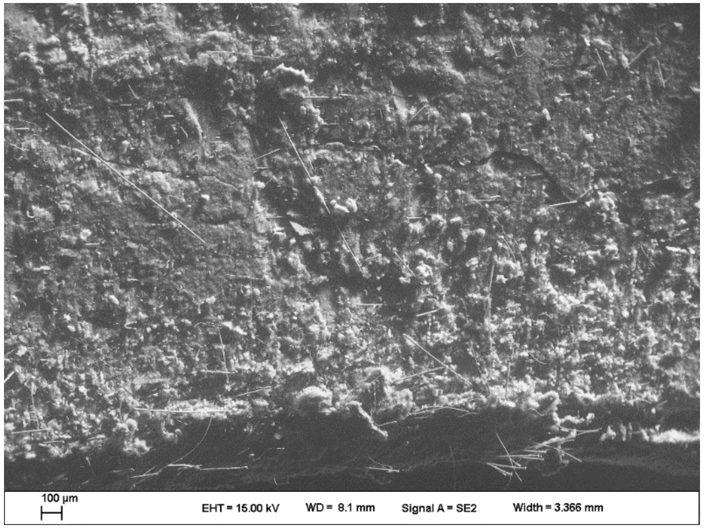
Fiberfrax board: Alumina fibers in silica matrix



Used in smaller batteries,
Traditionally higher closing forces

Focus on 900 psi, 700 psi, 500 psi
10 min, 10^4 min, 3 day hold times

Min-K board: Silica fibers in silica + titania matrix

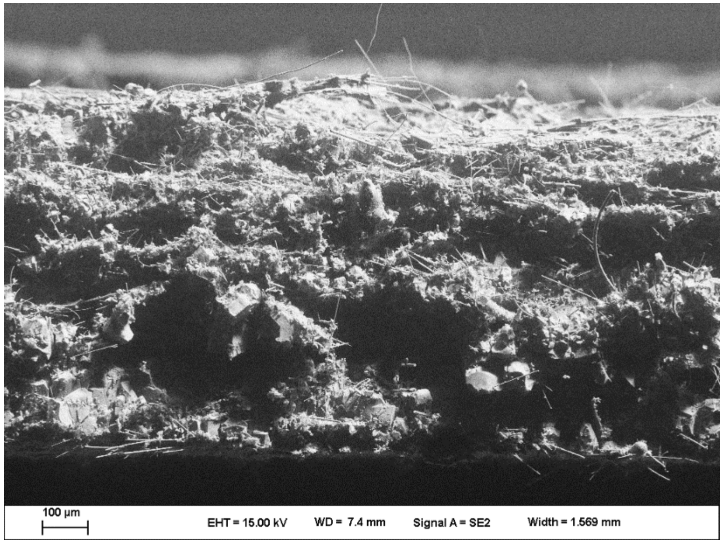


Used in larger batteries,
Traditionally lower closing forces

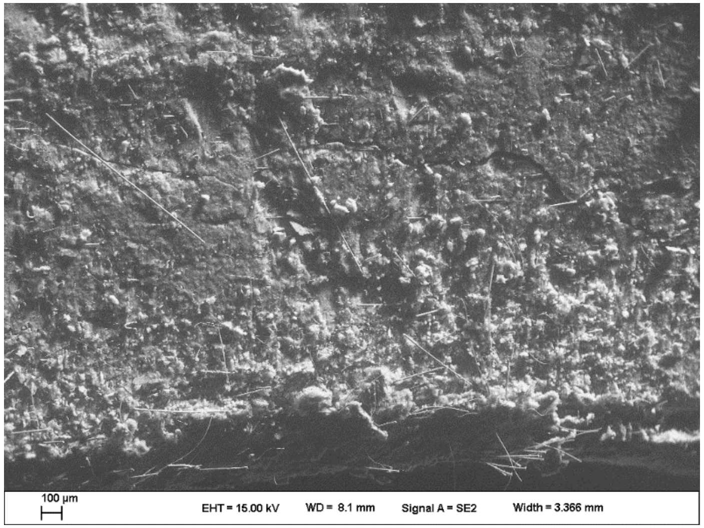
Focus on 500 psi, 250 psi, 100 psi
10 min, 10^4 min, 3 day hold times

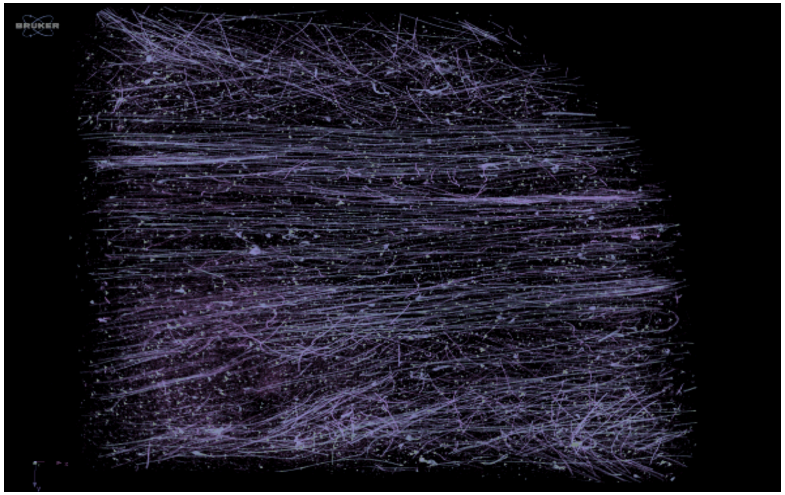
Axial Insulation Materials

Fiberfrax board: Alumina fibers in silica matrix



Min-K board: Silica fibers in silica + titania matrix





Top-down view: Fibers are preferentially aligned

Stress Relaxation of Axial Insulation Materials

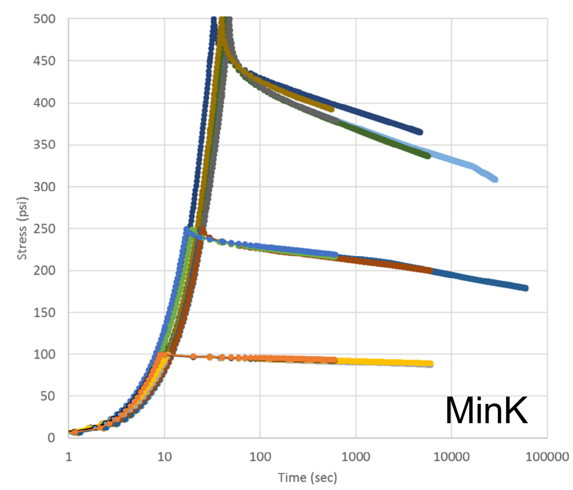
By how much does stress relaxation occur in compressed axial insulation during storage?

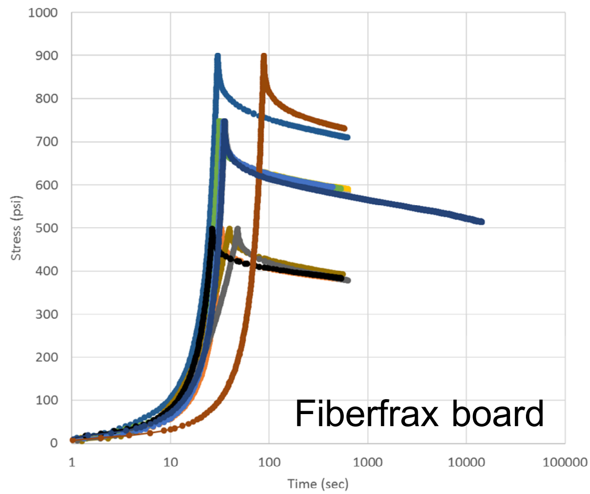
Instron data shows 1000 minute holds are not sufficient to complete stress relaxation

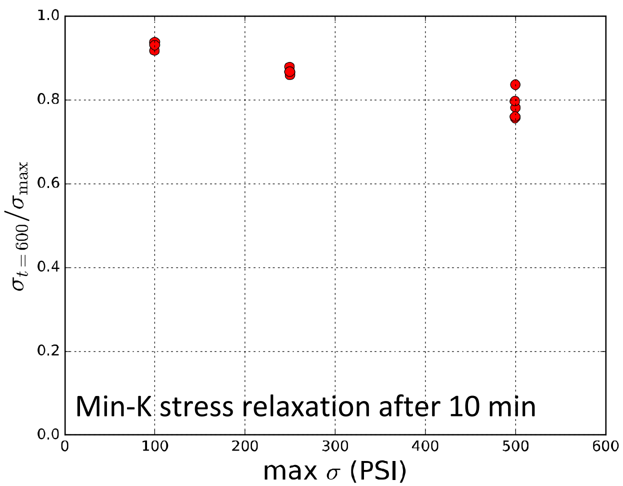
Longer-term studies are necessary

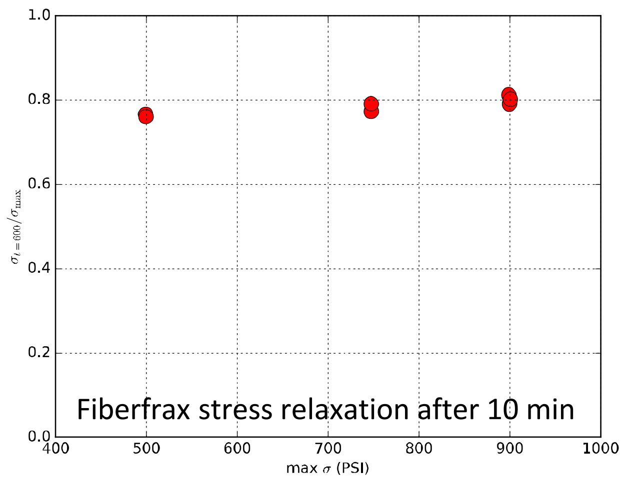
- Time-temperature superposition of uncertain efficacy for ceramic materials

Fundamentally different behavior seen for Fiberfrax and Min-K









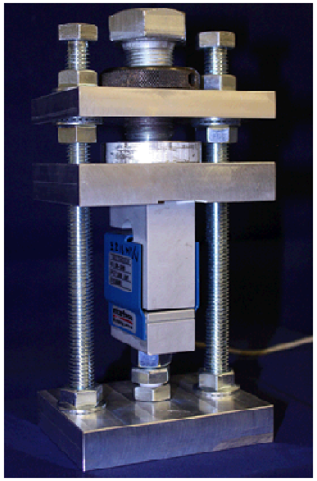
Long term stress relaxation studies

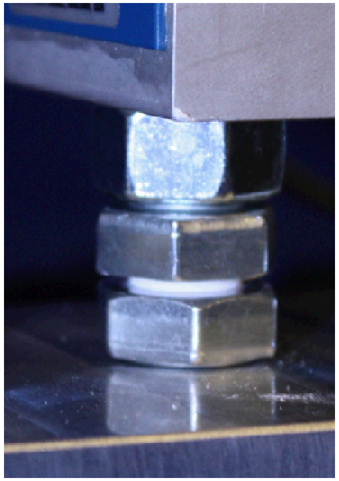
Methods for accelerated aging of insulation samples uncertain

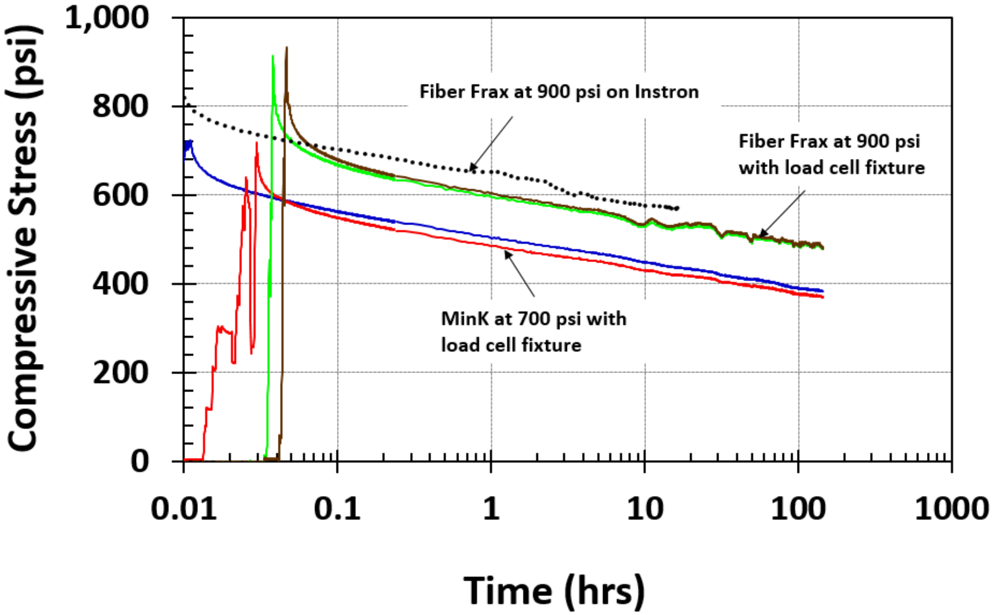
Custom constant strain fixture designed for dedicated long-term insulation stress relaxation studies.

Data matches instron behavior well.

To date, approximately 6 months of data have been collected on two samples. New fixtures ordered for more samples/capacity.





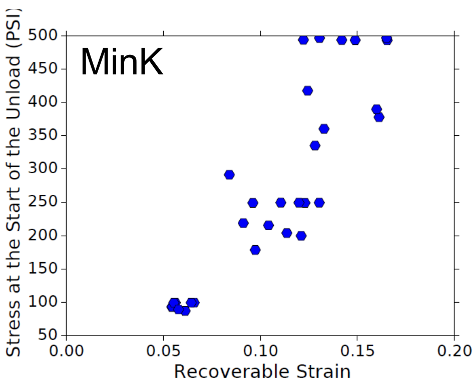


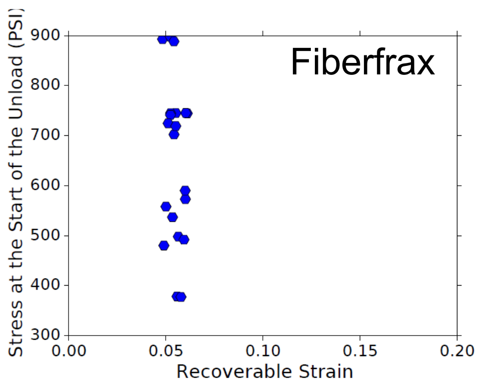
Unload behavior of Axial Insulation Materials

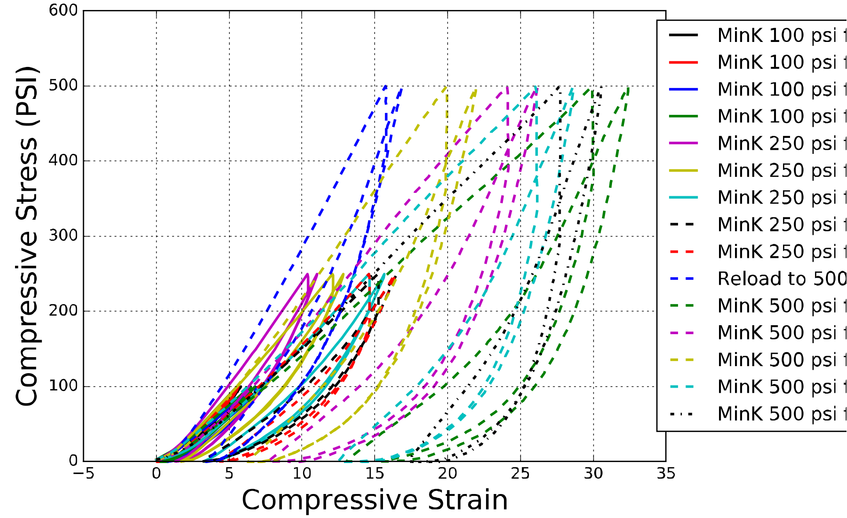
When the battery is activated and the strain on the insulation is relaxed, what is the remaining stress imposed on the electrochemical stack?

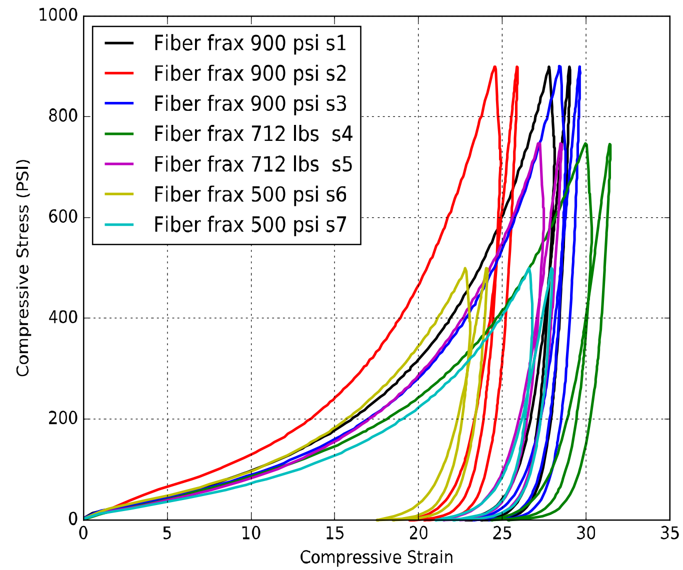
Recoverable strain does not seem to be a function of starting stress for fiberfrax insulation. (5%)

Min-K recoverable strain is a linear function of the stress









Insulation Mechanical Modeling

Can we derive and fit a constitutive model to match the unload behavior?

Represent stress relaxation with power law

$$\frac{\sigma}{\sigma_{max}} = a(t - t_{load})^m$$

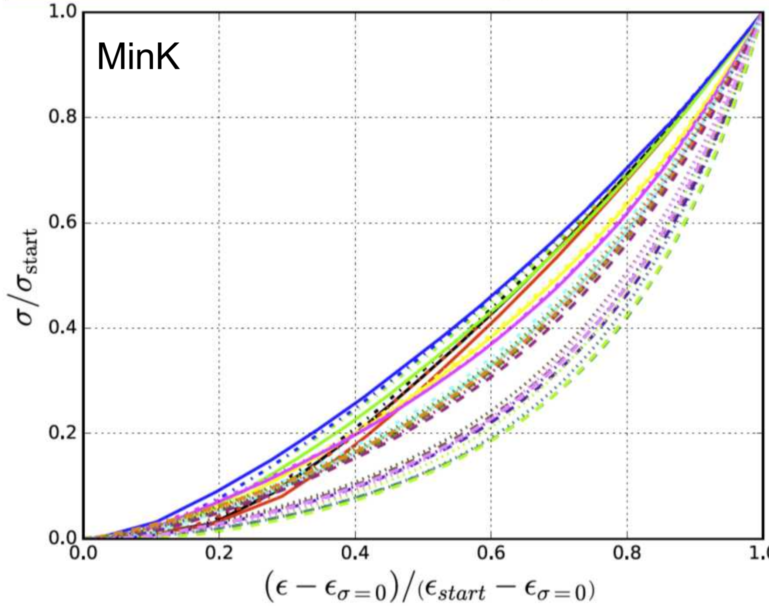
Scale unloading data appropriately to collapse

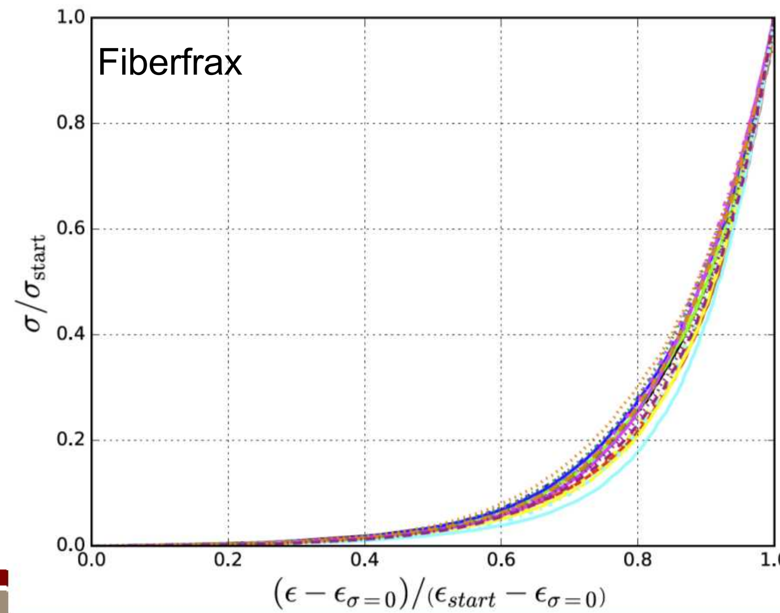
- Stress: σ/σ_{start}
- Strain: $(\epsilon - \epsilon_{\sigma=0})/(\epsilon_{start} - \epsilon_{\sigma=0})$

Fit unloading using simplified hyperfoam model [Storakers 1986]

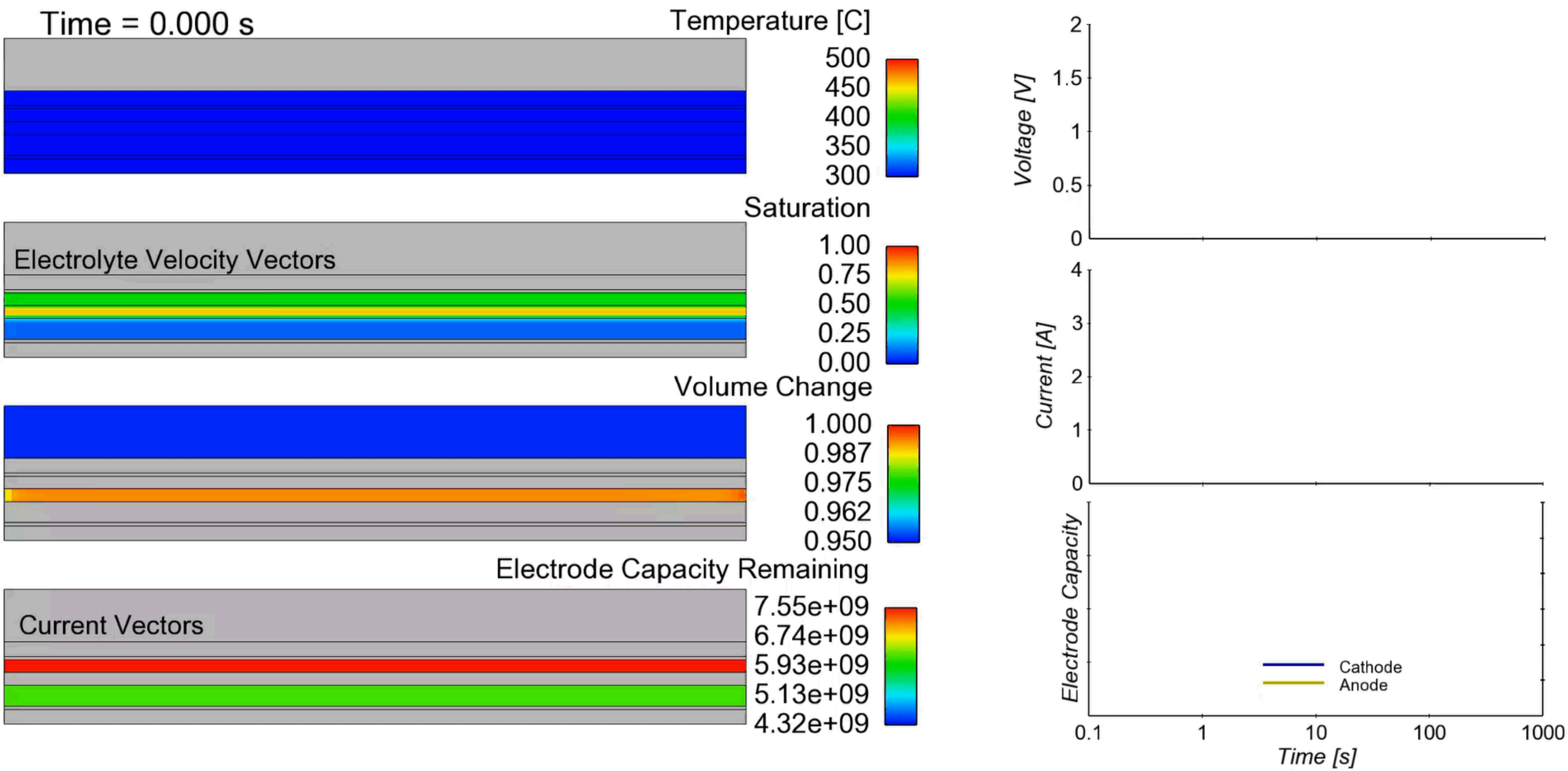
$$\sigma_{axial} = \sum_{i=1}^{N} \frac{2\mu_i}{\alpha_i} \left[\lambda_{axial}^{\alpha_i} - J^{\alpha_i \beta_i}\right] \qquad \beta_i = \frac{\nu_i}{1 - 2\nu_i}$$

Primitive modeling approach appears viable for Fiberfrax, questionable for MinK.





Full Multiphysics Single-Cell Simulation



Implications and Conclusions

Thermal batteries are specialized and complex multiphysics energy storage systems

- TABS design tool will facilitate battery design

Separator and insulation materials deform mechanically upon activation
Balance of material responses determines activated battery stack force

- Implications on
  - *Insulation thermal conductivity (porosity and thickness)*
  - *Electrolyte permeability and distribution in electrodes*
  - *Internal stresses: Robustness to mechanical environments*

Separator and Insulation have complex behaviors

- Insulation stress relaxation under constant strain
- Insulation nonlinear unloading behavior
- Separator: granular mechanics*

*Postdoc opportunity open at Sandia National Laboratories modeling separator mechanics
See Christine Roberts (ccrober@sandia.gov) for more information
US Citizenship is required