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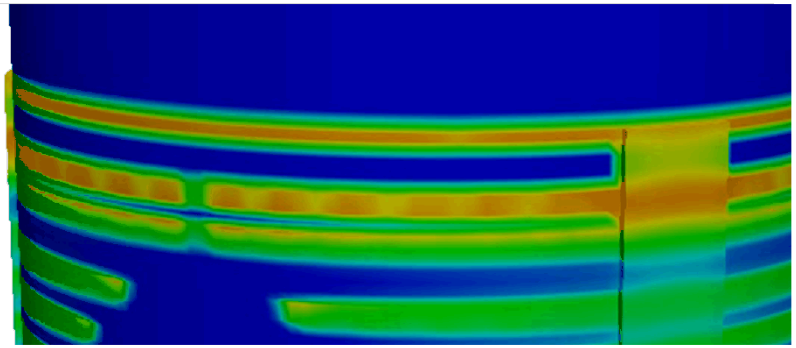

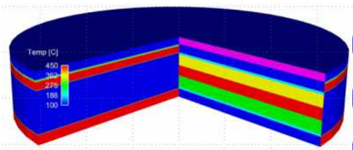

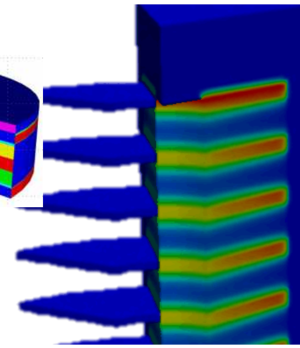

Developing a coupled thermal-mechanical-porous model for electrolyte flow in a molten salt battery

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U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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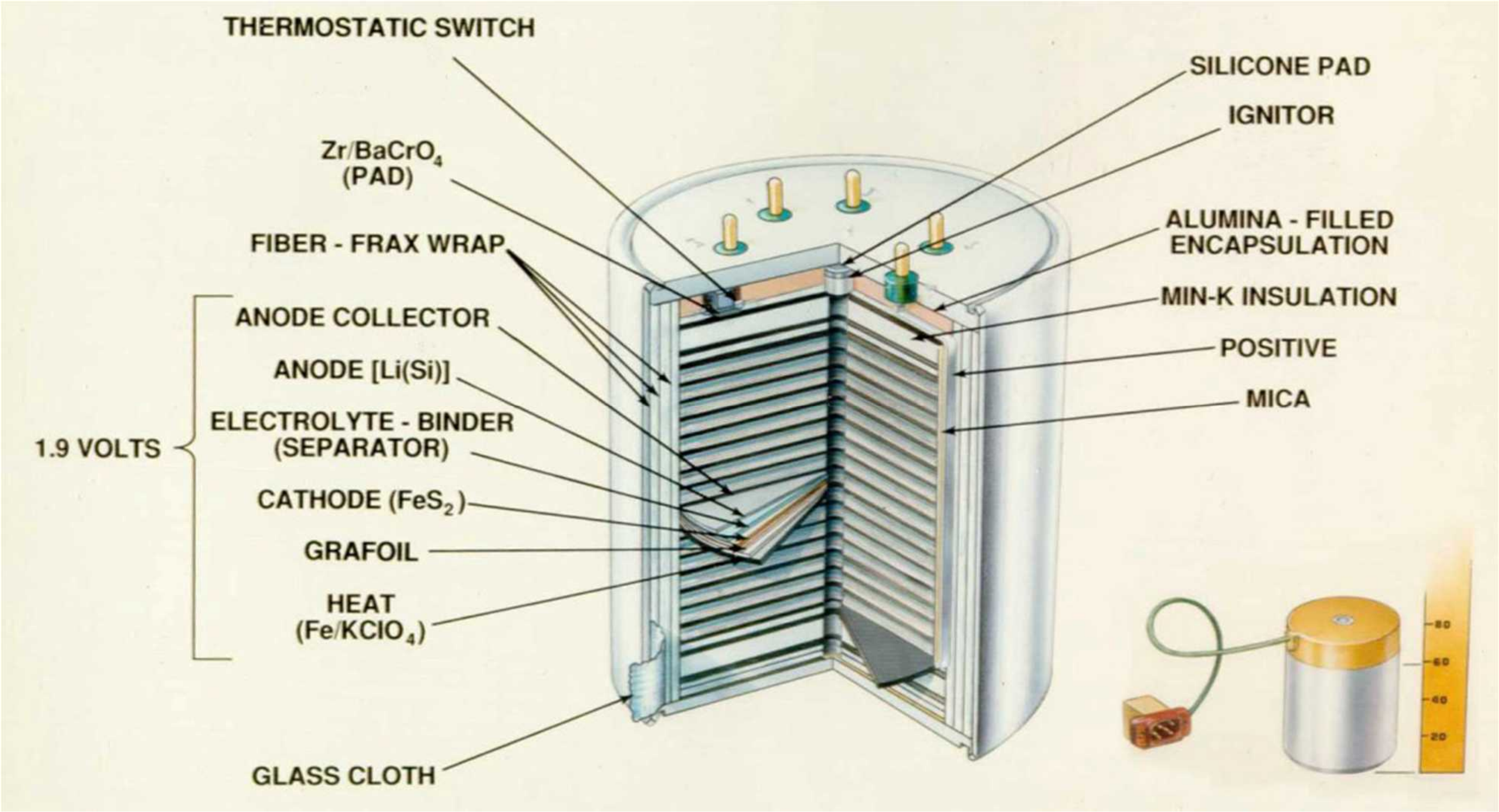
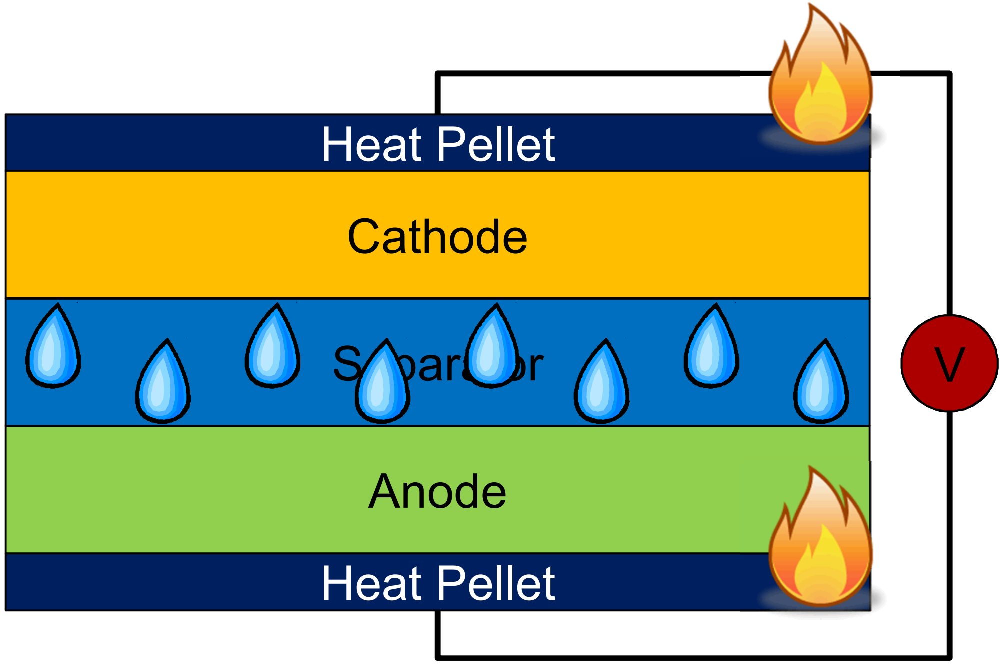
Molten Salt Battery

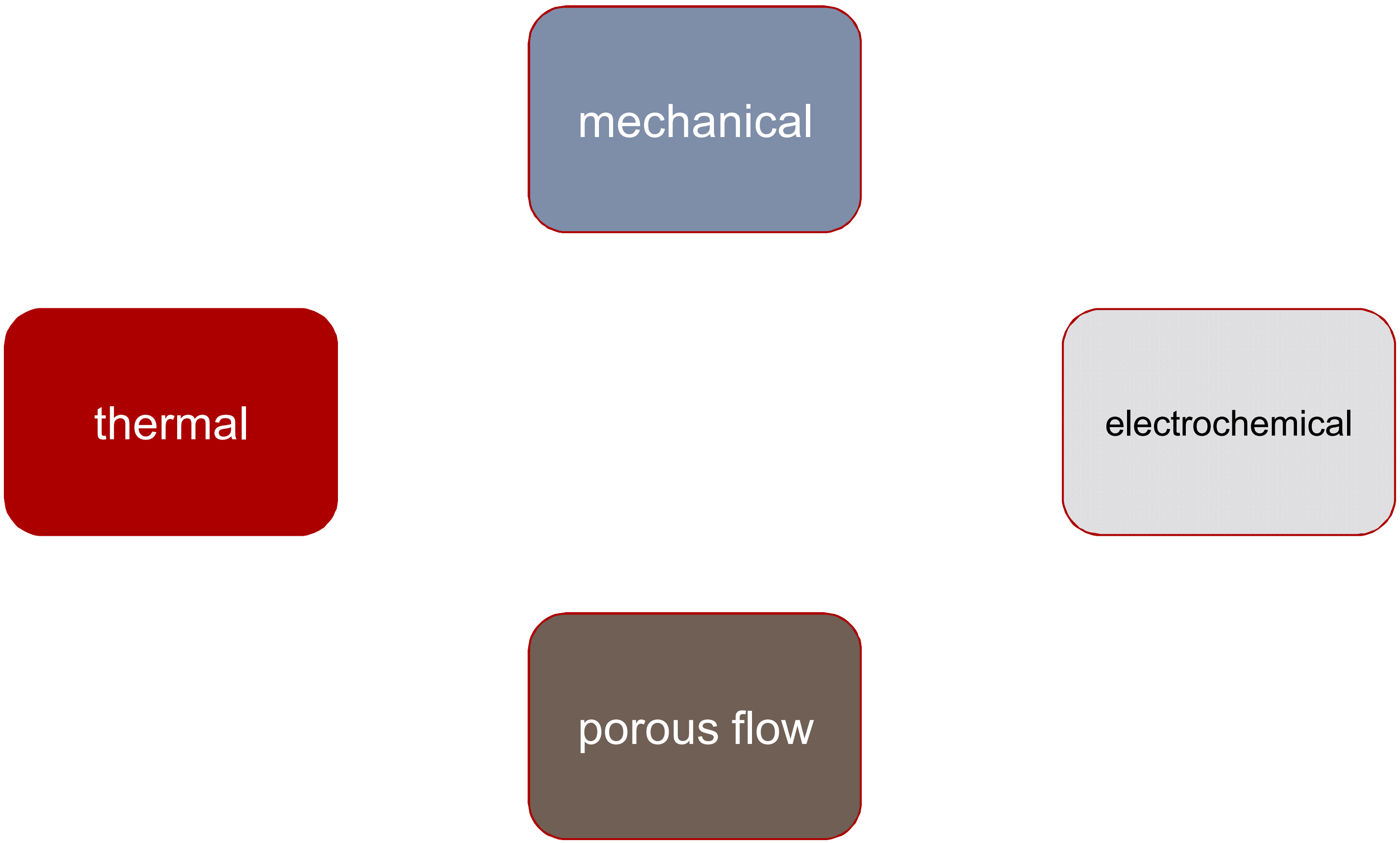


Physical Mechanisms

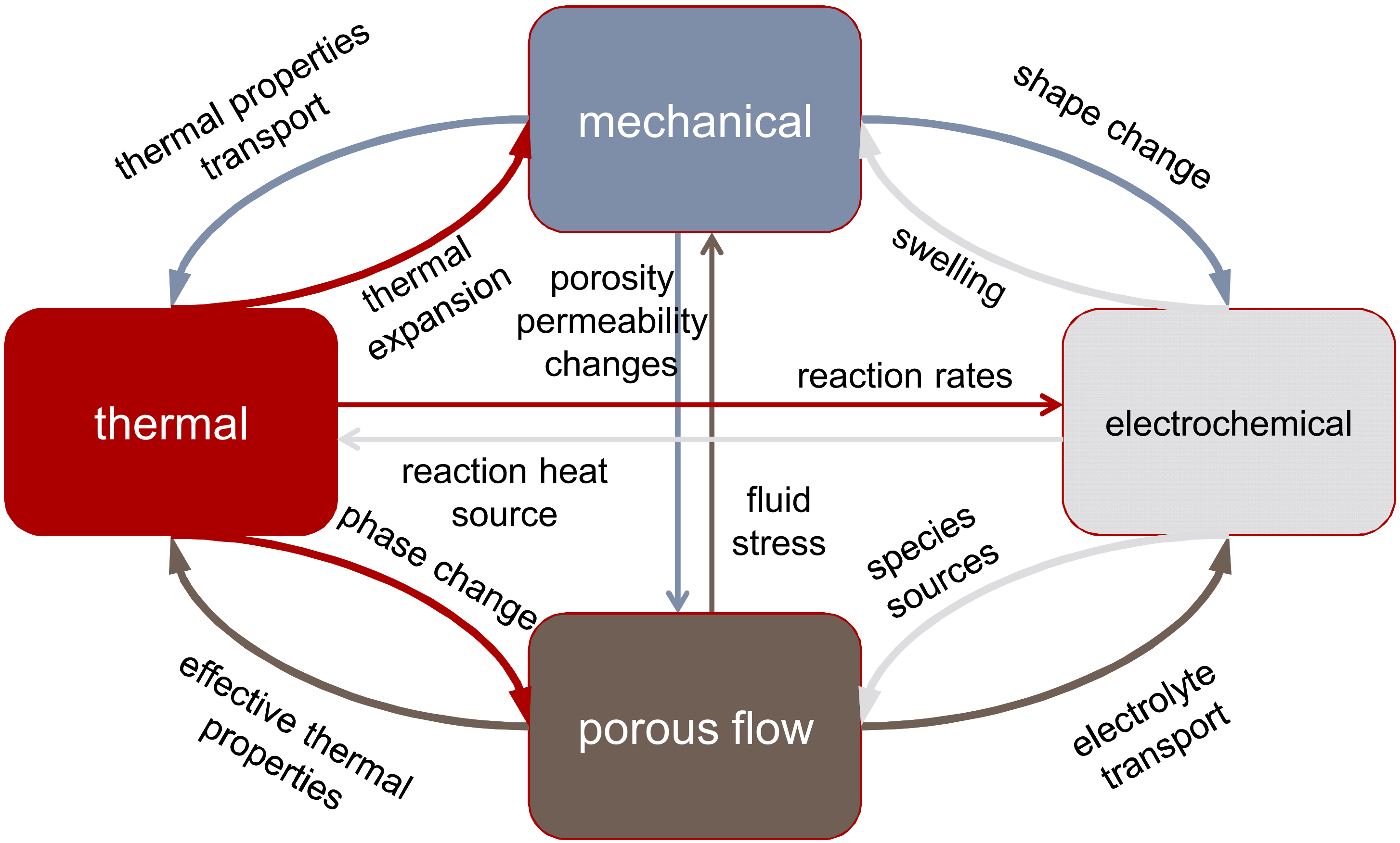
- Multi-physics problem
  - Thermal
  - Mechanical
  - Fluid
  - Electrochemical
- Modeling goals
  - Predict activation times
  - Optimize volume, insulation, manufacturing



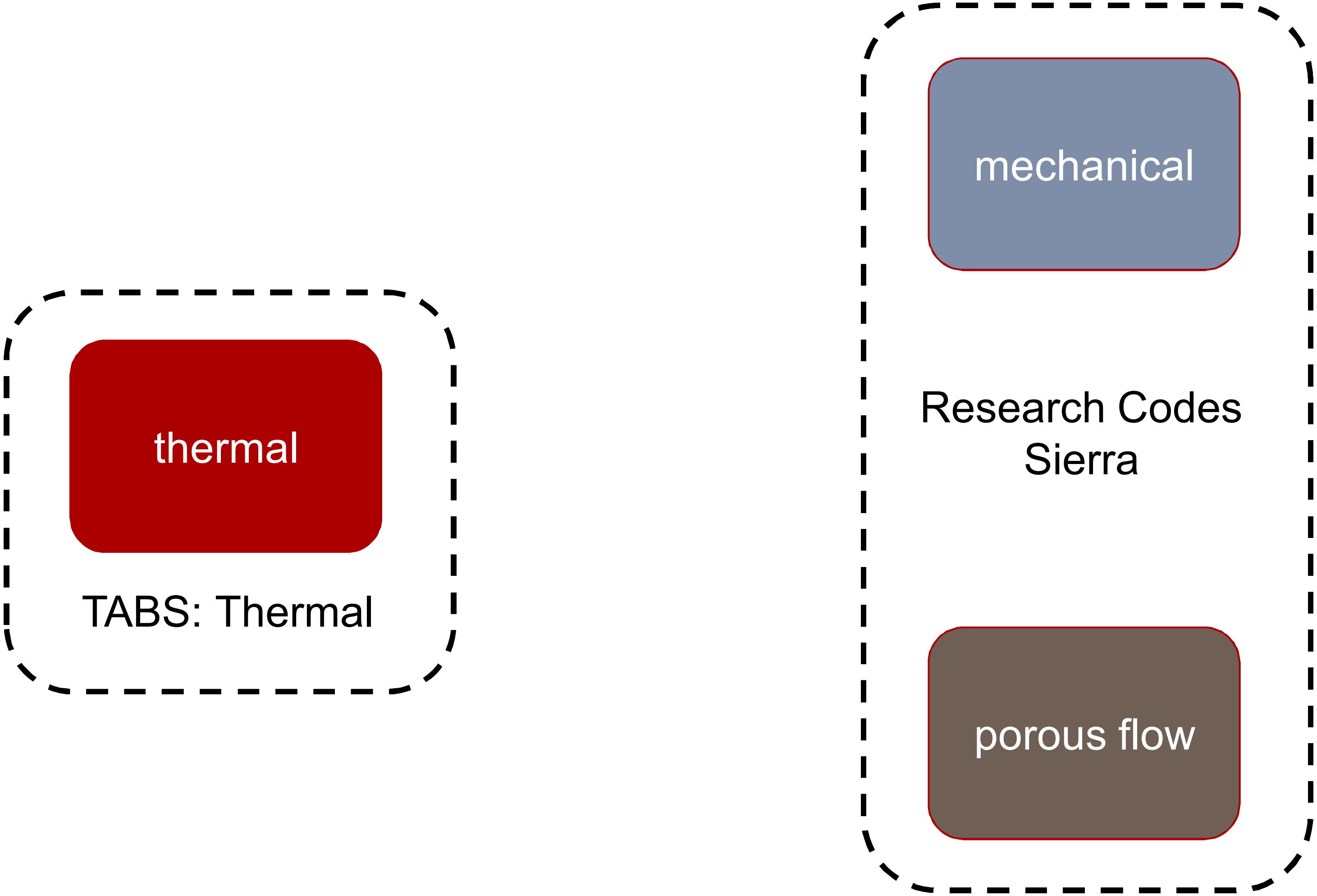
Multiphysics Coupling



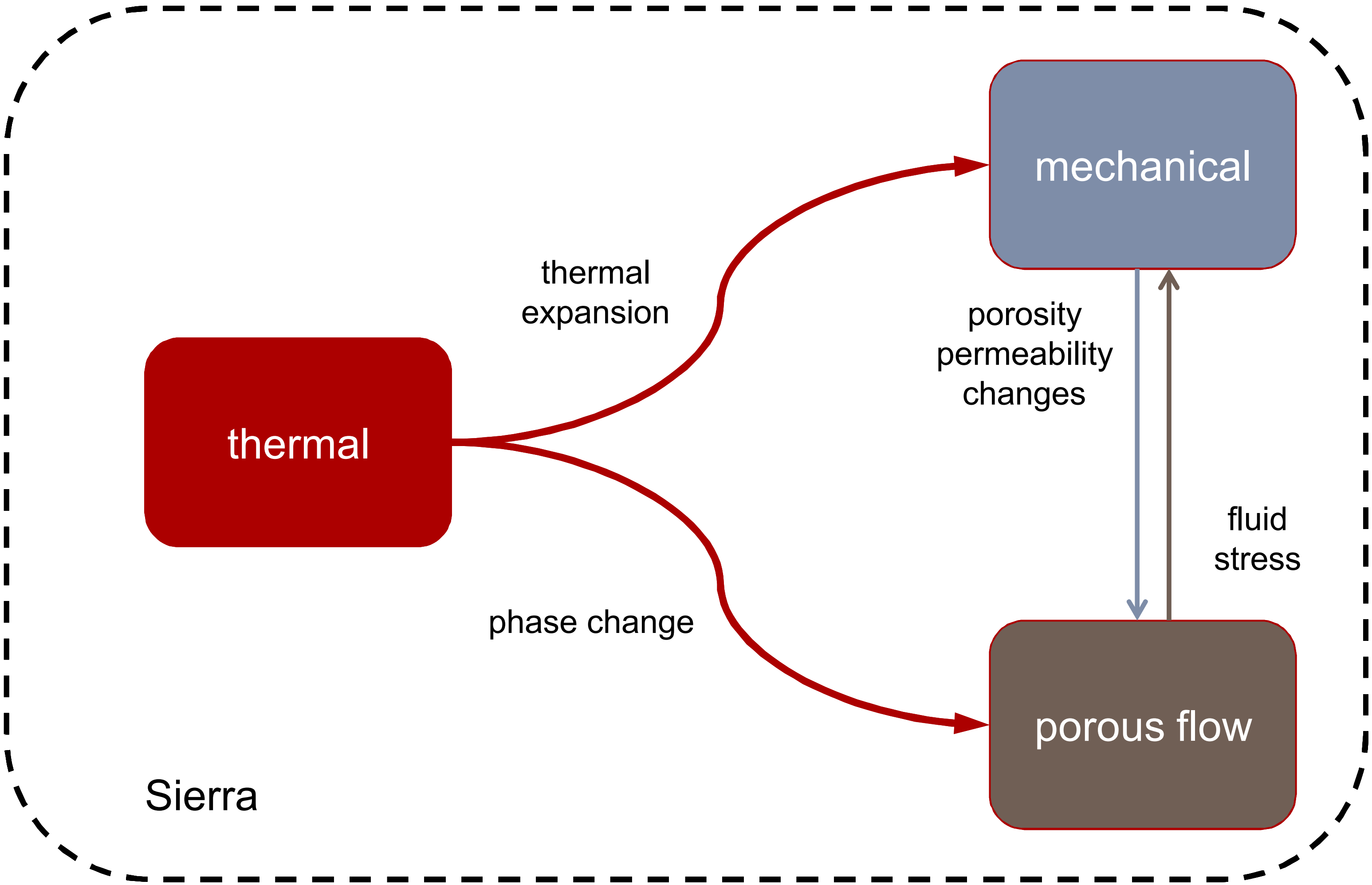
Multiphysics Coupling



Multiphysics Coupling



Multiphysics Coupling



Strongly coupled

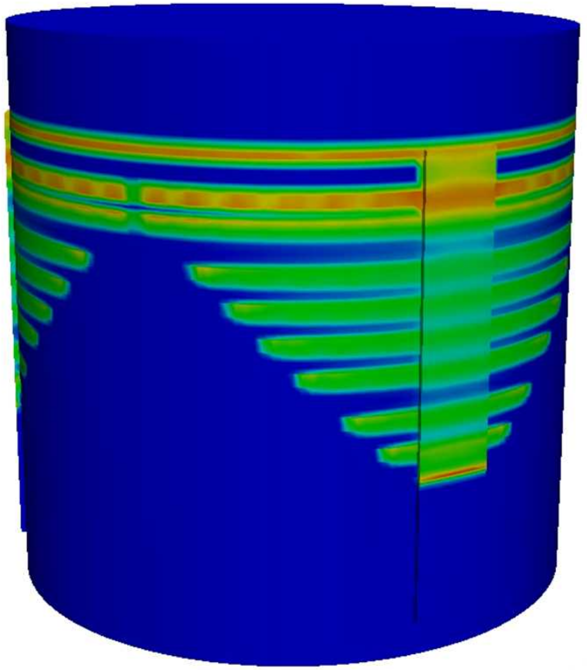
Models: Thermal

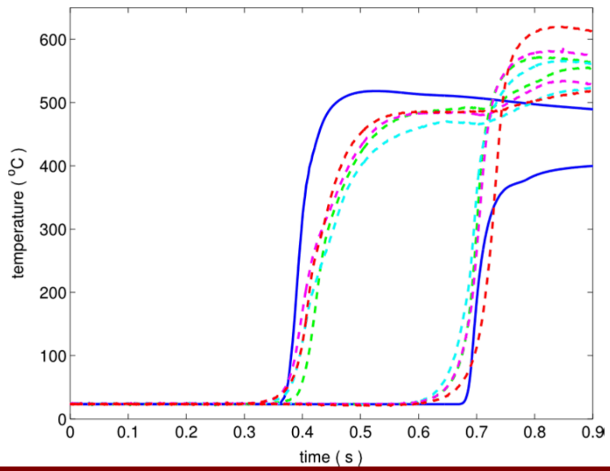
- Heat equation

$$\frac{\partial T}{\partial t} = \alpha \nabla^2 T + Q$$

  - Source term *Q* applies to heat pellet, paper

- Level set tracking of burn fronts
  - Constant propagation speed
  - Heat released over a narrow region near burn-front position





Model: Mechanical Deformation

- Solid constitutive model
  - inelastic volumetric and isochoric deformation of the *MgO skeleton* before, during, and after activation
  - Isotropic, thermal-elastic-plasticity
  - **Plasticity governs activation deformation**
  - Kinematic split of deformations

$$\underline{F} = \underline{F}^e \underline{F}^p \underline{F}^T$$

  - Rule of mixtures for phase decomposition

$$\chi = \frac{T - (T - T_w/2)}{T_w}$$

  - Kirchoff stress: $\underline{\underline{\tau}} = \mu_x(T)\mathrm{dev}(\underline{b}^3) + \frac{\kappa_x(T)}{2}(J_e^2 - 1)\underline{\underline{\delta}}$

- Conservation of momentum: $\underline{\nabla} \cdot \underline{\underline{\sigma}} = \underline{0}$
- Coupled to porous-flow through effective stress: $\underline{\underline{\sigma}} = \underline{\underline{\hat{\sigma}}} + p\underline{\underline{\delta}}$

Models: Porous flow

- Electrolyte and gas form two immiscible phases upon mel

$$\frac{\partial(\rho_w \phi S_w)}{\partial t} = \underline{\nabla} \cdot \left(\rho_w \frac{k_{rw}}{\mu_w} \underline{\underline{K}} \cdot (\underline{\nabla} p_w - \rho_w \underline{g}) \right) + Q_w$$

$$\frac{\partial(\rho_n \phi S_n)}{\partial t} = \underline{\nabla} \cdot \left(\rho_n \frac{k_{rn}}{\mu_n} \underline{\underline{K}} \cdot (\underline{\nabla} p_n - \rho_n \underline{g}) \right) + Q_n$$

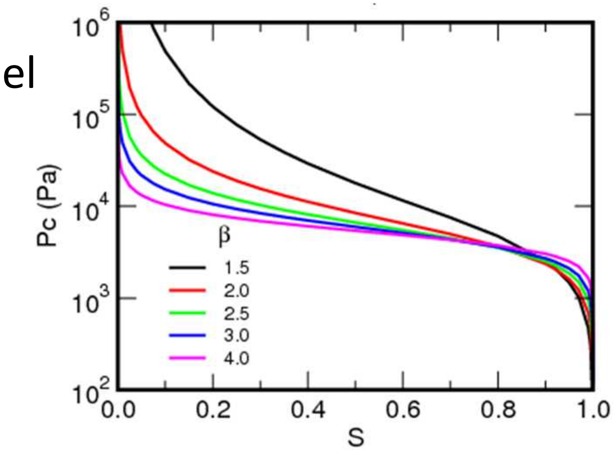
- Saturation and capillary pressure related to DOFs (wetting and non-wetting pressures) through model relations

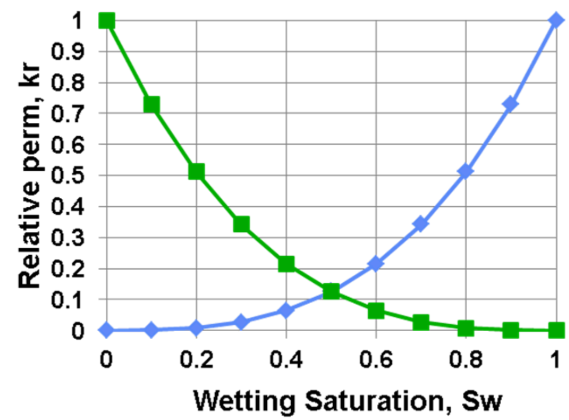
$$S = S(p_c); \quad p_c = p_n - p_w$$

- Coupling to other physics important!

$$\phi = \phi(\underline{d}); \quad \mu_i = \mu_i(T)$$

$$S_i = S_i(p_c, \underline{d}); \quad \underline{\underline{K}} = \underline{\underline{K}}(\underline{d})$$





Capillary pressure (top) and relative permeability (bottom) depend on wetting phase saturation and electrode pore structure

Numerics

- Thermal and Mechanical
  - GFEM method
- Porous Flow
  - Upwinded version of Darcy flux (Forsyth)

$$R_I^{flux} = -\sum_{J \neq I} \lambda^u_{(I,J)} K_{IJ}(P_J - P_I)$$

$$K_{IJ} = -\int_\Omega \nabla N_I \cdot \boldsymbol{k} \cdot \nabla N_J \, \mathrm{d}\Omega$$

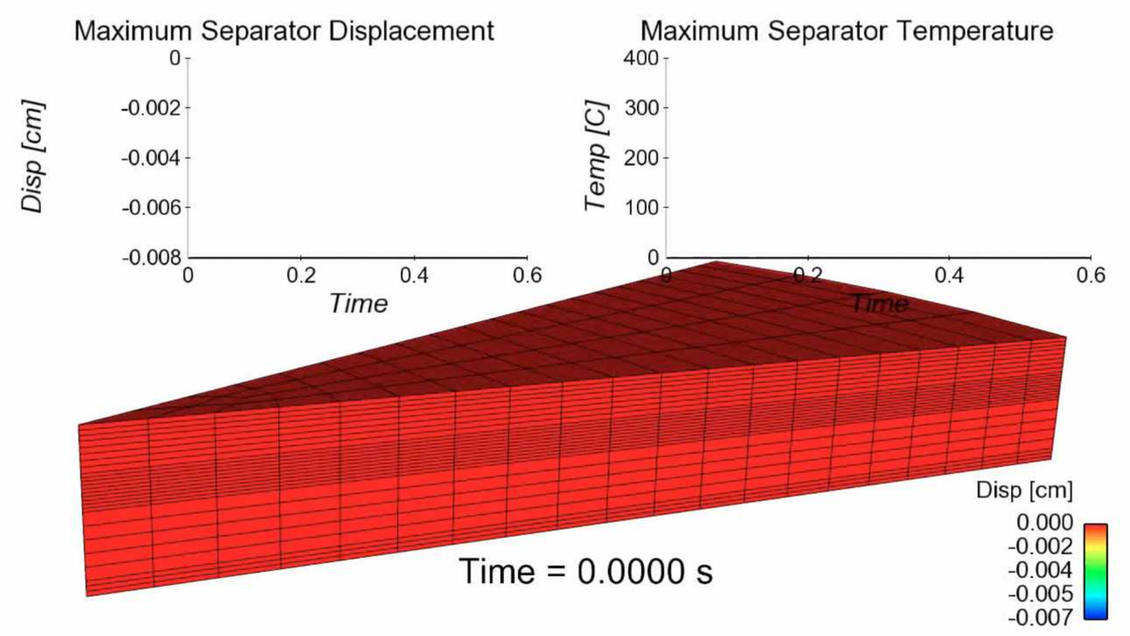
$$\lambda^u_{(I,J)} = \begin{cases} \lambda_J & \text{if } K_{IJ}(P_J - P_I) > 0 \\ \lambda_I & \text{if } K_{IJ}(P_J - P_I) < 0 \end{cases}$$

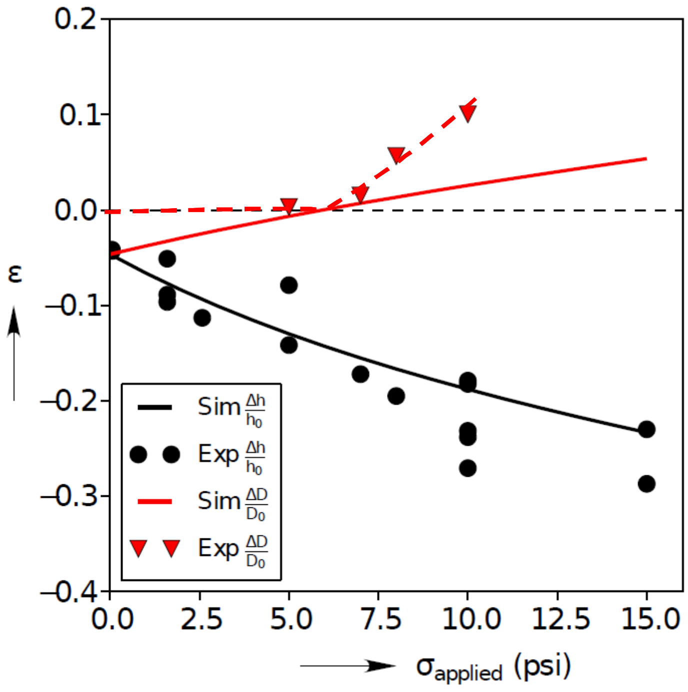
$$\lambda = \rho Y k_r / \mu$$

  - Vertex Quadriture
  - Discontinuous Saturations
    - pressure—pressure formulation

Demonstration: Themo-mechanical deformation

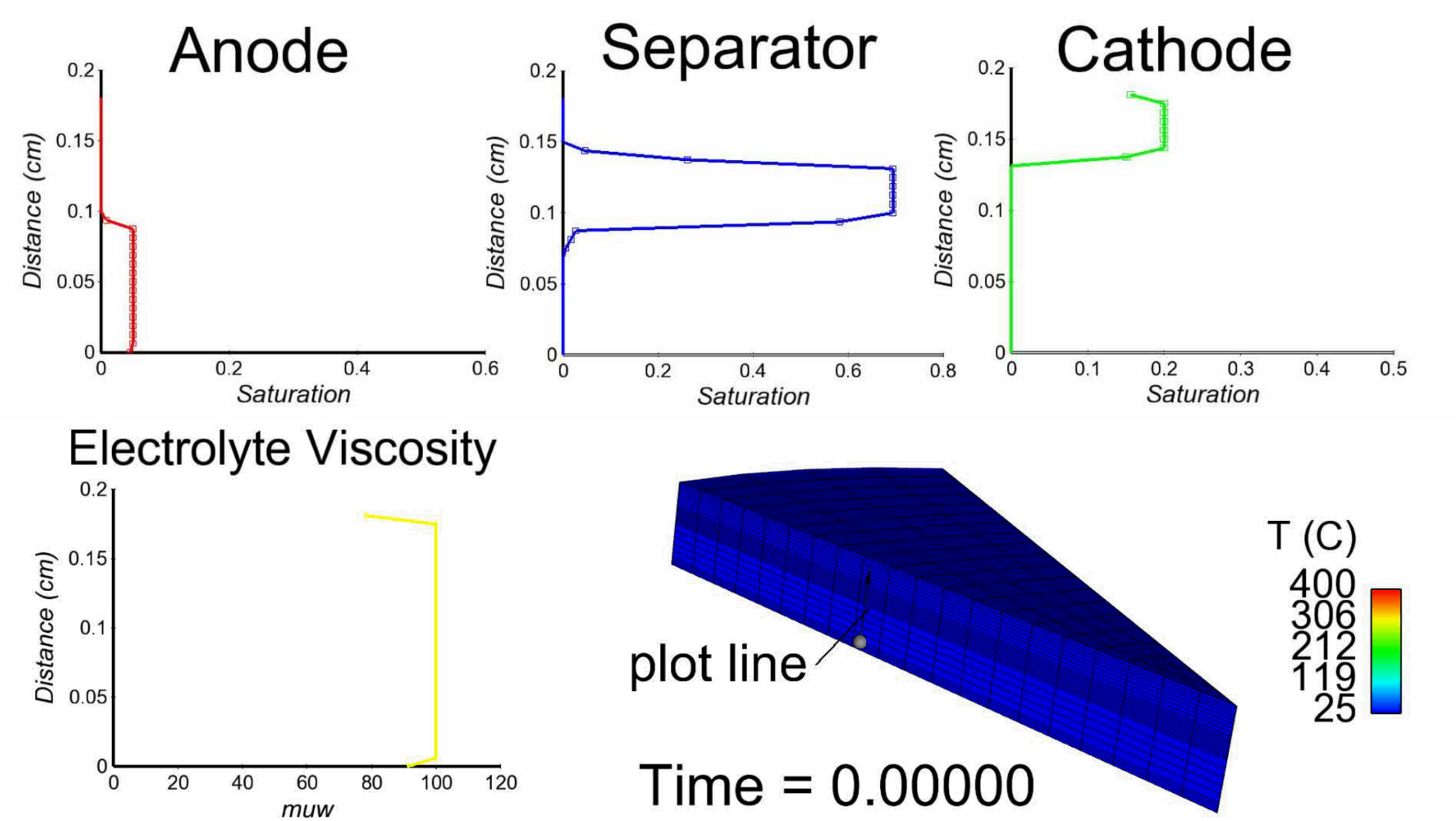
- Electrolyte melting causes separator deformation
- Height vs. diameter change
  - Missing effective stress





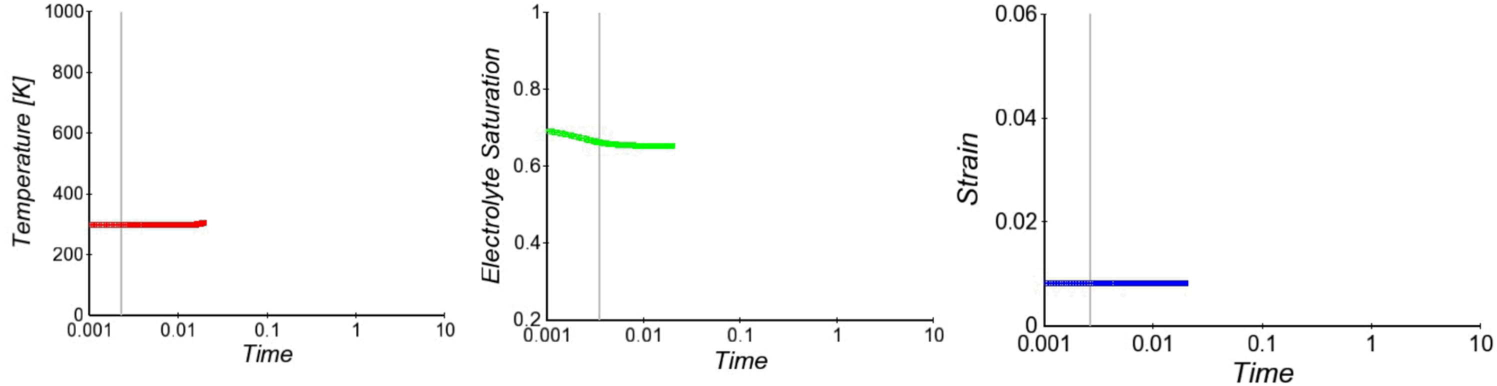
Demonstration: Thermo-porous flow

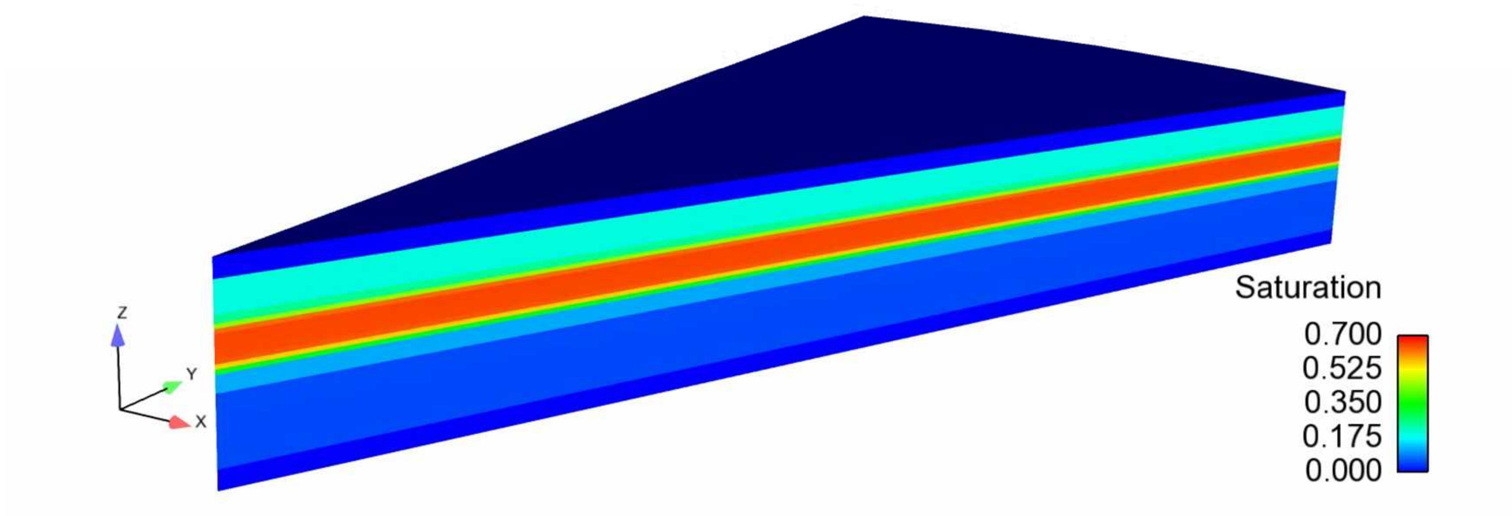
- Two-pressure porous-flow formulation enables stable solution of flow from the separator to the cathode and
-



Demonstration: Thermo-poro-mechanical coupling

- Thermo-poro-mechanical single-cell simulation with full coupling:





Conclusions & Future Work

- Proof of concept simulation
- Experimental determination of material properties
- Calibration of solid model via experiments
- Electrochemical modeling

- Acknowledgements:
  - DoD/DoE Joint Munitions Program, TCG V
  - ASC/IC, ASC/P&EM, WSEAT
  - Victor Brunini, Lindsay Erickson, Adrian Kopacz

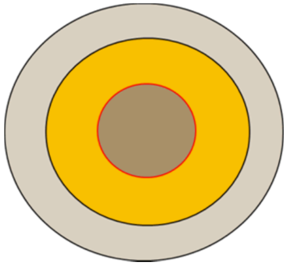
Models: Electrochemistry

- Reactions, especially for the cathode, are stoichiometrically complicated

$$\mathrm{Cathode:FeS_2 \leftrightarrows Li_3Fe_2S_4 \leftrightarrows Li_{2+x}Fe_{1+x}S_2 + Fe_{1-y}S \leftrightarrows Li_2FeS_2 \leftrightarrows Li_2S + Fe}$$

$$\mathrm{Anode:Li_1 3Si_4 \leftrightarrows Li_7Si_4 \leftrightarrows 4Si}$$

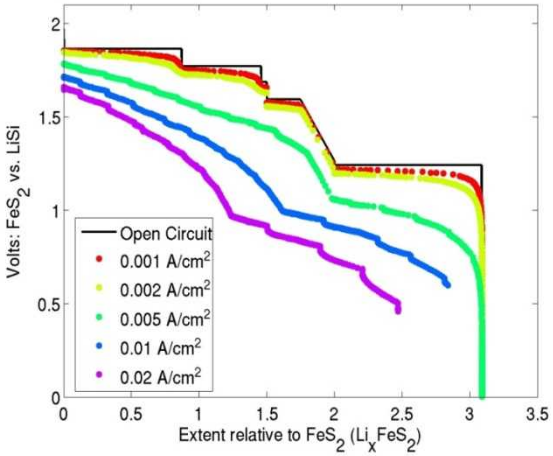
- Cantera's "Electrode Object" deploys multiple sub-grid models
  - Infinite capacity
  - Multi-plateau
  - Newman reaction extend
  - Finite capacity



Shrinking Core Model

- Multiple plateaus can react simultaneously
- Diffusional losses with transport

- Primary electrochemical coupling is the temperature
  - Cantera's thermodynamics all temperature-dependent
- Future: Use deformed geometry to affect porosity in electrochemical calculations



Demonstration: Thermo-electrochemical coupling

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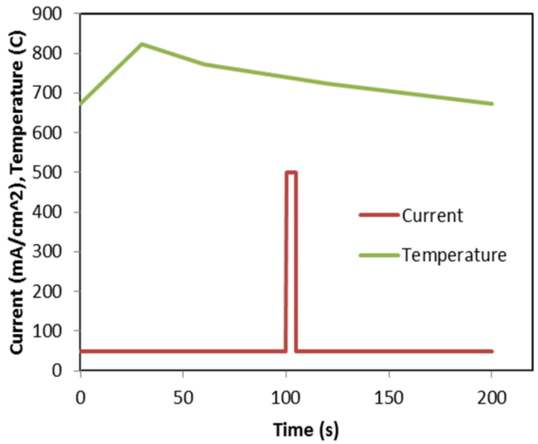
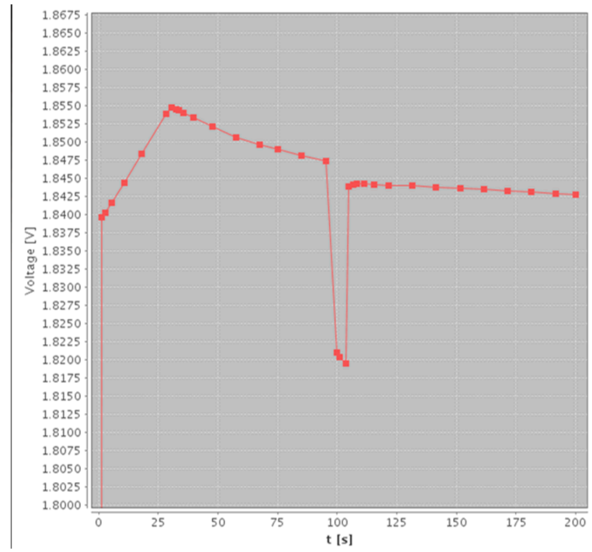
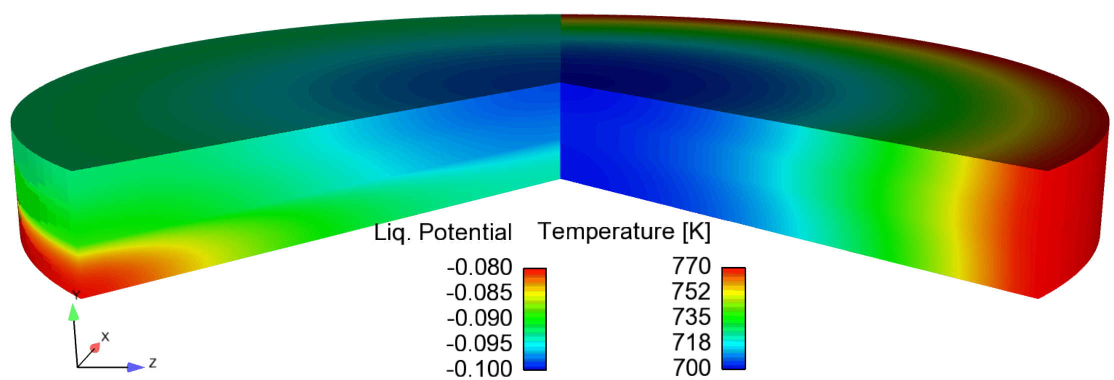
- Voltage responds to temperature and current





- Spatial temperature variations affect local potentials and current densities



Thermal-Mechanical Behavior of the Solid Skeleton

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Free Energy Density

$$\rho_0\psi = \mu_x[T](\bar{I}_{1e} - 3) + \frac{\kappa_x[T]}{4}\left(J_e^2 - 1 - 2\log J_e\right)$$

Kirchoff Stress

$$\boldsymbol{\tau} = 2\rho_0 \boldsymbol{b}\frac{\partial\psi}{\partial\boldsymbol{b}} = \mu_x[T]\mathrm{dev}[\boldsymbol{b}^e] + \frac{\kappa_x[T]}{2}\left(J_e^2 - 1\right)\mathbf{1}$$

Isochoric (Radial) Yield

$$\phi_\mu = \sqrt{J_2} - A_x\frac{I_1}{3} - B_x\left(\frac{I_1}{3}\right)^2 - Y_{ps\,x} - H_{\mu\,x}\epsilon_\mu^{m_x}$$

Plastic Flow Rules

$$\mathcal{L}\left[\boldsymbol{b}^e\right] = \boldsymbol{F}\dot{\boldsymbol{C}}^{p-1}\boldsymbol{F}^T = -2\left(\dot{\lambda}_{iso}\boldsymbol{n}_{iso} + \dot{\lambda}_{vol}\boldsymbol{n}_{vol}\right)\boldsymbol{b}^e$$

$$\boldsymbol{n}_{iso} = \frac{\mathrm{dev}\boldsymbol{\tau}}{||\mathrm{dev}\boldsymbol{\tau}||}, \qquad \boldsymbol{n}_{vol} = \frac{1}{3}\mathbf{1}$$

Kinematic Split of the Deformation Gradient: Thermal, Elastic, and Plastic Parts

$$\boldsymbol{F} = \boldsymbol{F}^e\boldsymbol{F}^p\boldsymbol{F}^\theta$$

Cold/Hot State Phase Decomposition

$$\begin{aligned} &\text{if} && T < T_m - T_w/2, && \chi = 0, \\ &\text{elseif} && T > T_m + T_w/2, && \chi = 1, \\ &\text{else} && && \chi = \frac{T - (T - T_w/2)}{T_w}, \end{aligned}$$

Volumetric Yield

$$\phi_\kappa = \frac{I_1}{3} - Y_{P\,x} - H_{\kappa\,x}\epsilon_\kappa^{n_x}$$

Net Yield Surface is the Phase Volume Fraction Weighted Sum

$$\phi = (1-\chi)\left(\phi_\mu^C + \phi_\kappa^C\right) + \chi\left(\phi_\mu^H + \phi_\kappa^H\right)$$

Model: Mechanical Deformation