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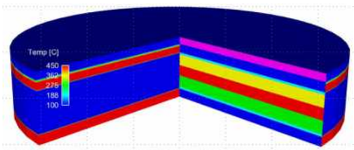
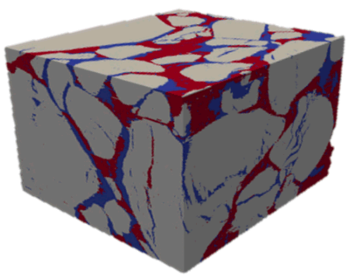


Multiphase Electrolyte Transport in Porous Electrode Batteries



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EERE Battery Project Meeting

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Mechanistic Modeling Framework for Predicting Extreme Battery Response: Multiphase transport in porous electrodes

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Objectives:

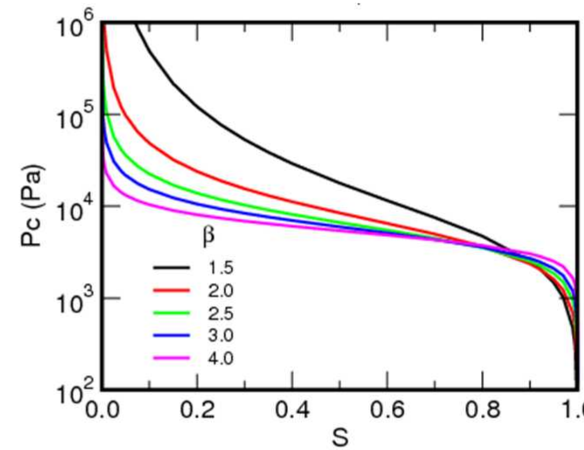
- Add partial saturation and solid mechanics models to CAEBAT to model gasification and stress-induced degradation phenomena
  - E.g., Hydrogen gas evolution
  - Some systems are two-phase initially, e.g. molten salt batteries
- Develop new models for thermal runaway processes that are based on consistent thermodynamics models.
- Develop consistent thermodynamic/transport models of the entire cell using CANTERA an open source constitutive modeling package

Overall Continuity of fluid phase in a Porous electrode

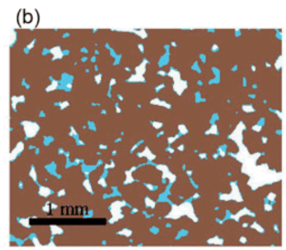
- Electrolyte and gas form two immiscible phases upon melting

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

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

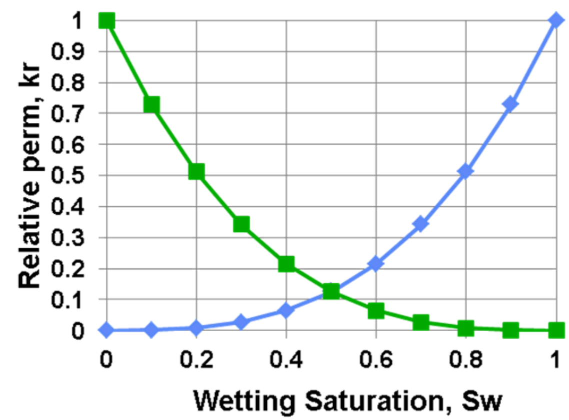


- Saturation and capillary pressure related to DOFs (wetting and non-wetting pressures) through model relations



Two-phase fluid system

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



- Coupling to other physics important!
  - Required:

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

  - Optional?:

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

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

Example: Molten Salt Batteries

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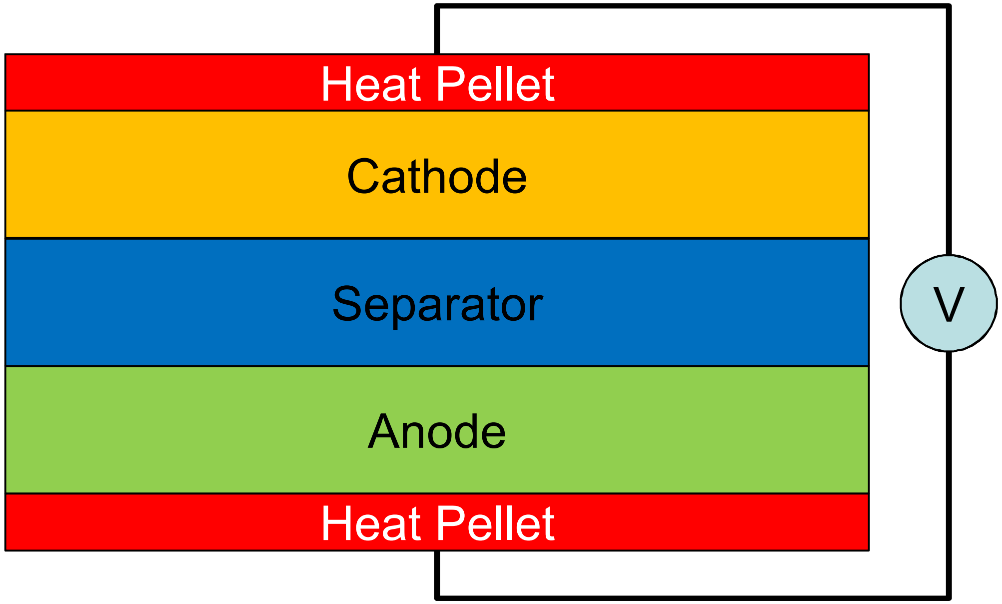
Physical mechanisms in molten salt battery activation:

- Battery activation is a complicated, multi-step process
  - Heat pellet burning
  - Thermal diffusion
  - Melting of the electrolyte
  - Deformation of the separator
  - Flow of the electrolyte
  - Activation



- A true multi-physics problem
  - Thermal
  - Mechanical
  - Fluid
  - Electrochemical

Example: molten salt battery activation

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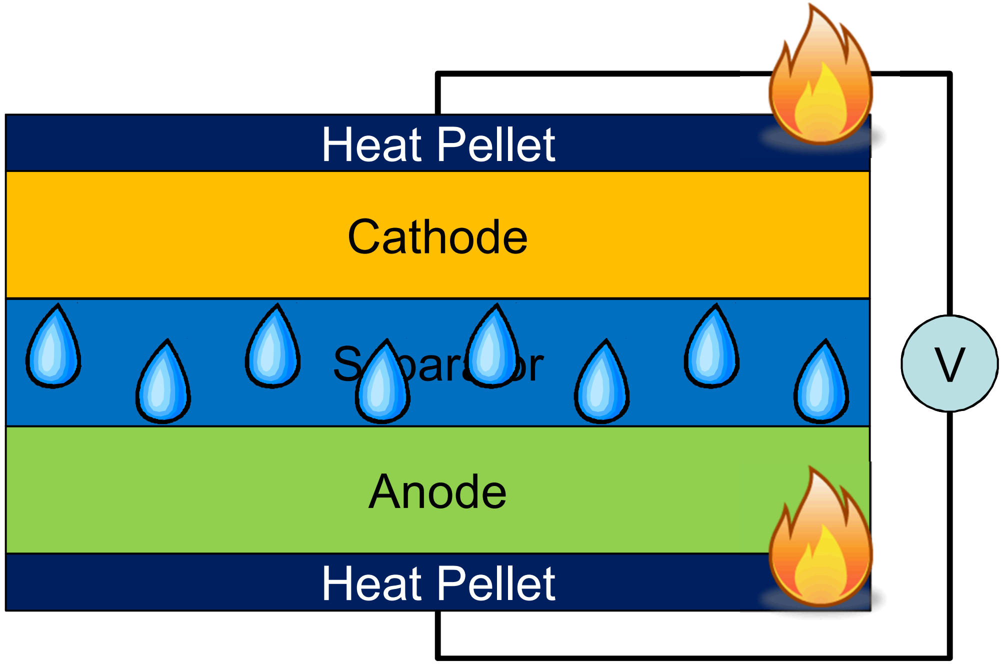
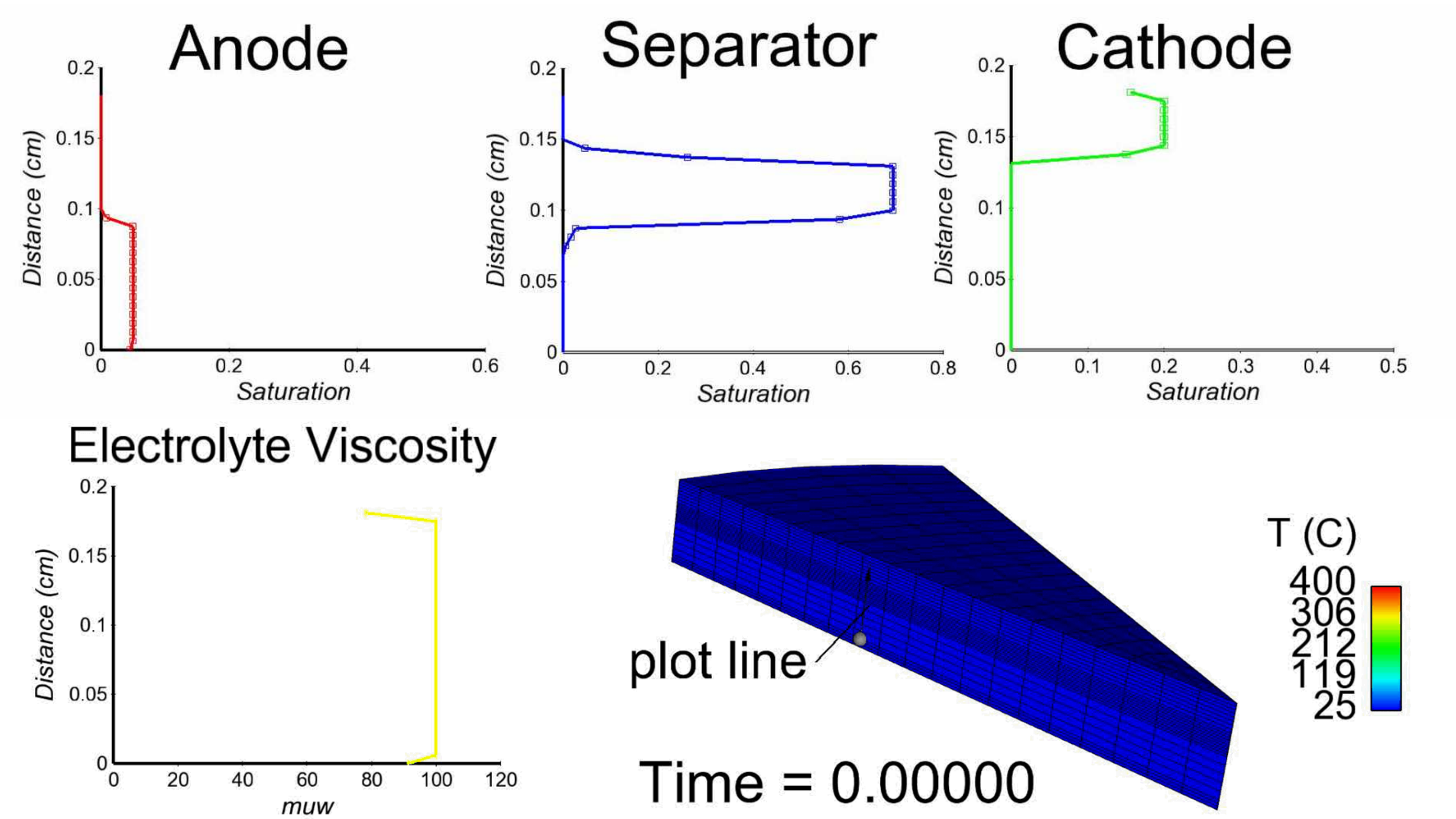


Demonstration: Thermo-porous flow

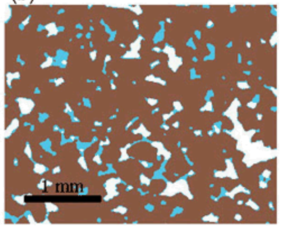
- Two-pressure porous-flow formulation enables stable solution of flow from the separator to the cathode and anode.
- Flow is “frozen” before activation by an artificially high viscosity. As the electrolyte melts, the viscosity drops.



Multiphase Electrolyte Transport

Transport of species *k* in phase *β* ($C_{\beta k}$):

$$\frac{\partial\left(\phi S_\beta C_{\beta k}\right)}{\partial t} + \nabla \bullet \left[C_{\beta k} \left(\mathbf{v}_\beta + \mathbf{V}_{\beta k}^{d} \right) \right] = \dot{r}_{\beta k} + Q_{\beta k}, \qquad \beta = l \text{ or } g$$



Two-phase fluid system
Blue: wetting phase
Whiite: nonwetting phase

Bulk phase velocity depends on phase concentration (C_β):

$$\mathbf{v}_\beta = -\frac{\mathbf{k}k_{r\beta}}{\mu_\beta}\left(\nabla p_\beta - C_\beta \mathbf{g}\right) \qquad C_\beta = \sum_k C_{\beta k}$$

Diffusion velocities ($\mathbf{V}^d$) can be modeled by Stephan-Maxwell, or Fickian with D_{eff}

Multiphase model introduces phase pressures (p_β) and phase saturations (S_β), but there are additional constraints:

- Fluid-saturated pore space: $S_l + S_g = 1$
- Unit sum of mole fractions: $\sum_k X_{\beta k} = 1, \quad \beta = l \text{ or } g$
- Electroneutrality: $\sum_k z_k^\beta C_{\beta k} = 0, \quad \beta = l \text{ or } g$

Pressure or saturation usually solved from overall continuity equation:

$$\frac{\partial\left(\phi S_\beta C_\beta\right)}{\partial t} - \nabla \bullet \left(C_\beta \frac{\mathbf{k}k_{r\beta}}{\mu_\beta}\left(\nabla p_\beta - C_\beta \mathbf{g}\right) \right) = Q$$

Partial Equilibrium

Some species can be in thermodynamic equilibrium and can partition between phases, e.g. in a aqueous system:

$$H_2O_{(g)} \rightleftharpoons H_2O_{(l)}$$

But thermodynamic equilibrium provides N_{eq} relationships for those species:

$$\mu_k^l = \mu_k^g$$

And the number of equilibrium transport equations is also reduced by N_{eq} by summing the phase transport equations:

$$\frac{\partial}{\partial t}\phi\left(S_l C_{lk} + S_g C_{gk}\right) + \nabla \bullet \left[C_{lk}\left(\mathbf{v}_l + \mathbf{V}_{lk}^d\right) + C_{gk}\left(\mathbf{v}_g + \mathbf{V}_{gk}^d\right)\right] = Q_k$$

Mechanical deformation and swelling

A possible continuum formulation following poroelastic theory (Coussy):

- Conservation of momentum: $\underline{\nabla} \cdot \underline{\sigma} = \underline{0}$
- Poroelastic constitutive theory:

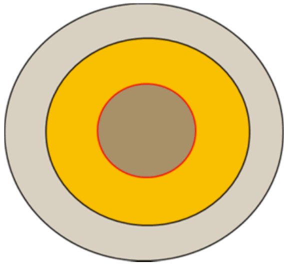
$$\sigma - \sigma_0 = K(\varepsilon - 3\alpha(T - T_0)) - b(p - p_0)$$

$$\phi - \phi_0 = b\varepsilon + \frac{1}{M}\left(p - p_0\right) - 3\alpha_\phi(T - T_0)$$

- A similar model could be postulated for Lithiation $\varepsilon_{Li} \square \beta\left(C_{Li} - C_{Li}^0\right)$

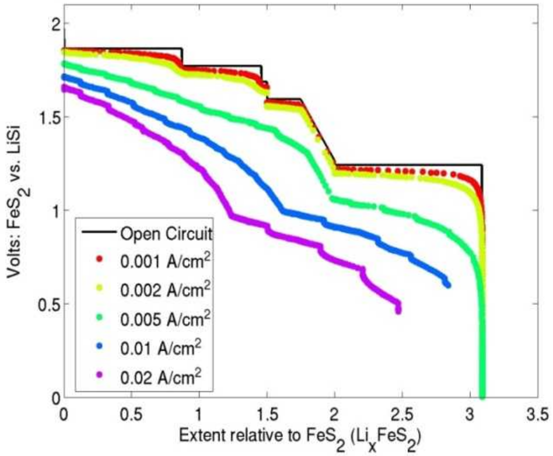
Models: Electrochemistry

- Cantera's "Electrode Object" deploys multiple sub-grid models
  - Infinite capacity
  - Multi-plateau
  - Newman reaction extend
  - Finite capacity
- Primary electrochemical coupling is the temperature
  - Cantera's thermodynamics all temperature-dependent



Shrinking Core Model

- Multiple plateaus can react simultaneously
- Diffusional losses with transport



Summary

Multiphysics coupling can provide higher-fidelity models, enabling a tool to investigate abnormal conditions in Li-ion batteries such as Lithiation cracking, thermal runaway, gas generation and leakage.

- Future:
  - Multiphase electrochemistry
  - Thermo-poro-mechanics
  - Couple electrochemistry to the thermo-poro-mechanics