

Modeling Separator Deformation and Electrolyte Flow in Thermally-Activated Batteries

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Abstract

When a thermal battery is activated, mechanical deformation occurs in the cell stack, which in turn affects the electrochemical performance of the battery. The most substantial change is observed in the separator component, which resides between the anode and cathode. This separator is typically composed of a solid MgO powder and a solid (at room temperature) electrolyte which are pressed together to make a pellet. During thermal activation, the electrolyte melts, the separator pellet compresses, void space is removed, and electrolyte flows within the separator, into the anode and cathode, and potentially into surrounding materials. Mechanical constitutive equations are developed that describe this mechanical process and response. Deformation of the separator pellet solid structure is modeled using a linear elastic model with temperature-dependent properties derived from experimental data. Flow of the electrolyte is captured using saturated and partially-saturated flow models. Simulations for a single cell stack are used to examine the effect of the deformations on electrolyte transport within the battery.

Keywords

thermally-activated battery; computational model; separator; mechanical deformation; porous flow; electrolyte

INTRODUCTION

Molten salt batteries manufactured by pressed pellet technology typically consist of multiple electrochemical cells stacked into a cylinder and packaged under a closing force. When they are activated and the electrolyte melts, the electrochemical stack exhibits a significant mechanical rearrangement with the separator losing up to 30% of its original height [3]. The consolidation is important to battery performance. Too much deformation can cause separator material or just electrolyte to leak out of the electrochemical stack, potentially resulting in a short circuit across battery cells. If the deformation is too small, there is poor interfacial contact between the layers, resulting in higher internal resistance in the battery [3]. In order to better understand the activation

process and resulting consolidation of the separator, we have built upon experimental characterization of thermal battery components [4] to develop new mechanical models for both the separator layer and a single electrochemical cell. Three mechanical models are examined ranging from a simple linear elastic model to two more complex models. A generalized thermal elastic mode is used to predict with greater fidelity the activation response but is limited to linear elastic deformation after melting. The Kayenta model is used to capture the non-linear response of the molten separator. Additionally electrolyte transport in response to the mechanical deformation will also be examined in a single battery cell.

MODEL

In this section we describe the models developed for this paper, including solid mechanics models to study separator deformation and a porous flow model for understanding electrolyte movement within the battery.

Solid mechanics model

A model for the mechanical deformation of the separator material must be compiled. While standard models, such as those of elastic solids, are considered, a more complex or novel model might need be developed to capture the observed behaviors. Roberts [4] describes the mechanical responses that are observed in the separator during laboratory testing. They key behaviors of the separator that we must capture include:

- The amount of deformation during melting of the electrolyte as a function of the applied force.
- The modulus prior to activation.
- The modulus after activation.

In this section, we describe three models of increasing complexity that we investigate for these purposes.

Simple linear elastic model

While more realistic constitutive equations for the separator were being developed and validated, a simple linear elastic model was used for the purposes of studying electrolyte transport. Here, we use the standard conservation equations for a linear elastic solid,

$$\nabla \cdot \sigma = 0, \quad (1)$$

with

$$\sigma = 2\mu\varepsilon + \lambda\text{tr}(\varepsilon)\mathbf{I}. \quad (2)$$

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Here, σ and ε are the stress and strain tensors, μ and λ are the first and second Lamé parameters (moduli), and \mathbf{I} is the identity tensor. The first Lamé parameter μ is also known as the shear modulus. A modification to this model is the use of a temperature dependent shear modulus, $\mu(T)$. This function was derived in two parts. First, the post-activation modulus was fit to the experimental data of Fig. 3 in Roberts [4] using the analytical solution for the strain of a linear elastic disk,

$$\gamma = \frac{Fh_0}{F + 2\mu_0(1 + \nu)}, \quad (3)$$

where γ is the engineering strain, F the applied force, μ_0 the post-activation value of the shear modulus, and ν Poisson's ratio. To include the temperature dependence, the modulus was artificially increased pre-activation to prevent deformation until the electrolyte melts. This function consists of three linear pieces,

$$\mu(T) = \begin{cases} M \times \mu_0 & T < T_m - \delta T \\ \mu_0 & T > T_m + \delta T \\ \frac{((1+M)\delta T + (M-1)(T_m - T))\mu_0}{2\delta T} & \text{else} \end{cases} \quad (4)$$

Here, M is a parameter (typically taken to be 1000) increasing the shear modulus prior to melting, T_m is the melting temperature of the electrolyte, and $2\delta T$ is the temperature range over which we consider the electrolyte to melt. This model shows very little deformation prior to melting of the electrolyte and yields a deformation consistent with data [4] after melting.

Thermal elastic model

To capture the three key physical behaviors described above, a novel phenomenological material model was developed that accounts for deformation arising from three sets of physics: non-linear thermal expansion, volume and shape change due to the melting of the electrolyte, and finite deformation elasticity. The mechanical behavior of the separator material is modeled as the volume fraction weighted sum the material in the cold state (A) and in the hot state (B). These states are distinguished with different elastic constants and possibly different mechanical behaviors. The transition between the two states is modeled via first-order reaction kinetics with thermally-activated rate constants. It is observed experimentally that an initial void fraction in the microstructure irreversibly disappears on the initial heating from the cold state to the hot state. Associated with this process is both a volume and shape change, each of which are captured with evolution rules associated with the rate at which the void fraction is shrinking.

To track the deformation associated with each of these processes, the deformation gradient associated with a separator material point is multiplicatively decomposed as shown in Fig. 1 into submaps associated with the corresponding set of

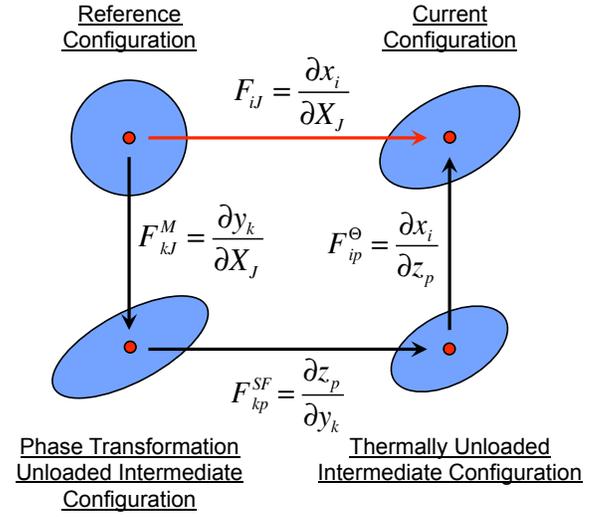


Figure 1. Kinematics of a material point (red dot) and its immediate neighborhood. Einstein notation is used for the components of the position vectors

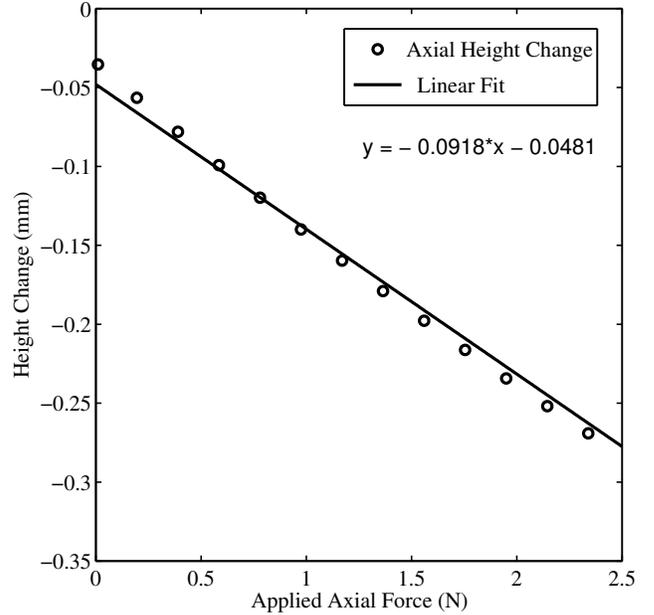


Figure 2. Plot of the separator height change through melting as a function of the applied axial force, using the thermal elastic solid model. Data points are model results while the line is a fit to those results.

physics,

$$\mathbf{F} = \mathbf{F}^\ominus \mathbf{F}^{\text{SF}} \mathbf{F}^{\text{M}} = F_{iJ} = \frac{\partial x_i}{\partial z_p} \frac{\partial z_p}{\partial y_k} \frac{\partial y_k}{\partial X_J} = \frac{\partial x_i}{\partial X_J} \quad (5)$$

The thermal expansions of the materials is captured by the first submap \mathbf{F}^\ominus . The phase transformation of the composite separator is captured by the second submap \mathbf{F}^{SF} . As the separator melts for the first time, the evolution of the void fraction is captured by an evolution rule which controls the total deformation of the separator on melting. Finally, the submap \mathbf{F}^{M} determines the linear elastic (neo-Hookean) deformation as a response to applied force capturing the transition between solid and molten moduli. The results of an example simulation using this model can be found in Fig. 2.

Kayenta model

The Kayenta model was first developed at Sandia National Laboratories as a geomechanics model geared towards understanding fractured rock [1]. The equations that make up the Kayenta model are too complex and numerous to repeat here, so we instead direct the reader to the key publication by Brannon et al.[1] for details on the model. For the purposes of this work, the Kayenta model could be used to investigate non-linear material deformations that may not be captured in the previous thermal elastic model. Work is currently ongoing to obtain a proper fit of the numerous model parameters to these data.

Porous flow model

Movement of the molten electrolyte is modeled using the standard Darcy porous flow model [2].

$$-\nabla p = \frac{\mu}{k} \mathbf{v}, \quad (6)$$

where p is the liquid pressure, μ is the liquid viscosity, k is the permeability of the liquid through the porous structure, and \mathbf{v} is the liquid velocity. As the separator pellet begins with unfilled pore space, a partially-saturated model is required. In this model, the liquid-phase pressure is the independent variable, and is correlated to the saturation of the pores through a capillary-pressure/saturation relationship.

Pre-activation, the electrolyte is solid and does not flow. However, post-activation, the electrolyte is molten and flows throughout the MgO binder. In order to accommodate this behavior, the liquid viscosity is modified to be significantly higher prior to activation, preventing significant flow. This modification uses a form similar to (4), with a high viscosity at low temperatures, the measured viscosity at high temperatures, and a linear transition during melting.

Numerical implementation

These models are implemented in a variety of Galerkin/Finite Element Method codes. The linear elastic solid model and the porous flow model were implemented in Goma [5]. The Kayenta and thermal elastic models were implemented in

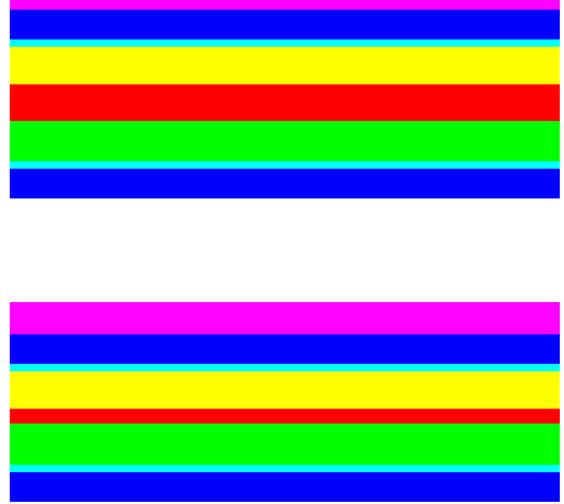


Figure 3. Schematic of the cell stack before (top) and after (bottom) activation, with the layer deformation magnified five times. Layers are (from top to bottom) insulation, heat pellet, collector, anode, separator, cathode, collector, and heat pellet.

Sierra/Adagio [6]. Work is ongoing to consolidate all of the models into the Sierra suite.

NUMERICAL EXAMPLES

In order to demonstrate the capabilities of the models presented here, a single cell of a thermally-activated battery is modeled. This battery cell consists of six layers, the cathode, separator, anode, and collector pellets, a heat generating pellet, and an elastic insulator layer. The primary component of this cell is the separator pellet, which is modeled with the linear elastic model for the mechanical response and the porous flow model for the electrolyte flow. The adjoining anode and cathode layers, along with the current collector layer, are impermeable to electrolyte and do not deform under mechanical stress. The insulation layer is impermeable to the electrolyte but deforms as a linear elastic material. This insulation is pre-stressed (compressed) prior to the simulation. A schematic of this cell stack is in Fig. 3.

Transient behaviors in this model are driven by the temperature gradients generated by the heat pellet. This pellet is initialized to a very high temperature (1100°C) and the heat is allowed to diffuse through the other pellets.

Results from this example simulation are shown in Fig. 4. The first plot (Fig. 4a) shows the mean separator temperature growing with time. This temperature increase is driven by the high initial temperature of the heat pellet, which is allowed

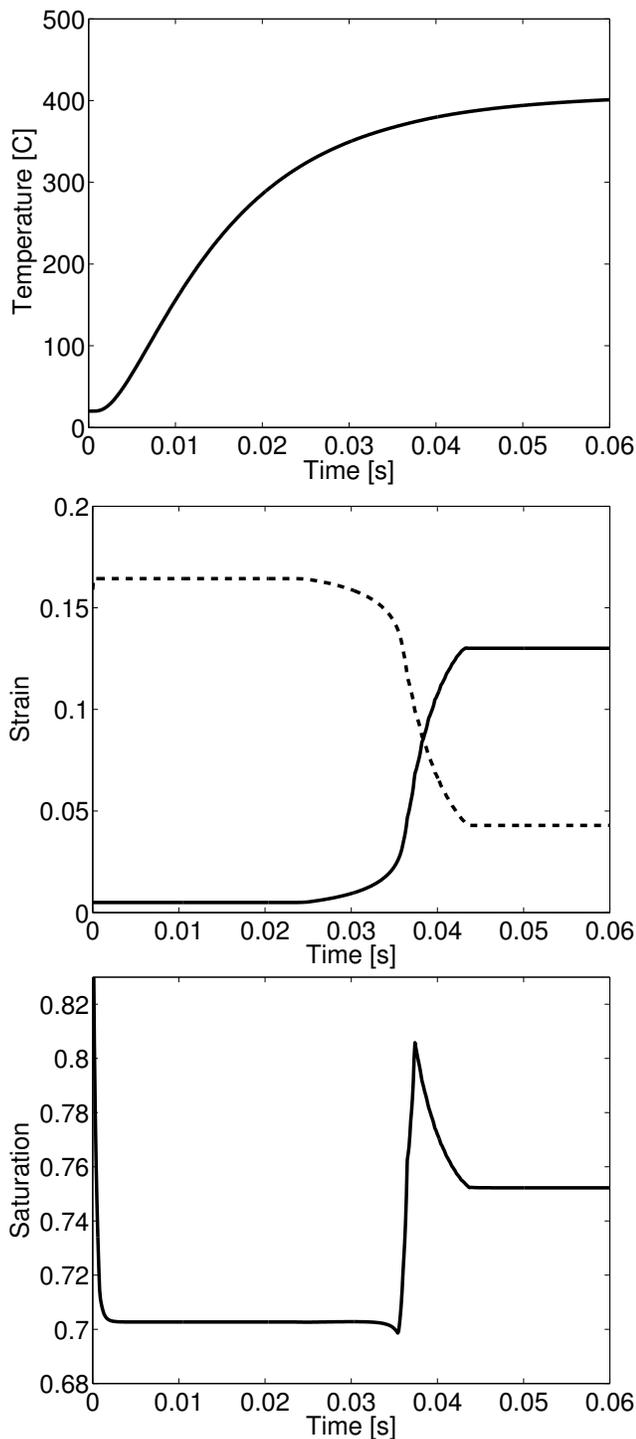


Figure 4. Results from example simulation. a) Mean separator temperature. b) Strain of the separator (solid) and insulation (dashed) layers. c) Mean saturation of the separator.

to diffuse through the cell stack. The second plot (Fig. 4b) shows the strain of the separator and insulation layers. As the insulation was pre-stressed at the beginning of the simulation, it starts with $\approx 17\%$ strain. As the electrolyte reaches its melting temperature, T_m , the modulus of the separator drops drastically (4), causing the separator to deform. Since the entire cell stack is a fixed height, the insulation expands to accommodate this deformation of the separator, and the pressure in the cell stack decreases. Finally, the last plot (Fig. 4c) shows the saturation of the pores in the separator. When the electrolyte melts, the separator deformation drives a flow of the electrolyte, which eventually leaves the separator more saturated than it initially was.

CONCLUSIONS

In this paper, we have described a variety of solid and porous models which may be used to understand the mechanical deformations that take place upon activation of a thermal battery. Three solid models were described that capture different phenomena at increasing levels of complexity, and all of them may be used to drive the flow of molten electrolyte using the porous flow model. These models are based on numerous experimental observations of these materials.

Acknowledgments

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